

Per- and Polyfluoroalkyl Substances (PFAS)

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Prepared by

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Per- and Polyfluoroalkyl Substances (PFAS) Team

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About ITRC

The Interstate Technology and Regulatory Council (ITRC) is a state-led coalition working to reduce barriers to the use of innovative environmental technologies and approaches so that compliance costs are reduced and cleanup efficacy is maximized. ITRC produces documents and training that broaden and deepen technical knowledge and expedite quality regulatory decision making while protecting human health and the environment. With private and public sector members from all 50 states and the District of Columbia, ITRC truly provides a national perspective. More information on ITRC is available at www.itrcweb.org. ITRC is a program of the Environmental Research Institute of the States (ERIS), a 501(c)(3) organization incorporated in the District of Columbia and managed by the Environmental Council of the States (ECOS). ECOS is the national, nonprofit, nonpartisan association representing the state and territorial environmental commissioners. Its mission is to serve as a champion for states; to provide a clearinghouse of information for state environmental commissioners; to promote coordination in environmental management; and to articulate state positions on environmental issues to Congress, federal agencies, and the public.

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This Interstate Technology and Regulatory Council (ITRC) online document includes the PFAS Technical and Regulatory Guidance Document, PFAS Fact Sheets and Explainer Videos, Training Module Videos and external tables of data and information prepared by the ITRC PFAS Team. Internal links in the online document will help the reader locate interrelated topics, refer back to key concepts, and locate references, while external links provide connection to the training module videos, see below, on key topics. Finally, the web-based nature of this document lends itself to updating of key information in this rapidly evolving subject. It is the intention of ITRC to periodically update the document as significant new information and regulatory approaches for PFAS develop. The guidance document can be downloaded as a PDF.

The Technical and Regulatory document is designed specifically to support state and federal environmental staff, as well as others (including stakeholders, project managers, and decision makers), to gain a working knowledge of the current state of PFAS science and practice. Developed by a team of over 400 environmental practitioners drawn from state and federal government, academia, industry, environmental consulting, and public interest groups, it also provides a summary of the current understanding of all aspects of PFAS from a broad perspective. While every effort was made to keep the information accessible to a wide audience, it is assumed the reader has some basic technical background in chemistry, environmental sciences, and risk assessment.

An Introduction is provided for the document.

The document addresses these questions:

Questions	Document Sections
What are PFAS?	<ul style="list-style-type: none">• Naming Conventions and Use• Chemistry, Terminology, and Acronyms• PFAS Uses• PFAS Releases to the Environment
How do they behave in the environment?	<ul style="list-style-type: none">• Physical and Chemical Properties• Environmental Fate and Transport Processes• Media-Specific Occurrence
Why are we concerned about PFAS?	<ul style="list-style-type: none">• Human and Ecological Health Effects• Basis of Regulations• Site Risk Assessment
How do we evaluate PFAS in the environment?	<ul style="list-style-type: none">• Site Characterization• Sampling and Analytical Methods
How do we remediate PFAS?	<ul style="list-style-type: none">• Treatment Technologies
What are the major concerns of communities and Tribes and how do we share what we know about PFAS?	<ul style="list-style-type: none">• Stakeholder Perspectives• Risk Communication
Special topics	<ul style="list-style-type: none">• Firefighting Foams• Case Studies

PFAS Training Module Videos

The PFAS Team developed training module videos to accompany this Technical and Regulatory Document. The following links will redirect you to ITRC's PFAS Training Module Videos on Youtube:

- PFAS introduction
- Naming Conventions and Physical and Chemical Properties
- Production, Uses, Sources and Site Characterization
- Sampling and Analysis

- Fate and Transport
- Human and Ecological Effects
- Risk Assessment and Regulations
- Treatment Technologies
- Aqueous Film-Forming Foam
- Risk Communication

Archived Round Table Sessions

- Roundtable Session 1
- Roundtable Session 2

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1 Introduction

A PFAS introduction Video is available.

Per- and polyfluoroalkyl substances (PFAS) are a very large family of thousands of chemicals that vary widely in their chemical and physical properties, as well as their potential risks to human health and the environment. Buck et al. (2011) provides a definition of PFAS (see text box) stating that all PFAS contain within their molecular structure a straight or branching chain of carbon atoms in which one or more of the carbon atoms have fluorine atoms attached at all bonding sites not occupied by another carbon atom and the fluorinated part of the molecule (the “perfluoroalkyl moiety”) can be expressed as C_nF_{2n+1} .

The persistence and mobility of some PFAS, combined with decades of widespread use in industrial processes, certain types of firefighting foams, and consumer products, have resulted in their being present in most environmental media at trace levels across the globe. PFAS have only recently come to the attention of investigators and the public in large part due to the fact that until the early 2000s analytical methods to detect low levels of PFAS in the environment were available only in a few select research institutions. It was not until the early 2010s that these methods became widely available and had detection limits in water low enough to be commensurate with levels of potential human health effects. Toxicological studies have raised concerns regarding the bioaccumulative nature and potential health concerns of some PFAS. As a result, our understanding of PFAS and the risks they may pose is rapidly evolving.

PFAS are “... highly fluorinated aliphatic substances that contain one or more carbon (C) atoms on which all the hydrogen (H) substituents (present in the nonfluorinated analogues from which they are notionally derived) have been replaced by fluorine (F) atoms, in such a manner that they contain the perfluoroalkyl moiety C_nF_{2n+1} .” (Buck et al. 2011)

This guidance document is designed specifically to support state and federal environmental staff, as well as others (including stakeholders, project managers, and decision makers), to gain a working knowledge of the current state of PFAS science and practice. Developed by a team of over 400 environmental practitioners drawn from state and federal government, academia, industry, environmental consulting, and public interest groups, it also provides a summary of the current understanding of all aspects of PFAS from a broad perspective. While every effort was made to keep the information accessible to a wide audience, it is assumed the reader has some basic technical background in chemistry, environmental sciences, and risk assessment. The document addresses the following questions:

Questions	Document Sections
What are PFAS?	<ul style="list-style-type: none">• Naming Conventions and Use• Chemistry, Terminology, and Acronyms• PFAS Uses• PFAS Releases to the Environment
How do they behave in the environment?	<ul style="list-style-type: none">• Physical and Chemical Properties• Environmental Fate and Transport Processes• Media-Specific Occurrence
Why are we concerned about PFAS?	<ul style="list-style-type: none">• Human and Ecological Health Effects• Basis of Regulations• Site Risk Assessment

Questions	Document Sections
How do we evaluate PFAS in the environment?	<ul style="list-style-type: none"> • Site Characterization • Sampling and Analytical Methods
How do we remediate PFAS?	<ul style="list-style-type: none"> • Treatment Technologies
What are the major concerns of communities and Tribes and how do we share what we know about PFAS?	<ul style="list-style-type: none"> • Stakeholder Perspectives • Risk Communication
Special topics	<ul style="list-style-type: none"> • Firefighting Foams • Case Studies

The thousands of chemicals that make up the large family known as PFAS can be divided into two major classes: nonpolymers and polymers. This document focuses primarily on those nonpolymer PFAS that, to date, are most commonly detected in the environment, particularly the highly persistent perfluoroalkyl acids (PFAAs), some of the better known replacements for phased-out long-chain PFAAs, and some of the “precursor” chemicals—PFAS that can break down to form PFAAs. These precursors include *poly*fluorinated alkyl substances and a subset of polymer PFAS known as side-chain fluorinated polymers (Washington et al. 2018). Many polymer PFAS, especially certain high-molecular weight fluoropolymers, are insoluble in the environment and not bioavailable, and therefore less of a concern to human and ecological health (Henry et al. 2018), so are not discussed in detail in this document. As this paragraph illustrates, it is important to be very clear about which PFAS is being discussed and what its particular physical and chemical properties are, and that is where this document begins.

The physical and chemical properties that make some PFAS persistent and mobile in the environment also make them particularly challenging to analyze and remediate. Analytical methods sensitive enough to detect environmentally relevant concentrations became widely available in the early 2010s. Although analyte lists continue to expand, currently available methods still only allow identification of a small fraction of the thousands of PFAS that have reportedly been created and used since the 1950s. As existing analytical methods improve and new, nontargeted analyses become commercially available, it is likely that additional PFAS and new release sites will be identified.

Concerns have been raised regarding human health and ecological risks associated with certain PFAS. These are based on widespread detections of some PFAS in humans and wildlife, evidence that certain PFAS bioaccumulate in individuals and bioconcentrate in the food chain, and studies reporting multiple toxicological effects in animals and potential health effects in humans. However, risk assessment of PFAS is hampered by the unique physical and chemical properties of many PFAS, which result in uncertainty in identifying sources and quantifying source area mass, complex fate and transport in the environment, poorly understood biological and chemical transformation pathways, and unique bioaccumulation processes. Moreover, the widespread presence of some PFAS in environmental media and the many potential PFAS sources also complicate interpretation of site data. Data evaluation methods to help distinguish between site-specific anthropogenic “background” PFAS, PFAS that are site-related, and PFAS from another nearby source are still being developed.

As with other emerging contaminants, our evolving understanding of PFAS and the volume of scientific studies makes it difficult for most environmental practitioners to stay current with the critical information about these chemicals. Meanwhile, public concern about PFAS has created pressure on state and federal agencies to take action, resulting in a patchwork of evolving regulatory approaches and regulatory standards, screening values, and guidance values. As with any new and evolving area of science, our knowledge is far from complete. We have attempted to alert the reader to areas where information is still uncertain or conflicting interpretations exist.

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2 PFAS Chemistry and Naming Conventions, History and Use of PFAS, and Sources of PFAS Releases to the Environment

The PFAS Team developed two training module videos with content related to this section, they are the Naming Conventions and Physical and Chemical Properties video and the Production, Uses, Sources and Site Characterization video.

PFAS chemistry was discovered in the late 1930s. Since the 1950s, many products commonly used by consumers and industry have been manufactured with or from PFAS, as the unique physical and chemical properties of PFAS impart oil, water, stain, and soil repellency, chemical and thermal stability, and friction reduction to a range of products. These products have application in many industries, including the aerospace, semiconductor, medical, automotive, construction, electronics, and aviation industries, as well as in consumer products (such as carpets, clothing, furniture, outdoor equipment, food packaging), and firefighting applications (3M Company 1999a; Buck et al. 2011; KEMI 2015a; USEPA 2017b).

The number of PFAS and their uses have expanded over the years. It has been estimated that the PFAS family may include approximately 5,000-10,000 chemicals (USEPA 2018i). A recent inventory of PFAS identified Chemical Abstracts Service (CAS) Registry Numbers for more than 4,700 PFAS that could have been, or may be, on the global market (OECD 2018), although the uses of each of these PFAS may not be known (KEMI 2015a). Publicly available health and toxicity studies are limited to only a small fraction of these PFAS, and modern commercially available analytical technologies typically identify only about 20-30 PFAS.

Scientific, regulatory, and public concerns have emerged about potential health and environmental impacts associated with chemical production, product manufacture and use, and disposal of PFAS-containing wastes. These concerns have led to efforts to reduce the use of or replace certain PFAS, such as the two most widely produced, commonly encountered, and most studied compounds: perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) (USEPA 2016e; WA DER 2017).

The objective of this section is to lay a foundation for identifying potential PFAS sources in the environment.

Section Number	Topic
2.1	Environmental Significance
2.2	Chemistry, Terminology, and Acronyms
2.3	Emerging Health and Environmental Concerns
2.4	PFAS Reductions and Alternative PFAS Formulations
2.5	PFAS Uses
2.6	PFAS Releases to the Environment

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2.1 Environmental Significance

PFAS have been and still are widely used, but not all types and uses of PFAS result in the same level of environmental impact and exposure. When considering potential environmental impacts from PFAS, it is critical to be as specific as possible not only about the particular PFAS involved, but also where and how they are released to the environment. For example, a stable, insoluble fluoropolymer such as polytetrafluoroethylene (PTFE) may pose little environmental or health risk once it is in a product, but potentially significant environmental releases may occur if controls are not used during PTFE manufacturing, when nonpolymer PFAS, such as PFAAs, are used to make the PTFE. Such considerations may help to focus investigation resources on major sources.

Figure 2-1 illustrates a conceptual PFAS lifecycle beginning at PFAS synthesis (raw materials). These raw materials are then used in a variety of manufacturing processes and industrial/commercial applications to create commercial and consumer products that contain or were treated with PFAS. Throughout this life cycle, variable types and amounts of PFAS may be released to the environment from manufacturing waste streams, fugitive emissions, spills, disposal of PFAS-containing or -treated materials, and general wear and tear of consumer products. Sometimes the intended use of the PFAS product (for example, firefighting foams) requires direct release to the environment. PFAS from a host of sources also may be aggregated in wastewater treatment plant effluent and sludges, creating secondary release sources. The volume, concentration, and mixture of PFAS released to the environment varies based on the source (process, material, or product), release mechanism(s), and environmental controls employed throughout this life cycle. Exposure to PFAS may occur as (1) direct interaction with the manufacturing process, (2) professional or intensive use of PFAS-containing materials, (3) use of or contact with commercial and consumer products containing PFAS, or (4) exposure (human or ecological) to environmental media that has been impacted by PFAS. The relative significance of these exposures will also vary widely.

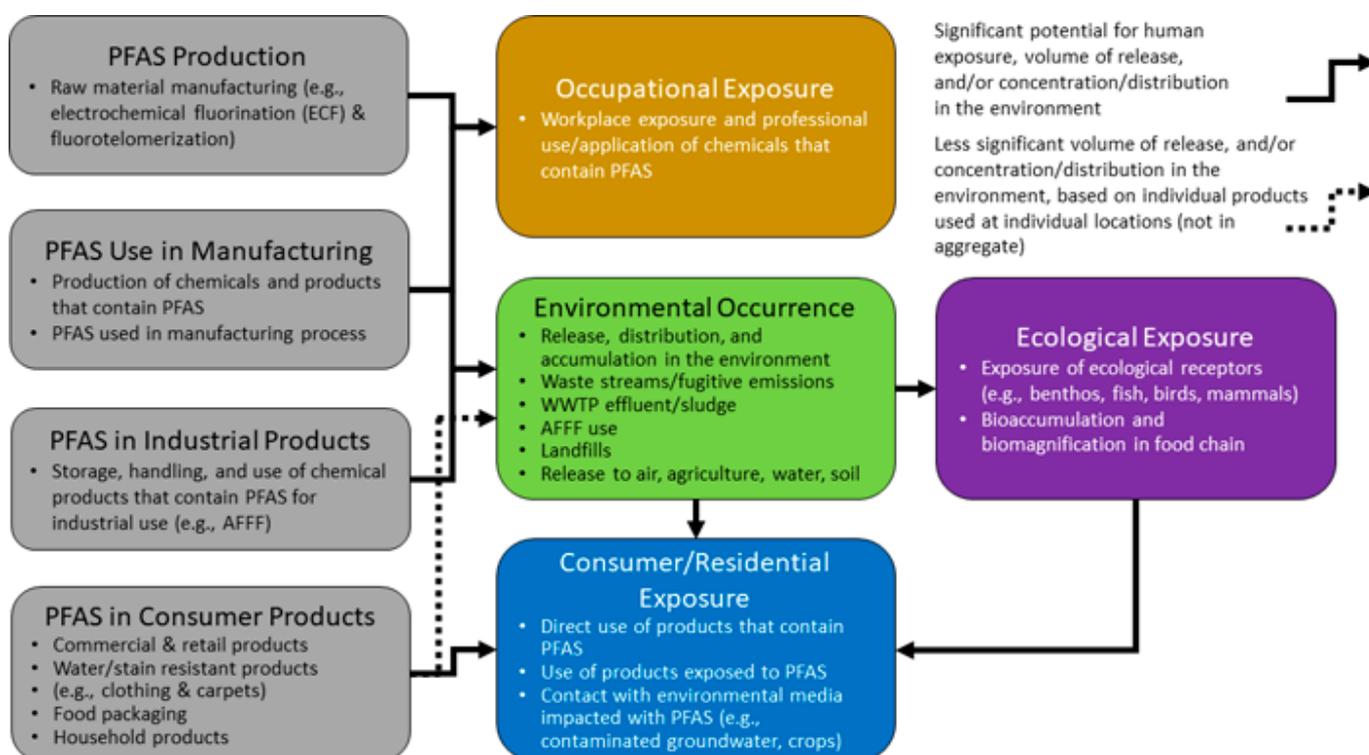


Figure 2-1. Generalized PFAS uses and relative exposure and environmental impact potential from PFAS life cycle.

This figure is not exhaustive with regard to all sources or release mechanisms from those sources. Multiple sources may exist at a site, and the relative potential of exposure and environmental impact may vary based on several considerations.

Due to the widespread use of PFAS in commercial and consumer products, other minor point and diffuse releases of PFAS to the environment may occur during use and disposal of some PFAS-containing products. Although these may result in locally significant environmental impacts, these releases typically affect smaller geographic areas and have lower total PFAS mass than major sources, such as PFAS chemical manufacturing, PFAS use in certain industries, and application of certain firefighting foams.

Different PFAS products and sources differ in their relative environmental significance, volumes released, distribution mechanisms, area affected, and relative concentration of impacted media. For instance, application of Class B firefighting foam may impact a moderate area relative to air dispersion from fluoropolymer production, but may exhibit higher associated groundwater concentrations near the source area.

The type of PFAS involved also determines the relative environmental significance. Nonpolymer PFAS (both per- and polyfluorinated) and some side-chain fluorinated polymer PFAS are likely to pose greater risks when released to the environment than certain fluoropolymer sources, such as the fluoropolymers PTFE, fluorinated ethylene-propylene (FEP), perfluoroalkoxy polymer (PFA), and ethylene tetrafluoroethylene (ETFE). These fluoropolymers are considered to be polymers of low concern (Section 2.2.2.1) because they are relatively stable, insoluble in the environment, and not bioavailable (Henry et al. 2018). However, environmental impact from the production or manufacturing uses of some fluoropolymers can pose a significant risk if emissions are not properly controlled at the industrial site. Also, releases to the environment from the disposal of fluoropolymers cannot be ruled out, as nonpolymer PFAS (such as the PFAAs used as polymerization aids) may be found at trace levels as impurities and byproducts in some fluoropolymer products (3M Company 1999a). Research suggests side-chain fluorinated polymers and fluorotelomer-based polymers are likely to break down into nonpolymer PFAS with time (Li et al. 2018; Washington et al. 2018), although it is documented that one fluoropolymer (PTFE) did not degrade to significant levels of PFAAs during incineration (Aleksandrov et al. 2019).

Finally, another consideration regarding environmental impacts is the issue of anthropogenic (human-caused, not naturally occurring) ambient or “background” levels of PFAS. As discussed in Section 6, the long duration of PFAS use and their release from many types of sources may have resulted in low-level contamination of environmental media worldwide. The implications of such ambient levels of PFAS should be considered in evaluating exposures and risk levels, establishing site action levels and cleanup goals, and identifying PFAS sources.

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2.2 Chemistry, Terminology, and Acronyms

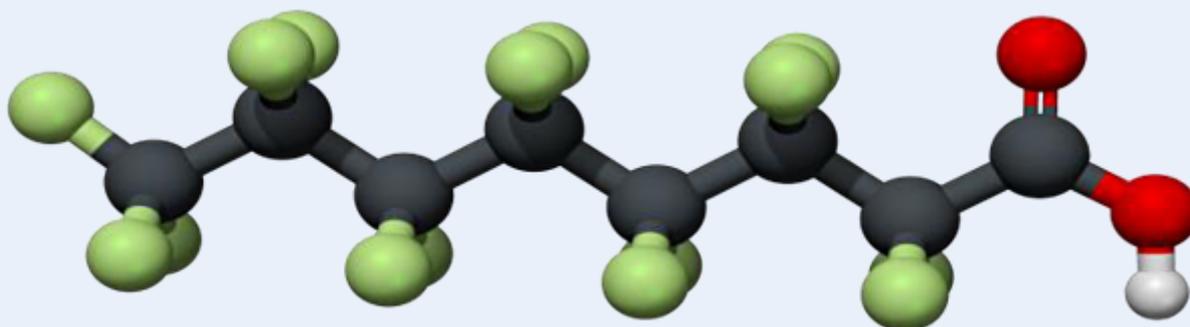
This section focuses on chemistry, terminology, names, and acronyms for those PFAS most commonly reported in the environment, identified in scientific literature, and those PFAS most commonly tested for by current analytical methods. Other important classes of PFAS are introduced. This section also introduces the chemical manufacturing processes that influence the types of PFAS that are found in the environment.

PFAS are characterized by carbon atoms that are linked together with fluorine atoms attached to the carbons. A more specific and technical definition of PFAS states that PFAS are defined as “highly fluorinated aliphatic substances that contain one or more carbon (C) atoms on which all the hydrogen (H) substituents (present in the nonfluorinated analogues from which they are notionally derived) have been replaced by fluorine (F) atoms, in such a manner that they contain the perfluoroalkyl moiety C_nF_{2n+1} .” (Buck et al. 2011).

The definition of PFAS may evolve to reflect continued study of these compounds. For example, the definition of PFAS used in one study (OECD 2018) also included chemicals that contain $-C_nF_{2n}-$ in addition to the C_nF_{2n+1} , which includes chemicals with both ends of the carbon-fluorine chain connected to a functional group, such as cyclic analogs of linear PFAS.

General Concepts of Organofluorine Chemistry for PFAS

Organofluorine Chemistry: A branch of organic chemistry involving organic molecules with a carbon-fluorine bond. Organofluorine molecules have many commercial uses. They include PFAS, such as PFOA, shown below:



EXAMPLE: 3D model of a PFOA (perfluorooctanoic acid) molecule, in its acid form.

Source: Manuel Almagro Rivas (Own work using: Avogadro, Discovery Studio, GIMP) [CC BY-SA 4.0] (<https://creativecommons.org/licenses/by-sa/4.0/>), via Wikimedia Commons. <https://commons.wikimedia.org/wiki/File:PFOA-3D.png>

Gray spheres represent carbon atoms linked together in a chain; there are eight of them, so “octane” is used in the name. Green spheres represent fluorine atoms bonded to carbon atoms. Red spheres represent oxygen atoms. White sphere represents a hydrogen atom that dissolves away in water, which makes this an acid. Fluorine atoms are attached to all possible bonding sites, making this **per**fluorinated. If some of the fluorine atoms were replaced by other atoms (such as oxygen or hydrogen), it would be **poly**fluorinated. Without the hydrogen, the “head end” takes on a negative charge and can bond to things through electrostatic attraction. The fluorine “tail end” is strong and stable, giving it lipid- and water-repelling properties, but also making it persistent in the environment.

Isomer: A molecule with the same molecular formula as another molecule, but with a different chemical structure. Isomers contain the same number of atoms of each element, but have different arrangements of their atoms. See Figure 2-13 for an example; linear and branched PFOS contain the same number of carbon, fluorine, oxygen, and sulfur atoms, but these atoms are arranged differently depending on whether it is a linear or branched isomer of

PFOS.

Homologue Groups and Homologous Series: A group of organic compounds, usually listed in order of increasing size, that has a similar structure (and therefore also similar properties) and whose structures differ only by the number of carbon atoms in the chain. For example, all of the linear and branched isomers of PFOS would be in the C₈ homologue group, while all of the linear and branched isomers of perfluorohexane sulfonic acid (PFHxS) would be in the C₆ homologue group. The C₄-C₁₂ PFASs are a homologous series of perfluorosulfonates.

2.2.1 Naming Convention Considerations

There is confusion among the environmental community and the public due to overgeneralization when describing PFAS and the lack of consistent naming of specific PFAS. The use of consistent naming conventions would reduce confusion and support clearer communication (Buck et al. 2011) (Wang, DeWitt, et al. 2017).

“PFAS,” not “PFASs”: The acronym “PFAS” stands for “per- and polyfluoroalkyl substances.” No single chemical within the PFAS family can be both perfluorinated and polyfluorinated, so by definition “PFAS” is plural and a small “s” is not needed. Some authors elect to add a small “s” to this acronym (PFASs) to emphasize the fact that it is plural, but it is not needed. When referring to a single chemical within the PFAS family, it is more accurate to simply name that specific chemical.

Consistent naming also helps to distinguish PFAS from other organic compounds that contain fluorine. As defined in the literature, PFAS include only fluorinated aliphatic (carbon chain) substances. PFAS do not include fluorinated compounds that contain aromatic (carbon ring) features in their structures (for example, active pharmaceutical ingredients, crop protection agents, or chlorofluorocarbons (refrigerants)). This definition distinguishes PFAS from the more generic term “PFC,” which can include aromatic compounds.

The use of nonspecific acronyms, such as perfluorinated compound (PFC), has hampered clarity of investigative results. The acronym “PFC” is poorly defined in the scientific literature, but typically refers to “perfluorinated compounds.” It does not include “polyfluorinated substances,” which are increasingly recognized as important contaminants at many PFAS sites.

In the future, it may be necessary to expand the current naming conventions and acronym approaches to ensure that standardized naming is available for additional members of the PFAS family of compounds. Buck et al. (2011) is an open-access paper that provides a more detailed explanation of PFAS terminology, classification, and origins, and recommends specific and descriptive terminology, names, and acronyms for PFAS.

CAS numbers are another helpful tool for clearly identifying the chemical that is being referenced; however, care must be taken in selecting the correct CAS number to avoid confusion regarding the chemistry and behavior of the chemical being described. Some PFAS may occur in various ionic states, such as acids, anions (negatively charged), cations (positively charged), and zwitterions (both positively and negatively charged dipolar molecules), and each has its own CAS number (and some have no CAS number). The ionic state determines electrical charge and physical and chemical properties, which in turn control fate and transport in the environment and potential human health and ecological effects. The ionic state of individual PFAS can result in significantly different physical and chemical properties, such as solubility, volatility, and bioaccumulative potential.

Chemicals in the PFAS family can exist in various ionic states (for example, acids, anions, cations), which have important implications for their chemical and physical properties. In most cases for PFAAs, this section uses the anionic form of a given PFAS name, as this is the state in which most PFAAs exist in the environment.

2.2.2 Introduction to the PFAS Family

PFAS encompass a wide universe of substances with very different physical and chemical properties (Section 4), including

gases (for example, perfluorobutane), liquids (for example, fluorotelomer alcohols), and solid material high-molecular weight polymers (for example, PTFE). For this reason, it is helpful to group PFAS that share similar chemical and physical properties.

As shown in Figure 2-2, the PFAS family may be divided into two primary classes: polymers and nonpolymers. Each class may contain many subclasses, groups, and subgroups, some of which are shown in the figure. This document focuses primarily on those nonpolymer PFAS most commonly detected in the environment and those PFAS that may be significant as “precursors” that can transform to more persistent forms.

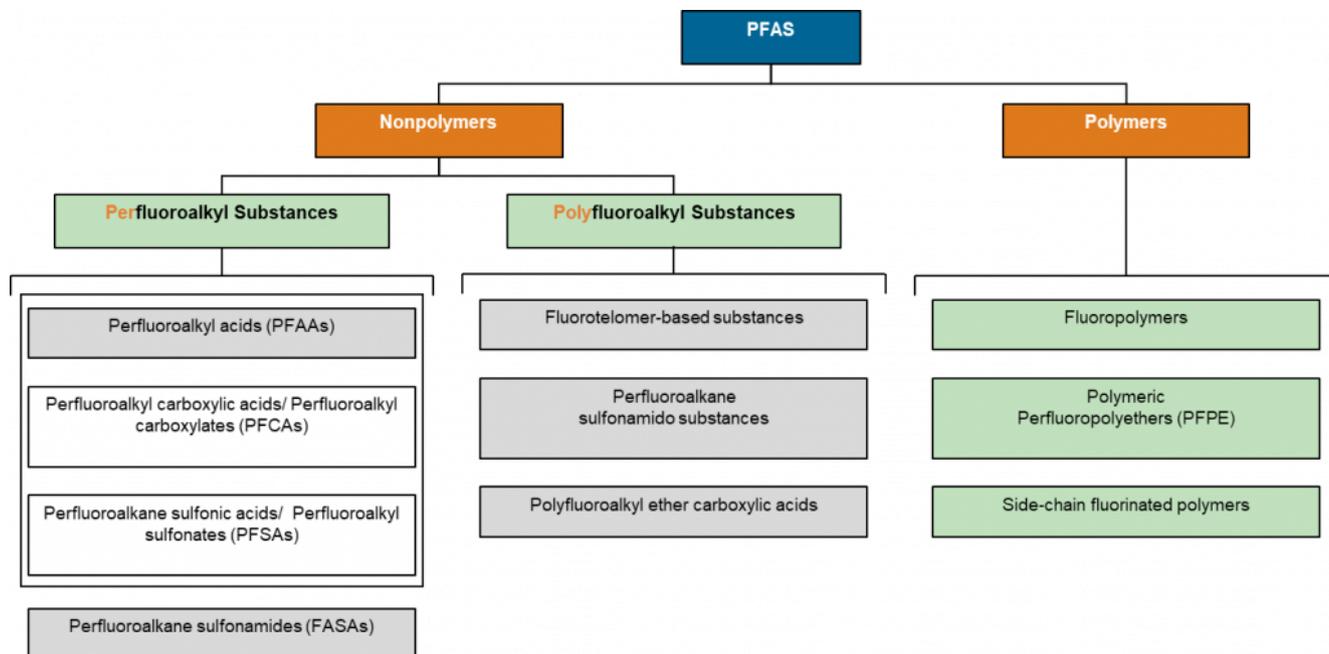


Figure 2-2. The PFAS family.

The family tree is further expanded in Figure 2-3, based on nomenclature provided in Buck et al. (2011), Organization for Economic Co-operation and Development OECD (2015b), and Wang, DeWitt, et al. (2017), with further introduction to some of these chemicals provided later in this section.

Future updates to the family tree and nomenclature are expected to be necessary given the evolving public knowledge of these compounds. For example, other PFAS without analytical standards are being identified using nontarget analyses by research laboratories (Section 11). These PFAS do not necessarily have an associated CAS number but are being identified by molecular structure.

Figure 2-3. PFAS family tree.

Adapted from a graphic provided courtesy of Paul Caprio, EA Engineering.

A stand-alone PDF version of Figure 2-3 is available.

2.2.2.1 Polymer PFAS

Polymers are large molecules formed by combining many identical smaller molecules (or monomers (which are shorter chain molecules with no repeating units)) in a repeating pattern. Oligomers are smaller polymers, with relatively fewer repeating units.

The PFAS polymer class includes fluoropolymers, polymeric perfluoropolyethers, and side-chain fluorinated polymers (Henry et al. 2018; Buck et al. 2011; Wang, Cousins, et al. 2013):

- Fluoropolymers contain a carbon-only polymer backbone with fluorines directly attached to the carbon. Fluoropolymers include polymers like PTFE, ETFE, copolymer FEP, and PFA, which were historically made using ammonium perfluorooctanoate (APFO) or sodium perfluorooctanoate (NaPFO), which are salts of perfluorooctanoate (PFOA). Fluoropolymers also include polyvinylidene fluoride (PVDF), which was historically made using ammonium perfluoronanoate (APFN), the ammonium salt of perfluoronanoate (PFNA) (OECD 2015b), (Buck et al. 2011).
- The specific fluoropolymers PTFE, FEP, ETFE, and PFA have been referred to as “polymers of low concern” because they have high molecular weight and are extremely stable. PTFE has been demonstrated to not be bioavailable (Henry et al. 2018). Based on this, Henry et al. (2018) suggest polymers of low concern should be considered separately from other PFAS when evaluating risk. Polymers of low concern are reported to pose little environmental or health risk once in a consumer product.
- Polymeric perfluoropolyethers (PFPE) contain a carbon and oxygen polymer backbone with fluorines directly attached to carbon. Relatively little is known about these chemicals in the environment.
- Side-chain fluorinated polymers contain a nonfluorinated polymer backbone, off of which fluorinated side chains branch. These PFAS include fluorinated urethane polymers, fluorinated acrylate/methacrylate polymers, and fluorinated oxetane polymers. Some side-chain fluorinated polymers may become precursors for PFAAs, Section 2.2.3.1, when the point of connection of a fluorinated side chain on a polymer is broken to release a PFAA.

During the manufacture and manufacturing uses of some fluoropolymers, controls are necessary to mitigate potential releases of nonpolymer PFAS. Nonpolymer PFAS may be used as processing aids in the manufacture of some fluoropolymer PFAS, and may be found as impurities in some fluoropolymer products, and due to potential degradation of some fluoropolymers (3M Company 1999b; CalEPA 2018; Washington et al. 2018), see also Section 5.4.5.

2.2.2.2 Nonpolymer PFAS

Nonpolymer PFAS encompass two major subclasses: **perfluoroalkyl substances** and **polyfluoroalkyl substances**, which include many groups and subgroups of chemicals. Figure 2-4 provides general classification and chemical structures, examples of each group, and examples of the primary uses of the nonpolymer PFAS highlighted in Figure 2-2 and Figure 2-3.

Nonpolymer PFAS were selected as the focus of this document because:

- they are the PFAS most commonly detected (to date) in humans, biota, and other environmental media and appear to be relatively more abundant at PFAS investigation sites (Section 6)
- data may be available regarding potential human health and ecological effects from environmental exposure for some of these chemicals (Section 7)
- state or federal standards or guidance values may exist for some of these chemicals (Section 8)
- they are included in most laboratory PFAS analyte lists (Section 11).

Nonpolymers

Perfluoroalkyl Substances

Perfluoroalkyl acids (PFAAs)

Perfluoroalkyl carboxylic acids/ Perfluoroalkyl carboxylates (PFCAs)

Example	Chemical Structure	Uses
Perfluorooctanoic acid (PFOA)	$C_7F_{15}COOH$	Surfactant
Perfluorooctanoate (PFOA)	$C_7F_{15}CO_2^-$	Surfactant

Perfluoroalkane sulfonic acids (PFSAAs)/ Perfluoroalkane sulfonates (PFSAs)

Example	Chemical Structure	Uses
Perfluorooctane sulfonic acid (PFOS)	$C_8F_{17}SO_3H$	Surfactant
Perfluorooctane sulfonate (PFOS)	$C_8F_{17}SO_3^-$	Surfactant

Perfluoroalkyl ether carboxylic acids (PFECAs)

Example	Chemical Structure	Uses
Hexafluoropropylene oxide dimer acid (HFPO-DA)	$CF_3CF_2CF_2OCF_2COOH$	Surfactant

Perfluoroalkane sulfonamides (FASAs)

Example	Chemical Structure	Uses
Perfluorooctane sulfonamide (FOSA)	$C_8F_{17}SO_2NH_2$	Major raw material for surfactant and surface protection products

Polyfluoroalkyl Substances

Polyfluoroalkyl ether carboxylic acids

Example	Chemical Structure	Uses
4,8-dioxa-3H-perfluorononanoic acid (ADONA)	$CF_3OCF_2CF_2CF_2-OCHFCF_2COOH$	Surfactant

Fluorotelomer-based substances

n:2 Fluorotelomer alcohols (FTOHs)

Example	Chemical Structure	Uses
10:2 Fluorotelomer alcohol	$C_{10}F_{21}CH_2CH_2OH$	Major raw material for surfactant and surface protection products

n 2: Fluorotelomer carboxylic acids (FTCAs)

Example	Chemical Structure	Uses
8:2 Fluorotelomer carboxylic acid (8:2 FTSA)	$C_8F_{17}CH_2COOH$	Surfactant and environmental transformation products

n:2 Fluorotelomer sulfonic acids (FTSAs)

Example	Chemical Structure	Uses
8:2 Fluorotelomer sulfonic acid (8:2 FTSA)	$C_8F_{17}CH_2CH_2SO_3H$	Surfactant and environmental transformation products

Perfluoroalkane sulfonamido substances

N-Alkyl perfluoroalkane sulfonamides (FASAs), (MeFASAs, EtFASAs, BuFASAs)

Example	Chemical Structure	Uses
N-Ethyl perfluorooctane sulfonamide (nEtFOSA)	$C_8F_{17}SO_2N(C_2H_5)H$	Major raw material for surfactant and surface protection products

N-Alkyl perfluoroalkane sulfonamidoethanols (FASEs), (MeFASEs, EtFASEs, BuFASEs)

Example	Chemical Structure	Uses
N-Ethyl perfluorooctane sulfonamidoethanol (nEtFOSE)	$C_8F_{17}SO_2N(C_2H_5)CH_2CH_2OH$	Major raw material for surfactant and surface protection products

N-Alkyl perfluoroalkane sulfonamido acetic acids (FASAAAs), (MeFASAAAs, EtFASAAAs, BuFASAAAs)

Example	Chemical Structure	Uses
N-Ethyl perfluorooctane sulfonamido acetic acid (nEtFOSAA)	$C_8F_{17}SO_2N(C_2H_5)CH_2CO_2H$	Intermediate environmental transformation product

Figure 2-4. Nonpolymer PFAS subclasses discussed in this document.

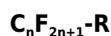
Source: Adapted with permission from Buck, R.C., J. Franklin, U. Berger, J. M. Conder, I. T. Cousins, P. de Voigt, A. A. Jensen, K. Kannan, S. A. Mabury, and S. P. van Leeuwenet. 2011. "Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins." *Integrated Environmental Assessment and Management*, 7:513-541. Open access. Copyright 2011 SETAC. <http://dx.doi.org/10.1002/ieam.258>

2.2.3 Perfluoroalkyl Substances

Perfluoroalkyl substances are fully fluorinated alkane molecules that include (but are not limited to):

- perfluoroalkyl acids (PFAAs) and
- perfluoroalkane sulfonamides (FASAs).

The basic chemical structure is a chain (or *tail*) of two or more carbon atoms with a charged functional group (or *head*) attached at one end. The functional groups commonly are carboxylates or sulfonates, but other forms are also detected in the environment. Fluorine atoms are attached to all possible bonding sites along the carbon chain of the tail, except for one bonding site on the last carbon where the functional group head is attached. This structure, which is illustrated in Figure 2-5 for PFOS and PFOA, can be written as:



where " C_nF_{2n+1} " defines the length of the perfluoroalkyl chain tail, " n " is ≥ 2 , and " R " represents the attached functional group head. Note that the functional group may contain one or more carbon atoms, which are included in the total number of carbons when naming the compound.

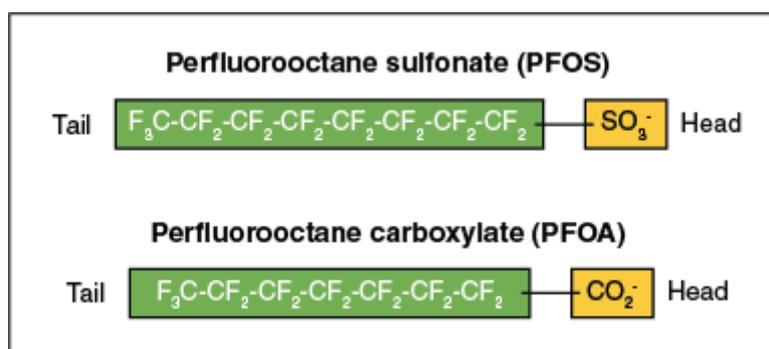


Figure 2-5. The tail and head structure of PFOS and PFOA molecules.

2.2.3.1 Perfluoroalkyl Acids (PFAAs)

PFAAs are some of the least complex PFAS molecules. They are essentially non-degradable under normal environmental conditions. Biotic and abiotic degradation of many polyfluoroalkyl substances may result in the formation of PFAAs. As a result, PFAAs are sometimes referred to as "terminal PFAS" or "terminal degradation products," meaning no further degradation products will form from them under environmental conditions. Polyfluoroalkyl substances that degrade to create terminal PFAAs are referred to as "**precursors**." Longer chain PFAAs do not degrade to shorter chain PFAAs.

The PFAA group is divided into two major subgroups (as shown in Table 2-1 and Figure 2-3).

- **Perfluoroalkyl carboxylic acids** (PFCAs), or perfluoroalkyl carboxylates, are used commercially and can be formed as terminal degradation products of select precursor polyfluoroalkyl substances, such as FTOHs. An example PFCA is PFOA.
- **Perfluoroalkane sulfonic acids** (PFSAs), or perfluoroalkyl sulfonates, also are used commercially and can be formed as terminal degradation products of select precursor polyfluoroalkyl substances, such as perfluoroalkyl sulfonamide ethanols (PFOSEs). An example PFSA is PFOS.

Other subgroups of PFAAs are introduced in Section 2.2.3.3. Some of those are compounds that are receiving increasing

attention, are being added to commercial laboratory target analyte lists, and are being detected in the environment.

PFAAs are the group of PFAS that make up the majority of PFAS typically included in commercial laboratory target analyte lists and are the primary PFAS for which federal or state health-based guidance values have been established. As a result, PFAAs tend to drive site investigation and remediation decisions, so it is helpful to understand the naming conventions for this class. Many of the commonly detected PFAAs are denoted using the structural shorthand:

PFXY where:

PF = perfluoro

X = the carbon chain length (using the same naming conventions as hydrocarbons based on the number of carbons (for example, *B* for butane or 4 carbons, *Pe* for pentane or 5 carbons)

Y = the functional group (for example, *A* = carboxylate or carboxylic acid and *S* = sulfonate or sulfonic acid)

Table 2-1 illustrates how this naming structure works for the PFCAs and PFSAs, which collectively are referred to as PFAAs.

Table 2-1. Basic naming structure and shorthand for PFAAs

X	Y	Acronym	Name	Formula	CAS No.
B = buta (4 carbon)	A = carboxylate or carboxylic acid	PFBA	Perfluorobutanoate ¹	$C_3F_7CO_2^-$	45048-62-2
			Perfluorobutanoic acid ¹	C_3F_7COOH	375-22-4
	S = Sulfonate or sulfonic acid	PFBS	Perfluorobutane sulfonate	$C_4F_9SO_3^-$	45187-15-3
			Perfluorobutane sulfonic acid	$C_4F_9SO_3H$	375-73-5
Pe = penta (5 carbon)	A = Carboxylate or carboxylic acid	PFPeA	Perfluoropentanoate	$C_4F_9CO_2^-$	45167-47-3
			Perfluoropentanoic acid	C_4F_9COOH	2706-90-3
	S = Sulfonate or sulfonic acid	PFPeS	Perfluoropentane sulfonate	$C_5F_{11}SO_3^-$	175905-36-9
			Perfluoropentane sulfonic acid	$C_5F_{11}SO_3H$	2706-91-4
Hx = hexa (6 carbon)	A = Carboxylate or carboxylic acid	PFHxA	Perfluorohexanoate	$C_5F_{11}CO_2^-$	92612-52-7
			Perfluorohexanoic acid	$C_5F_{11}COOH$	307-24-4
	S = Sulfonate or sulfonic acid	PFHxS	Perfluorohexane sulfonate	$C_6F_{13}SO_3^-$	108427-53-8
			Perfluorohexane sulfonic acid	$C_6F_{13}SO_3H$	355-46-4
Hp = hepta (7 carbon)	A = Carboxylate or carboxylic acid	PFHpA	Perfluoroheptanoate	$C_6F_{13}CO_2^-$	120885-29-2
			Perfluoroheptanoic acid	$C_6F_{13}COOH$	375-85-9
	S = Sulfonate or sulfonic acid	PFHpS	Perfluoroheptane sulfonate	$C_7F_{15}SO_3^-$	146689-46-5
			Perfluoroheptane sulfonic acid	$C_7F_{15}SO_3H$	375-92-8
O = octa (8 carbon)	A = Carboxylate or carboxylic acid	PFOA	Perfluorooctanoate	$C_7F_{15}CO_2^-$	45285-51-6
			Perfluorooctanoic acid	$C_7F_{15}COOH$	335-67-1
	S = Sulfonate or sulfonic acid	PFOS	Perfluorooctane sulfonate	$C_8F_{17}SO_3^-$	45298-90-6
			Perfluorooctane sulfonic acid	$C_8F_{17}SO_3H$	1763-23-1

X	Y	Acronym	Name	Formula	CAS No.
N = nona (9 carbon)	A = Carboxylate or carboxylic acid	PFNA	Perfluorononanoate	$C_8F_{17}CO_2^-$	72007-68-2
			Perfluorononanoic acid	$C_8F_{17}COOH$	375-95-1
	S = Sulfonate or sulfonic acid	PFNS	Perfluorononane sulfonate	$C_9F_{19}SO_3^-$	474511-07-4
			Perfluorononane sulfonic acid	$C_9F_{19}SO_3H$	68259-12-1
D = deca (10 carbon)	A = Carboxylate or carboxylic acid	PFDA	Perfluorodecanoate	$C_9F_{19}CO_2^-$	73829-36-4
			Perfluorodecanoic acid	$C_9F_{19}COOH$	335-76-2
	S = Sulfonate or sulfonic acid	PFDS	Perfluorodecane sulfonate	$C_{10}F_{21}SO_3^-$	126105-34-8
			Perfluorodecane sulfonic acid	$C_{10}F_{21}SO_3H$	335-77-3
Un = undeca (11 carbon)	A = Carboxylate or carboxylic acid	PFUnA or PFUnDA	Perfluoroundecanoate	$C_{10}F_{21}CO_2^-$	196859-54-8
			Perfluoroundecanoic acid	$C_{10}F_{21}COOH$	2058-94-8
	S = Sulfonate or sulfonic acid	PFUnS PFUnDS	Perfluoroundecane sulfonate	$C_{11}F_{23}SO_3^-$	441296-91-9
			Perfluoroundecane sulfonic acid	$C_{11}F_{23}SO_3H$	749786-16-1
DoD = dodeca (12 carbon)	A = Carboxylate or carboxylic acid	PFDoDA	Perfluorododecanoate	$C_{11}F_{23}CO_2^-$	171978-95-3
			Perfluorododecanoic acid	$C_{11}F_{23}COOH$	307-55-1
	S = Sulfonate or sulfonic acid	PFDoDS	Perfluorododecane sulfonate	$C_{12}F_{25}SO_3^-$	343629-43-6
			Perfluorododecane sulfonic acid	$C_{12}F_{25}SO_3H$	79780-39-5
TrD = trideca (13 carbon)	A = Carboxylate or carboxylic acid	PFTrDA	Perfluorotridecanoate	$C_{12}F_{25}CO_2^-$	862374-87-6
			Perfluorotridecanoic acid	$C_{12}F_{25}COOH$	72629-94-8
	S = Sulfonate or sulfonic acid	PFTrDS	Perfluorotridecane sulfonate	$C_{13}F_{27}SO_3^-$	NA
			Perfluorotridecane sulfonic acid	$C_{13}F_{27}SO_3H$	NA
TeD = tetradeca (14 carbon)	A = Carboxylate or carboxylic acid	PFTeDA	Perfluorotetradecanoate	$C_{13}F_{27}CO_2^-$	365971-87-5
			Perfluorotetradecanoic acid	$C_{13}F_{27}COOH$	376-06-7
	S = Sulfonate or sulfonic acid	PFTeDS	Perfluorotetradecane sulfonate	$C_{14}F_{29}SO_3^-$	NA
			Perfluorotetradecane sulfonic acid	$C_{14}F_{29}SO_3H$	NA
NA = not available					
¹ Older nomenclature may use butyrate or butyric acid.					

Note that for PFCAs, the total number of carbons used for naming the compound includes the carbon in the carboxylic acid functional group (COOH). For example, although PFOA has seven carbons in its fluoroalkyl tail, all eight of the carbons in the molecule are used to name it, hence *perfluorooctanoate*. But in terms of chemical behavior, PFOA would be more analogous to seven-carbon perfluoroheptane sulfonate (PFHpS) than to eight-carbon perfluorooctane sulfonate (PFOS).

Table 2-1 shows the PFAA names and formulas in both the anionic (also referred to as “deprotonated” or negatively charged) and acid (also referred to as protonated or neutral) forms. The anionic form is the state in which PFAAs are found in the environment, except in very rare situations (for example, extremely low pH). The anionic and acid forms of PFAA names are often incorrectly used interchangeably (for example, perfluorooctane sulfonate and perfluorooctane sulfonic acid), and the same acronym (in this case, PFOS) applies to both forms. However, as discussed below and in Section 4, their physical and

chemical properties are different, and it is important to know which form is being described.

Until recently, PFCAs and PFSAs have been the subgroups most commonly tested for in the environment; however, a wide range of PFAS with other functional groups exists for which the same “PFXY” shorthand shown above may or may not apply. For naming conventions for these compounds, please refer to Buck et al. (2011).

2.2.3.2 Long-Chain Versus Short-Chain Distinction

PFAS, predominantly PFAAs, are sometimes described as *long-chain* and *short-chain* as a shorthand way to categorize PFCAs and PFSAs that may behave similarly in the environment; however, it is important not to generalize about PFAA behavior based only on chain length. As recent research suggests, other factors besides chain length may affect bioaccumulation potential of PFAS (Ng and Hungerbühler 2014).

According to the OECD (2013):

- *Long-chain* refers to:
 - PFCAs with eight or more carbons (seven or more carbons are perfluorinated)
 - PFSAs with six or more carbons (six or more carbons are perfluorinated)
- *Short-chain* refers to:
 - PFCAs with seven or fewer carbons (six or fewer carbons are perfluorinated)
 - PFSAs with five or fewer carbons (five or fewer carbons are perfluorinated)

Table 2-2 illustrates the differences in the short-chain and long-chain PFCAs and PFSAs.

Table 2-2. Short-chain and long-chain PFCAs and PFSAs

Number of Carbons	4	5	6	7	8	9	10	11	12
PFCAs	Short-chain PFCAs				Long-chain PFCAs				
	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA
PFSAs	PFBS	PFPeS	PFHxS	PFHpS	PFOS	PFNS	PFDS	PFUnS	PFDoS
	Short-chain PFSAs			Long-chain PFSAs					

Anions Versus Acids

As noted above, the names for the anionic and acid forms of PFAAs are often used interchangeably, but it is critical to know which form is being discussed because of differences in their physical and chemical properties and behavior in the environment (Section 6). Some important things to keep in mind regarding the anionic versus acid forms are:

- Most PFAAs are present in environmental and human matrices in their anionic form. For example, PFOS is present in the environment in the anionic form, perfluorooctane sulfonate.
- Although laboratories may be reporting PFOA or PFOS using the acid form of their name, they are actually measuring the anionic form (for example, perfluorooctanoate or perfluorooctane sulfonate), as this is the form that exists in the environment.
- The acid form and their associated cationic salts have CAS numbers, while the anionic forms may not (Table 2-1). For example, PFOS can exist as different salts (cationic), including sodium, lithium, potassium, or ammonium. Each of these salts will have a different CAS number:
 - PFOS, acid form CAS No.: 1763-23-1
 - PFOS, potassium salt CAS No.: 2795-39-3
 - PFOS, ammonium salt CAS No.: 29081-56-9
- When the salt or acid exists in water or other liquids, it will dissociate (lose its hydrogen atom), and the salt or acid will break off and form the anion (for example, COO⁻ or SO₃⁻). Figure 2-6 illustrates the dissociation of PFBA.

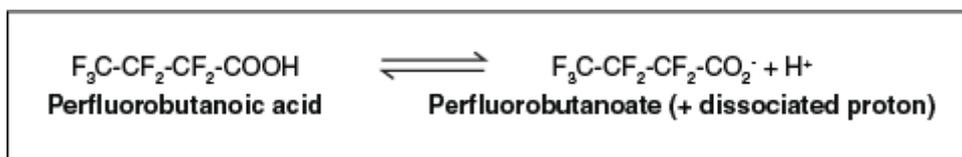


Figure 2-6. Dissociation of PFBA.

- It is most important to distinguish between the acid form and anionic form when reporting the physical and chemical properties. The discussion of PFAS properties in this guidance document generally refers to the anionic form; it will be specifically called out if the acid form is being discussed.

A Note About PFAS Naming in Laboratory Reports (see Section 11)

Even though PFAAs occur as anions in the environment, some laboratories report all of their results in the acidic form, while others may report PFCAs as acids (for example, **perfluorooctanoic acid**) and PFSAAs as anions (for example, **perfluorooctane sulfonate**). Different naming conventions in laboratory reports have led to confusion regarding exactly which form of the PFAA the labs are measuring. Although the lab is measuring the concentration of PFAA anions present in the sample, where the results are reported as an acid, the lab has adjusted for the H⁺ cation (which has so little mass, this does not affect the resulting concentration). It should be noted that the standards used by laboratories to perform analyses may be prepared from PFAA salts, as is often the case for sulfonate standards. If so, the lab must adjust the reported concentration to account for the mass of the counterion (typically Na⁺ or K⁺). The calculation to do this is described in Section 7.2.3 of EPA Method 537 (Shoemaker, Grimmer, and Boutin 2009).

2.2.3.3 Other PFAAs

Other PFAAs include:

- perfluoroalkyl sulfinic acids (PFSiAs), associated with the electrochemical fluorination (ECF) process and also occur as intermediate environmental transformation products
- perfluoroalkyl phosphonic acids (PFPAs) and phosphinic acids (PFPIAs), associated with the fluorotelomerization process and used as surfactants

2.2.3.4 Perfluoroalkane Sulfonamides (FASAs)

FASAs, such as perfluorooctane sulfonamide (FOSA), are used as raw material in the ECF process to make perfluoroalkyl sulfonamide substances that are used for surfactants and surface treatments. FASAs can degrade to form PFAAs such as PFOS.

2.2.3.5 Other Perfluoroalkyl Substances

Other perfluoroalkyl substances shown on Figure 2-3 include:

- perfluoroalkane sulfonyl fluorides [PASFs, such as perfluorooctane sulfonyl fluoride (POSF) and perfluorobutane sulfonyl fluoride (PBSF)], and perfluoroalkanoyl fluorides (PAFs), associated with the ECF process
- perfluoroalkyl iodides (PFAIs) and perfluoroalkane aldehydes (PFALs), associated with the fluorotelomerization process
- perfluoroalkyl ether carboxylic acids (PFECAs) and perfluoroalkyl ether sulfonic acids (PFESAs)

As discussed in Section 2.4, some PFECAs have been developed or used as replacements for other PFAS that are phased out of production and use. This includes GenX chemicals (see text box). Other emerging fluorinated replacement PFECAs more recently detected in the environment, such as perfluoro-2-methoxyacetic acid (PFMOAA), are described in Sun et al. (2016).

GenX Chemicals

A PFCECA, commonly referred to by the trade name “GenX,” has been used by one manufacturer as a replacement for APFO (PFOA) as a surfactant and polymerization aid in the production of their PTFE product. GenX actually refers to the GenX processing aid technology, while the major chemicals used include:

- hexafluoropropylene oxide (HFPO) dimer acid (HFPO-DA, CAS No. 13252-13-6, also known as 2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propanoic acid [PFPrOPrA] or FRD-903) and
- its ammonium salt (ammonium, 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy) propanoate [$\text{CF}_3\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{COO}^-\text{NH}_4^+$, CAS No. 62037-80-3, also known as FRD -902]) (Wang, Cousins, et al. 2013) (Buck 2015) (USEPA 2018d).

Prior to their use in PTFE production, GenX chemicals were produced as a byproduct of other manufacturing processes (NC DEQ 2018). HFPO also is used to manufacture other HFPO-DA derivatives, fluoropolymers (including polyethers), and other specialty agrochemical, semiconductor, and pharmaceutical applications (ATSDR 2018e). HFPO-trimer acid and longer polymer fluorides can be formed from reaction of HFPO-DA.

Further discussion of the GenX chemicals is provided in Section 2.4.6. The chemical structure of the ammonium salt is shown in Figure 2-7.

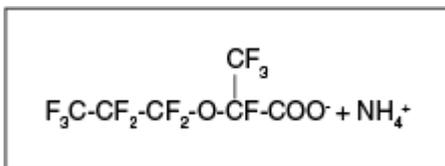


Figure 2-7. Example replacement chemistry structure for GenX Ammonium Salt.

2.2.4 Polyfluoroalkyl Substances

Polyfluoroalkyl substances and some side-chain fluorinated polymers are increasingly being identified as important to understanding the occurrence, fate, and transport of PFAS at release sites and in the environment (OECD 2013; Butt, Muir, and Mabury 2014; Liu and Mejia Avendaño 2013; Wang et al. 2011; Mejia-Avendaño et al. 2016). Figure 2-2 and Figure 2-3 highlight the groups of polyfluoroalkyl substances that, to date, have most commonly been detected at PFAS sites (see Barzen-Hanson et al. 2017; OECD 2018) indicates that of the approximately 4,700 PFAS identified in that study, about 90% were potential precursors to PFAAs.

Polyfluoroalkyl substances are distinguished from perfluoroalkyl substances by not being fully fluorinated. Instead, they have a nonfluorine atom (typically hydrogen or oxygen) attached to at least one, but not all, carbon atoms, while at least two or more of the remaining carbon atoms in the carbon chain tail are fully fluorinated (Figure 2-4).

The carbon-hydrogen (or other nonfluorinated) bond in polyfluoroalkyl molecules creates a “weak” point in the carbon chain that may be susceptible to biotic or abiotic degradation. As a result, many polyfluoroalkyl substances that contain a perfluoroalkyl $\text{C}_n\text{F}_{2n+1}$ group are potential precursor compounds that have the potential to be transformed into PFAAs.

Figure 2-8 provides examples of degradation pathways for environmentally relevant polyfluoroalkyl precursors derived from two PFAS production methods, fluorotelomerization and ECF, respectively (Buck et al. 2011; Liu and Mejia Avendaño 2013; Butt, Muir, and Mabury 2014). Note that these figures include some PFAS not discussed in this guidance document, but described in Buck et al. (2011). Refer to Section 5.4, for further information on transformation processes, noting that not all degradation products will be formed through every environmental transformation process.

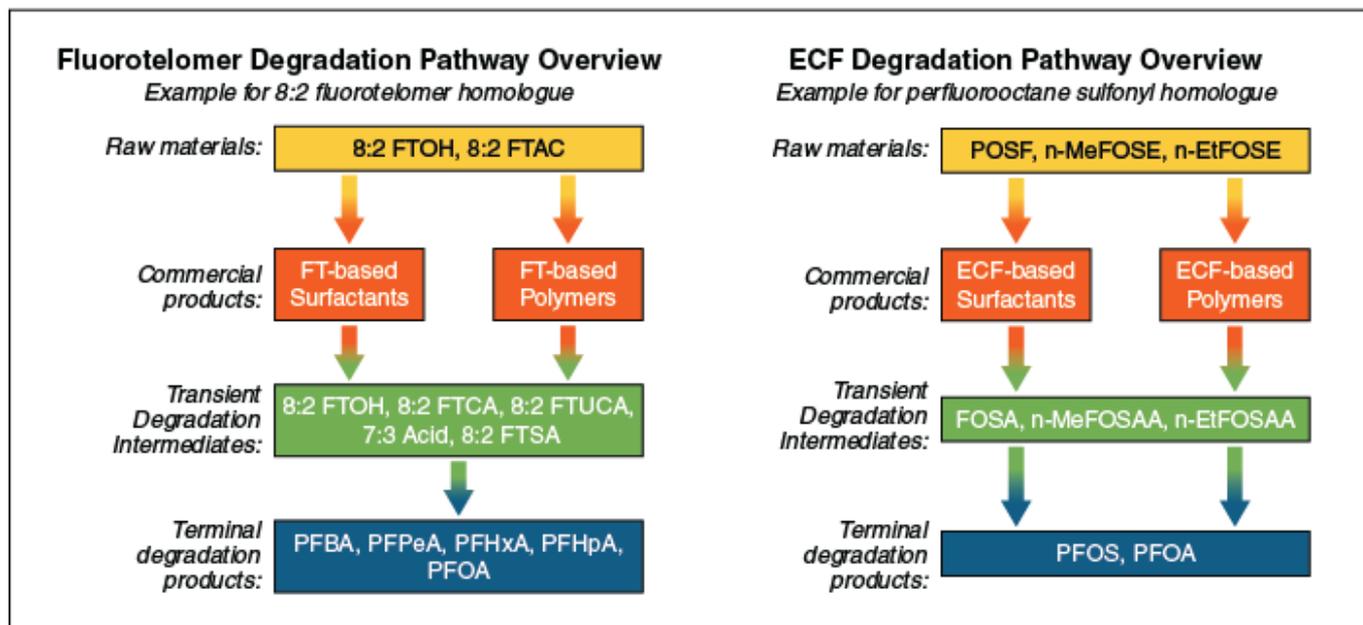


Figure 2-8. Example polyfluoroalkyl substance degradation pathways.

(Note that degradation of POSF-based products is for the terrestrial environment, but transformation into lower homologues of PFCAs and PFSA in the atmosphere is also possible.)

2.2.4.1 Fluorotelomer Substances

Fluorotelomer substances are polyfluoroalkyl substances produced by the fluorotelomerization process. As shown in Figure 2-8, the degradation of fluorotelomer-based substances is a potential source of PFCAs in the environment, but not PFSA (Buck et al. 2011).

Fluorotelomer-based polyfluoroalkyl substances are named using an “n:x” prefix where “n” indicates the number of fully fluorinated carbon atoms ($n \geq 2$) and “x” indicates the number of carbon atoms that are not fully fluorinated ($x \geq 1$). An example of a polyfluoroalkyl substance is shown in Figure 2-9, which also illustrates the “n:x” naming convention.

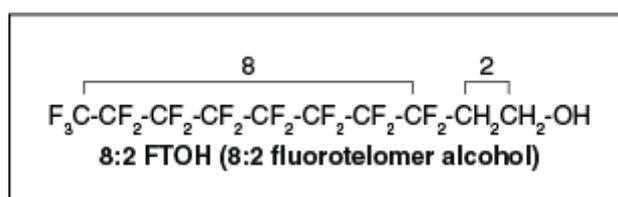


Figure 2-9. Example of a polyfluoroalkyl substance.

The following fluorotelomer substances are those most commonly detected in the environment to date (Section 6):

- *Fluorotelomer alcohols* (FTOH): The n:2 fluorotelomer alcohols (n:2 FTOHs) are key raw materials in the production of n:2 fluorotelomer acrylates and n:2 fluorotelomer methacrylates (Buck et al. 2011).
- *Fluorotelomer sulfonic acids* (FTSA): The n:2 fluorotelomer sulfonic acids (n:2 FTSA) have been detected in environmental matrices at sites where aqueous film-forming foam (AFFF) has been used, and also in wastewater treatment plant effluents and landfill leachate. FTSA are precursor compounds and can undergo aerobic biotransformation to form PFCAs (Buck et al. 2011).
- *Fluorotelomer carboxylic acids* (FTCA): These compounds form through the biodegradation of FTOHs (Figure 2-8; (Buck et al. 2011; Liu and Mejia Avendaño 2013) and have been detected in landfill leachate. Note that the -COOH functional group on these fluorotelomer compounds means they may have either an even or odd number of carbons, so they may have n:2 or n:3 prefixes.

2.2.4.2 Perfluoroalkane Sulfonamido Substances

The subgroups of perfluoroalkane sulfonamido substances shown in Figure 2-3 and discussed below have been detected in the environment and humans (Buck et al. 2011). Perfluoroalkane refers to the fully fluorinated carbon chain tail, but these compounds also contain one or more CH₂ groups in the head of the molecule attached to the sulfonamido spacer (Figure 2-10). They are either used as raw materials for surfactant and surface treatment products, or they are present as intermediate transformation products of these raw materials. As shown in the degradation pathways in Figure 2-8, some perfluoroalkane sulfonamido substances have been found to degrade to PFOS (Mejia Avendaño and Liu 2015). Environmentally relevant perfluoroalkane sulfonamido substances include:

- *N-Alkyl perfluoroalkane sulfonamides* (N-alkyl FASAs) are intermediate environmental transformation products that include N-methyl perfluorooctane sulfonamide (MeFOSA) and N-ethyl perfluorooctane sulfonamide (nEtFOSA).
- *Perfluoroalkane sulfonamido ethanols* (FASEs) and *N-alkyl perfluoroalkane sulfonamido ethanols* (MeFASEs, EtFASEs, BuFASEs) are raw materials for surfactant and surface treatment products (Buck et al. 2011). Figure 2-10 illustrates the structure of nEtFOSE
- *Perfluoroalkane sulfonamido acetic acids* (FASAAs) and *N-alkyl perfluoroalkane sulfonamido acetic acids* (MeFASAAs, EtFASAAs, BuFASAAs) are intermediate transformation products of FASEs, MeFASEs, EtFASEs, and BuFASEs (Figure 2-8) (Buck et al. 2011).

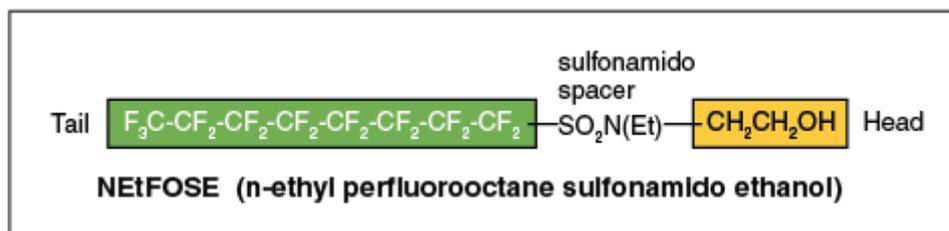


Figure 2-10. Example of a perfluoroalkane sulfonamido ethanol (FASE).

2.2.4.3 Other Polyfluoroalkyl Substances

Other polyfluoroalkyl substances shown in Figure 2-3 include:

- polyfluoroalkyl ether sulfonic acids (PFESAs)
- polyfluoroalkyl ether carboxylic acids
- other fluorotelomer (FT)-based substances.

As discussed in Section 2.4.6, some PFAS have been developed or used as replacements for other PFAS that are phased out of use and production.

One replacement compound for the use of PFOA as a polymerization aid in the production of PTFE is a polyfluoroether carboxylate surfactant: ammonium 4,8-dioxa-3H-perfluorononanoate ($CF_3OCF_2CF_2CF_2-OCHF_2COO^-NH_4^+$ (CAS No. 958445-44-8), commonly referred to by the trade name ADONA (Gordon 2011). The chemical structure is shown in Figure 2-11.

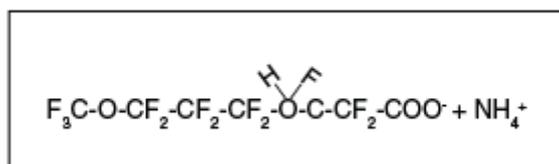


Figure 2-11. Chemical structure for ADONA.

Other replacement polymerization compounds for the manufacture of PTFE and polyvinylidene fluoride (PVDF) include cyclic or polymeric functionalized perfluoropolyethers (PFPEs) (Wang, Cousins, et al. 2013). A sample chemical structure is shown

in Figure 2-12.

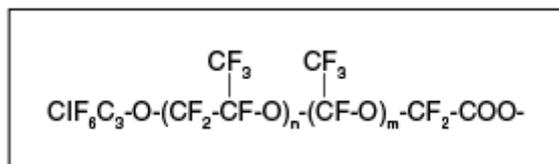


Figure 2-12. Sample chemical structure for a PFPE.

2.2.5 Chemical Manufacturing

To differentiate among PFAS in understanding a conceptual site model for environmental risk assessment, it is important to know about the chemical manufacturing processes. The various manufacturing processes produce different types of PFAS, such as linear and branched isomers (as discussed in this section), which may affect the environmental fate, treatment, toxicology, and site forensics for these chemicals. The type of PFAS that might be formed by the transformation of precursor PFAS at or related to an environmental release site also may depend on the manufacturing process (refer to the family tree in Figure 2-3).

2.2.5.1 Processes

Two major processes, *electrochemical fluorination (ECF)* and *fluorotelomerization*, have been (and are) used to manufacture PFAS substances that contain perfluoroalkyl chains: side-chain fluorinated polymers, perfluoroalkyl acids and polyfluoroalkyl surfactants (USEPA 2003b; Benskin, DeSilva, and Martin 2010; KEMI 2015b; OECD 2018). The fluorotelomerization process may also be characterized as “oligomerization,” as it involves using tetrafluoroethylene (TFE) monomer and adding one to nine TFE monomers to form a perfluoroalkyl chain (Kissa 2001; Rao and Baker 1994). ECF and fluorotelomerization can be used to create some of the same PFAS, as shown on Figure 2-3. PFSAs are produced only using the ECF process, whereas PFCAs can be produced by both ECF and fluorotelomerization (USEPA 2003b; CONCAWE 2016)

More than 600 intermediate processes have been used to further produce certain PFAS and the associated final products. Further discussion of the intermediate processes may be found in the general scientific literature and numerous textbooks specifically written about fluorinated organics and fluoropolymers (Banks, Smart, and Tatlow 1994).

Electrochemical Fluorination (ECF)

The Simons ECF process was licensed by 3M in 1945; 3M subsequently built an ECF pilot in 1949 and started commercial production in 1951 (3M Company 1999a) In the ECF process, an electric current is passed through a solution of an organic feedstock and liquid anhydrous hydrogen fluoride, which causes the hydrogen atoms to be replaced by fluorine atoms, thereby creating carbon-fluorine bonds (3M Company 1999a; USEPA 2003b; Buck et al. 2011). ECF is used to create perfluoroalkane sulfonyl fluorides (PASFs), which are the building blocks for other sulfonyl-based PFAS, as well as perfluoroalkyl carboxylate derivatives. These ECF-synthesized PFAS can contain a variable mixture of linear and branched perfluorinated isomers, as well as other homologues, byproducts, and impurities (USEPA 2003b; Buck et al. 2011). The variable composition is caused by the process conditions, raw materials, and equipment used by the ECF process (3M Company 1999a; CONCAWE 2016). Subsequent processes (for example, hydrolysis, base neutralization) are then used to refine the compounds (USEPA 2003b).

Historically, the ECF process was primarily used to produce POSF-based compounds. This includes PFOS, which is often a terminal degradation product of POSF-based compounds. ECF was also used to produce perfluorooctanyl derivatives (for example, using perfluorooctane carbonyl fluoride to produce PFOA and its salts, such as APFO). As part of the phaseout of production of select long-chain PFAS in the United States, 3M has ceased using ECF to make certain long-chain PFAS, such as POSF-based compounds (PFOS and PFHxS) and PFOA (Buck et al. 2011) (Section 2.4.1). 3M’s phaseout did not include other, shorter chain PASF-based products, such as those based on PBSF (3M Company 2018).

Fluorotelomerization

Fluorotelomerization involves the reaction of perfluoroethyl iodide (PFEI, $\text{CF}_3\text{CF}_2\text{-I}$) with tetrafluoroethylene (TFE, $\text{CF}_2=\text{CF}_2$) to yield a mixture of even-numbered carbon linear perfluoroalkyl iodides ($\text{C}_n\text{F}_{2n+1}\text{-I}$, $n = 4, 6, 8, 10$, etc.), commonly known as “Telomer A.” Telomer A is then reacted with ethylene to make “Telomer B” (perfluoroalkylethyl iodides (PFEIs),

$C_nF_{2n+1}CH_2CH_2-I$, $n = 4, 6, 8, 10$, etc.). Telomer B is reacted to make fluorotelomer alcohols (FTOHs, $C_nF_{2n+1}CH_2CH_2-OH$, $n = 4, 6, 8, 10$, etc.) Telomer A, Telomer B, and FTOHs are the basic raw materials used to manufacture fluorotelomer-based surfactant (nonpolymer) and polymer products (Kissa 2001; Rao and Baker 1994).

As part of the USEPA 2010/2015 Stewardship Program (USEPA 2018a; Section 2.4.3), eight major global fluorotelomer manufacturers phased out production of long-chain (Table 2-2) fluorotelomer-based products that were potential precursors to PFOA and other long-chain perfluorocarboxylic acids (PFCAs). Today, the major global fluorotelomer manufacturers are reported to have refined their processes and predominantly manufacture short-chain (C6) fluorotelomer-based products (<https://www.americanchemistry.com/ATCS/>). Some manufacturers outside of the United States (for example, China, India) have not phased out long-chain PFAS production (Song et al. 2018).

Fluorotelomerization has been primarily used to produce linear (straight-chain) PFAS isomers with an even number of carbon atoms (Buck et al. 2011), although some sources indicate that the process can also produce compounds with an odd number of carbons and branched chains (Lindstrom, Strynar, and Libelo 2011; Danish EPA 2015).

2.2.5.2 Linear and Branched Isomers of PFAS

Many PFAS may be present as mixtures of linear and branched isomers (Figure 2-13) depending on the manufacturing process that was used. These structural differences are important because they may affect how the compounds behave in the environment and may provide an indicator of their source. Structural differences are described below:

- A *linear isomer* is composed of carbon atoms bonded to only one or two carbons, which form a straight carbon backbone. There can be only one linear isomer in a C_n homologue (compounds with the same number of carbons in their tail) series.
- In a *branched isomer*, at least one carbon atom is bonded to more than two carbon atoms, which forms a branching of the carbon backbone. There can be many isomers per C_n homologue series.

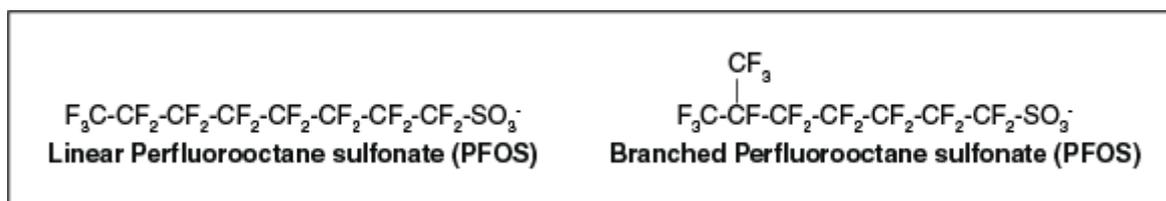


Figure 2-13. Linear and one branched isomer of PFOS.

For simplicity, both linear and branched isomers are abbreviated using the same acronym in this document. Note that other nomenclature conventions further identify PFAS by labeling linear isomers (for example, n-PFOS) and branched isomers based on the location of the branch in the carbon chain (for example, 5m-PFOS) (Benskin, DeSilva, and Martin 2010).

The formula " $C_nF_{2n+1}-$ " (where n is greater than or equal to 3) includes linear and branched structures. For example, PFOS and PFHxS are routinely present in environmental samples as a mixture of linear and branched isomers (Beesoon et al. 2011) (Beesoon et al. 2012) (Benskin, DeSilva, and Martin 2010).

Accurate quantification of PFAS that are mixtures of linear isomers and branched isomers in environmental matrices can be difficult (Riddell et al. 2009). However, the relative contributions of isomers may be useful in understanding sources of PFAS and the age of the source, because the production of isomers varies by manufacturing processes. For example, as discussed above, the fluorotelomerization process has been primarily used to produce mostly linear PFAAs, whereas the ECF process produces a mixture of linear and branched PFAA isomers (Table 2-3). Refer to Section 10.3 for more information on PFAS source identification. The presence of linear and branched isomers may also have implications for partitioning, transport, and bioaccumulation (Section 10.5).

Table 2-3. Manufacturing processes and potential PFAAs produced

Manufacturing Process	Commonly Found Polyfluorinated Substance (Precursors)	Potential PFAAs Produced
Fluorotelomerization	FTSA ¹	Linear PFCAs ³
	FTCA ²	Linear PFCAs ³
	FTOH	Linear PFCAs ³
Electrochemical fluorination	FASE	Branched and linear PFCAs Branched and linear PFSAs
	FASAA	Branched and linear PFCAs Branched and linear PFSAs
¹ Fluorotelomer sulfonate: for example, may be found at AFFF sites ² Fluorotelomer carboxylic acids: for example, 5:3 acid may be found in landfill leachate ³ Under certain instances, can produce mixture of linear and branched PFCAs		

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2.3 Emerging Health and Environmental Concerns

Like other emerging contaminants, knowledge and concern about PFAS in the environment has evolved through a series of phases discussed in this section:

- discovery and/or synthesis of PFAS, followed by growth in commercial production and use (Section 2.2.5)
- emerging health and environmental concerns, including:
 - awareness of potential health impacts (Section 2.3.1)
 - analytical developments (Section 2.3.2)
 - detection in the environment (Section 2.3.3)
 - response in science, regulatory, and legal actions (Section 2.3.4)
- subsequent efforts to reduce use of contaminants of concern and/or replace the contaminants of concern with alternate technologies and chemicals, accompanied by health and environmental questions about those chemicals (Section 2.4)

2.3.1 Awareness of Potential Health Impacts

Occupational studies in the 1970s found detections of some PFAS in the blood of exposed workers, and further studies in the 1990s reported detections in the blood of the general human population (Buck et al. 2011). In recent years, the presence of several long-chain PFAAs (PFOA, PFOS, PFNA, and PFHxS) have been measured in the low parts per billion (ppb, equivalent to nanograms per milliliter (ng/ml)) range in the blood serum of almost all residents of the United States and other industrialized nations (Kato 2015; CDC 2018). These PFAS are present whether or not people were exposed in the workplace, likely due to the widespread use of PFAS in consumer products and industries (Kannan et al. 2004; Kärman et al. 2006; Olsen et al. 2003). Further information and discussion of studies and human health effects can be found in Section 7.1.

These findings led to increased awareness of PFAAs in the environment, associated human exposure, and the potential for health effects. Occupational workers may be more highly exposed, and at risk, than other populations (ATSDR 2018b). Laboratory studies using animals and epidemiological studies of human populations show that exposure to some PFAS may be associated with a wide range of adverse human health effects (USEPA 2016c; USEPA 2016d; ATSDR 2018e). Toxicity studies have mostly focused on PFOS and PFOA, as well as some other long-chain PFAAs (Section 7.1). More recently, the toxicology of other PFAS, such as fluorotelomers and shorter chain PFAAs, as well as replacement PFAS chemicals (such as GenX chemicals, Section 2.4.6), have received increased attention (CONCAWE 2016; USEPA 2016e; USEPA 2018g).

ATSDR is undertaking a national, multi-site PFAS health study to study how PFAS-impacted drinking water may harm health (ATSDR 2020b). The study was authorized by the National Defense Authorization Acts of 2018 and 2019. According to ATSDR, “The information learned from the multi-site study will help all communities in the U.S. with PFAS exposures, including those that were not part of the study.” The multi-site health study builds on the Pease Health Study at former Pease Air Force Base in Newington, NH, which effectively serves as a pilot program. The health study is intended to provide a better understanding of the cause and effect relationship between PFAS at various concentration and specific health outcomes based on adults and children. The study is expected to improve upon epidemiological studies with limited information about exposure factors.

2.3.2 Analytical Developments

Early detection of PFAS in environmental media was hindered by the analytical capability challenges arising from the unique surface-active properties of PFAS (Giesy and Kannan 2001; 3M Company 2000b). Since the 2000s, methods have been, and continue to be, developed with lower detection limits (for example, parts per trillion (ppt)) in water, that are commensurate with levels of potential human health effects. More commercial laboratories now offer these analytical capabilities. For further information on analytical methods, refer to Section 11.

The list of PFAS that can be tested for has also evolved over time, with longer lists of compounds and changing commercial availability helping to drive the evolving health and environmental concerns. Early focus was on PFOA and PFOS, but nationwide testing of drinking water supplies under the USEPA’s Third Unregulated Contaminant Monitoring Rule (UCMR3)

led to four additional PFAAs (PFHpA, PFNA, PFBS, PFHxS) gaining greater attention. More information about UCMR3 is provided in Section 6.3, and a summary of the occurrence data for the six PFAAs analyzed during UCMR3 is provided in Section 8.2.2.2. In Germany, von der Trenck et al. (2018) presented health- and ecological-based PFAS significance thresholds for 7 of 13 priority PFAS for the assessment of contaminated groundwater.

Many state regulatory agencies now request or require testing for an expanded list of long- and short-chain PFAAs, and some potential precursors to PFAAs, such as fluorotelomers. Other polyfluoroalkyl substances are also receiving increased attention, as illustrated in Figure 2-14. Many of these PFAS are also summarized in Figure 2-4.

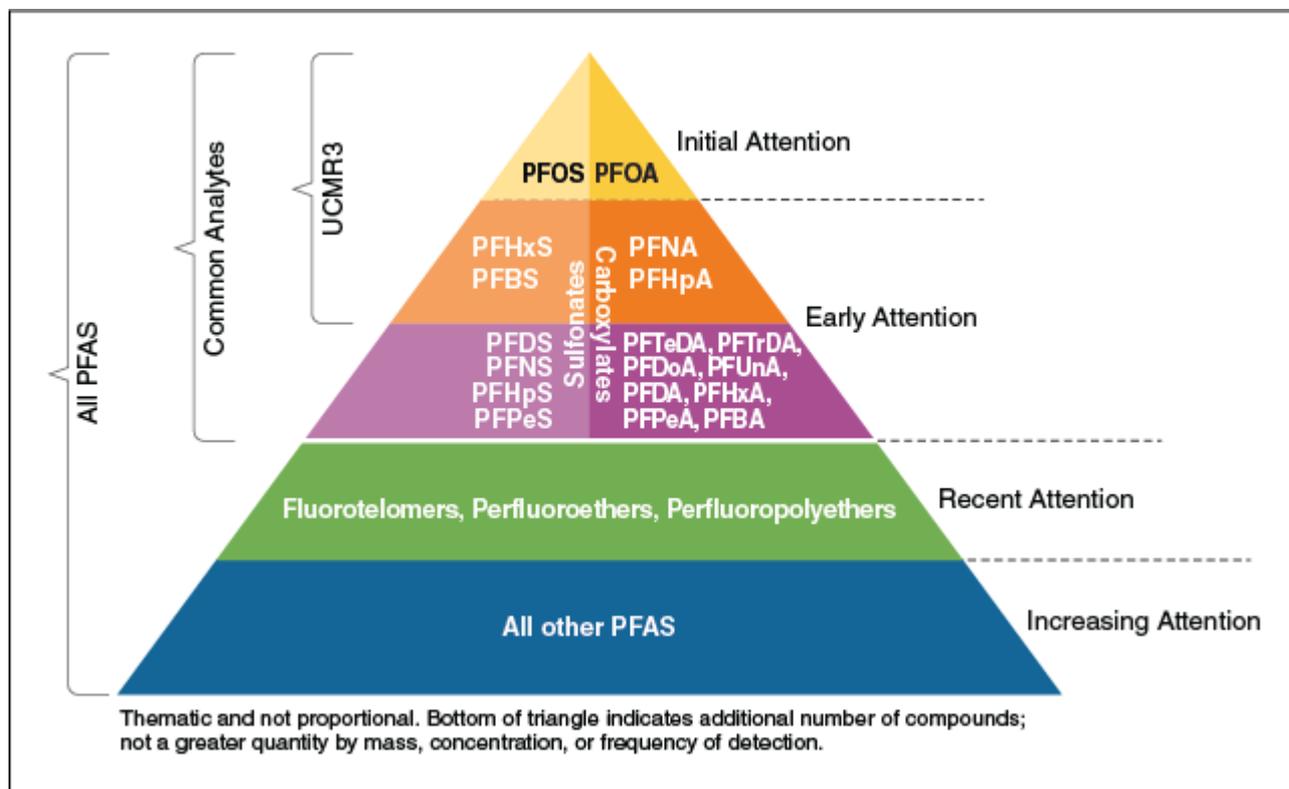


Figure 2-14. Emerging awareness and emphasis on PFAS occurrence in the environment.

Source: J. Hale, Kleinfelder. Used with permission.

2.3.3 Detection in the Environment

Although some PFAS have been manufactured since the 1950s, PFAS were not widely documented in environmental samples until the early 2000s, as PFAS testing was not widely available until that time. Since the early 2000s, however, the occurrence of PFAS in the environment has been a very active area of research. The occurrence of certain PFAS has been reported in a wide variety of matrices, including sediments, surface and groundwater, and wildlife (Kannan et al. 2004; Yamashita et al. 2005; Higgins et al. 2005; Rankin et al. 2016). As noted above, UCMR3 sampling detected PFAS in 4% of drinking water supplies across the country, including in 33 states, three territories, and one Native American community (Hu et al. 2016). Initially, investigations focused mainly on major releases from manufacturing sources and significant PFAS uses such as firefighting foam application sites.

In recent years, with more sensitive analytical methods available, studies have detected PFAS (especially PFAAs) in locations throughout the globe, even in areas well beyond where they were initially used or manufactured (Houde et al. 2011). Detections of certain PFAS in the environment in various media are detailed in Section 6, and ecological effects are described in Section 7.2.

2.3.4 Growing Awareness and Concern

Societal awareness and concern about PFAS have increased since regulatory activity began in the early 2000s. Societal awareness and response are documented in the form of scientific progress and health advisories, federal regulatory actions, and legal actions. Major milestones of these are summarized in Figure 2-15. Other milestones, such as the growth of

knowledge and investigation at major manufacturing and DOD sites in various U.S. states, are not discussed here.

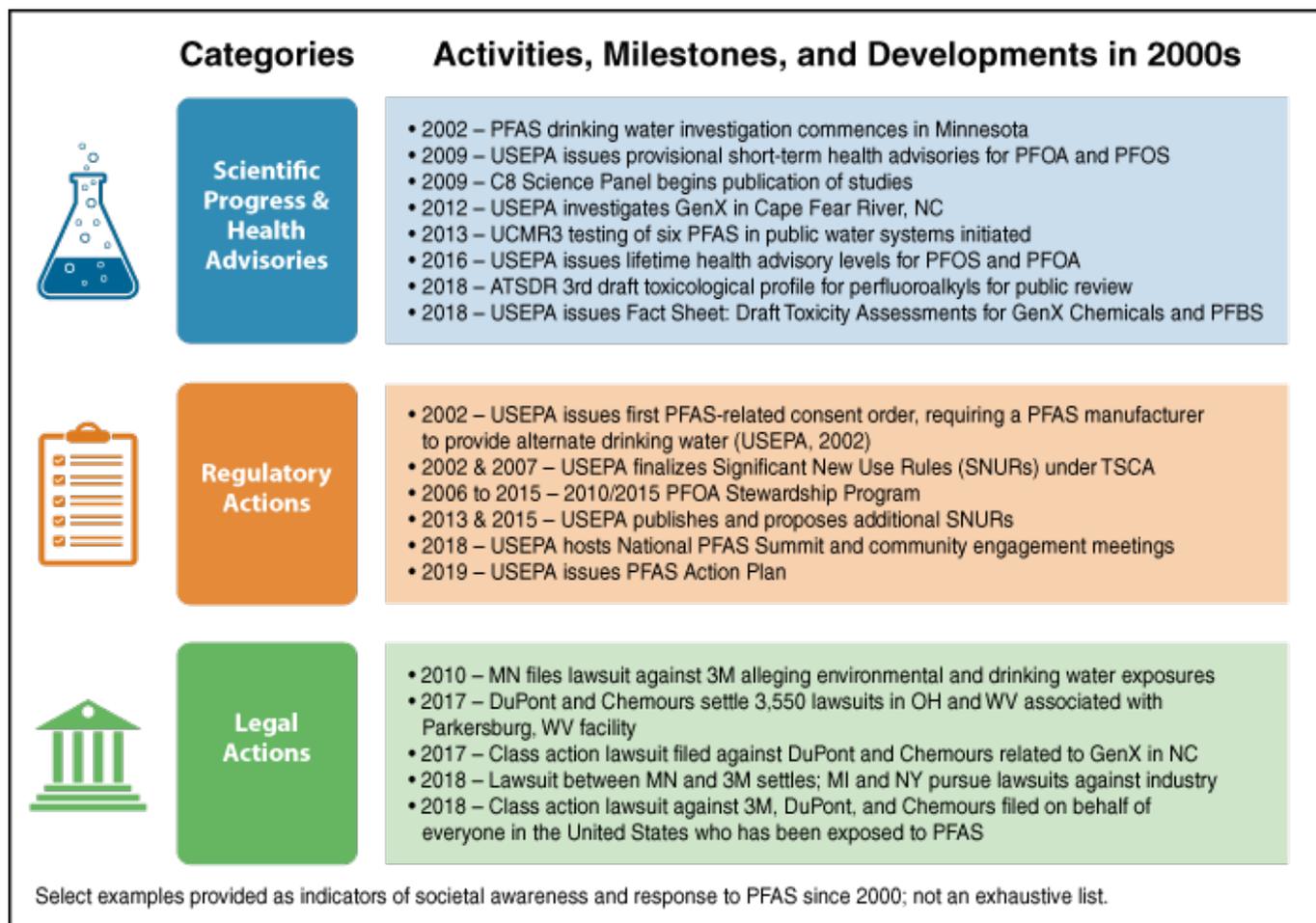


Figure 2-15. Growing awareness and concern since the early 2000s.

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2.4 PFAS Reductions and Alternative PFAS Formulations

Concern regarding the persistence, bioaccumulation, and possible ecological and human health effects of long-chain PFAAs has led manufacturers to use replacement PFAS chemistries, which include reformulating or substituting longer chain substances with generally shorter chain perfluoroalkyl or polyfluorinated substances that should not degrade to long-chain PFAAs, or replacing manufacturing processes with nonfluorinated chemicals or alternate methods (USEPA 2006a; OECD 2017). Manufacturing reductions and phaseouts are described in this section.

2.4.1 3M Voluntary Phaseout of Certain Long-Chain PFAS

In early 2000, 3M was the principal worldwide manufacturer of PFOA and POSF-derived PFAS (for example, PFOS) (Buck et al. 2011). This represented about 80–90% of global POSF-based production (Prevedouros et al. 2006), with 3M the sole U.S. manufacturer of PFOS (USEPA 2003b). In 2000, 3M announced a voluntary, unilateral phaseout (this only applied to 3M) of POSF-derived PFAS, which at the time represented more than 95% of the company's perfluorooctanyl production (3M Company 2000a). The 3M phaseout included the six-, eight-, and ten-carbon PFSAs (PFHxS, PFOS, and PFDS) and related precursors, as well as PFOA (Buck et al., 2011). 3M reportedly completed most of the phaseout by the end of 2002, with the remaining phaseout completed by 2008 (USEPA 2017e); (3M Company 2017).

At the time of the phaseout, 3M's POSF-derived PFAS were used in several applications:

- ~41% for paper and packaging protectors
- ~36% for textiles, leather, and carpet treatment and fabric protectors
- ~19% as industrial surfactants, additives, and coatings (including electroplating and etching surfactants, household additives, insecticides, and other applications)
- ~3% in firefighting foam (3M Company 2000a).

The paper and packaging protectors included POSF-based side-chain fluorinated polymers and phosphate diesters (Wang, Cousins, et al. 2013).

PFOA produced by 3M was primarily used as a fluoropolymer processing aid, with only about 3% of PFOA production used for other applications: mostly in antistatic coatings in medical films, with limited quantities used for electronics applications (for example, to create a humidity barrier on printed circuit boards and to coat precision bearings with silicone oil) (3M Company 2003).

This phaseout applied only to 3M, and only to select PFAS. 3M subsequently used (and reportedly continues to use) ECF to produce PBSF-based PFAS (for example, the four carbon PFSAs: PFBS) (OECD 2013), (Wang, Cousins, et al. 2015)). Any new manufacture and/or import of the PFAS phased out by 3M requires USEPA review based on the Significant New Use Rules (SNURs) described in Section 2.4.2. Based on the 2012 Chemical Data Reporting effort, no company reported manufacture or import of PFOS into the United States (reporting was required for quantities greater than 25,000 pounds) (USEPA 2018a).

When 3M stopped producing PFOA in the early 2000s, it is reported that the manufacture of PFOA was continued by other domestic producers using fluorotelomerization (USEPA 2003b). Domestic PFOA production was later phased out by the eight major domestic producers as described in Section 2.4.3.

2.4.2 USEPA Significant New Use Rules (SNURs)

In conjunction with these voluntary reductions and phase-outs, USEPA used its authority under the Toxic Substances Control Act (TSCA) to finalize four SNURs between 2002 and 2013 to require notification to USEPA before any manufacture (including import) of select PFAS, which include, but are not limited to, some of the PFAS included in 3M's voluntary phaseout of PFOS and related chemicals (Section 2.4.1). USEPA proposed another SNUR for select PFAS in 2015 that has yet to be finalized, primarily focused on certain PFCAs (e.g., PFOA) and their precursors included in the 2010/2015 PFOA Stewardship Program (Section 2.4.3). For further discussion of the SNURs, including 2020 developments, see Section 8.

2.4.3 USEPA PFOA Stewardship Program

In January 2006, USEPA initiated the 2010/2015 PFOA Stewardship Program (USEPA 2006b). Most PFOA produced in 2003 (around the time of the phaseout described in Section 2.4.1) was used as a processing aid in the manufacture of fluoropolymers, such as PTFE (USEPA 2003b), and this was likely still the case at the time the stewardship program began.

The eight major manufacturing or processing companies that participated in the program are reportedly those that manufactured or processed the majority of these chemicals, including Arkema, Asahi, BASF Corporation (successor to Ciba), Clariant, Daikin, 3M/Dyneon, DuPont, and Solvay Solexis (USEPA 2018a). There may be other manufacturing or processing companies that did not participate in the program (USEPA 2015d). USEPA indicated that the eight participating companies successfully met the program goals, meeting a 95% reduction by 2010 in global facility emissions and product content, and eliminating production (100% reduction) of PFOA, certain longer chain PFCAs (higher homologues such as PFNA and PFDA), and related PFOA precursors (for example, 8:2 FTOH) by 2015 (USEPA 2017e). Even though the program goals were met by the eight companies, the ongoing use of PFOA stock and imported materials has not been fully restricted (USEPA 2018a). Products manufactured and imported prior to 2015, and materials with ongoing uses, may still contain these PFAS (USEPA 2018b), and PFOA may be present as a trace contaminant in some other PFAS and fluoropolymer products (3M Company 2003). As discussed in Section 2.4.5, production is ongoing in other nations.

2.4.4 Stockholm Convention on Persistent Organic Pollutants

The Stockholm Convention on Persistent Organic Pollutants (POPs) is a United Nations treaty signed in 2001 aimed at reducing or eliminating the production, use, and release of key POPs. POPs are defined as synthetic, organic compounds that, to varying degrees, resist photolytic, biological, and chemical degradation (KEMI 2004, 2015b); (USEPA 2017j). Chemicals listed as POPs satisfy screening criteria for persistence, bioaccumulation, long-range environmental transport, and adverse effects (Stockholm Convention 2001). The Stockholm Convention targets PFAS in these ways:

- In 2009, *Annex B of the Stockholm Convention* (which restricts production and use) was amended to include PFOS (and its salts and POSF), because it is persistent in the environment and is not known to degrade at any environmental condition. Currently, the United States has not ratified the amendment (KEMI 2017)). Annex B is not an outright ban; it allows certain approved uses and exemptions of POPs. Prior to 2019, approved, ongoing uses for PFOS under Annex B included select applications in photoimaging, semiconductor coatings and etching agents, metal plating, insect baits, chemically driven oil production, aviation hydraulic fluids, some medical devices, and color printer electronic parts (UNEP 2008, 2009).
- According to the Stockholm Convention website:
 - In May 2019, Annex B was amended to discontinue several of the previously allowed ongoing uses (UNEP 2019a).
 - Annex A was amended in May 2019 to prohibit and/or eliminate the production and use of PFOA (its salts and PFOA-related compounds), with certain exemptions (UNEP 2019a).
 - the POPs Review Committee recommended in October 2019 to list PFHxS (and its salts and related compounds) in Annex A without specific exemptions (UNEP 2019b)

2.4.5 Global Manufacture and Use of PFAS

PFAS are still manufactured globally, despite some PFAS (most notably PFOA and PFOS) no longer being produced in the United States, Europe, and Japan (FluoroCouncil 2018). For further information, see OECD's "Risk Reduction Approaches for PFASs" (OECD 2015b). In addition to the domestic reductions discussed in Section 2.4.1 and 2.4.3, some of the phase-outs and restrictions are summarized below.

In 2017, the South Australia state government took initial steps to develop legislation banning environmentally harmful foams, such as Class B firefighting foams containing PFAS (SA EPA 2017).

Canada embarked on an Environmental Performance Agreement with four major manufacturers to phase out PFOA and related compounds from 2010 to 2015 (CEPA 2006). In 2008, Canada prohibited the use of most PFOS, with select exemptions such as use of existing stocks of PFOS-based firefighting foams, and then added PFOS to the Virtual Elimination List in 2009 and to the Prohibition of Certain Toxic Substances Regulations in 2016 (CEPA 2018). By 2016, Canada prohibited the import, manufacture, use and sale of PFOS, PFOA, and other long-chain PFCAs (and salts and precursors), with limited exemptions (CEPA 2018), and subsequently in 2018, Canada proposed further modification to those restrictions (Government of Canada 2018).

In 2009, the European Union (EU), through the European Chemicals Agency (ECHA), regulated PFOS as a POP, and use of PFOS is limited to certain restrictions (Vierke et al. 2012). In 2017, the EU banned the sale, use, and import of PFOA, its salts and PFOA-related substances through Annex XVII of the European Chemicals Regulation (REACH), with phase-outs occurring through 2032 and certain allowed uses. ECHA is currently considering restrictions for other long-chain PFCAs, their salts and precursors, as well as other compounds, such as PFHxA (ECHA 2018).

In Japan, there are restrictions on the manufacture, import, export, and use of PFOS and its salts (OECD 2015a).

The global reduction anticipated with the U.S. phaseout of PFOA has potentially been offset by increased production of PFOA and related PFAS in China, India, and Russia (OECD 2015b). PFAS manufacture began in China in the 1980s (World Bank 2017b) (2017a), and PFOS production in China increased coincident with the long-chain PFAA phaseout in the United States (CONCAWE 2016) (OECD 2015b). In 2016, PFOS and its derivatives were still being produced in Germany, Italy, and China (TTE 2016), but by early 2017, China was the only known producer of PFOS. China has ratified the Stockholm Convention on POPs and was awarded a grant from the Global Environment Facility (GEF) in 2017 to support the reduction of PFOS in China (World Bank 2017b). China has developed some guidance for restriction and limitations of some PFAS (OECD 2015b). In Brazil, EtFOSA, which is a precursor to FOSA and PFOS and used in the pesticide sulfluramid, which is still being produced on an industrial scale, is allowed as an approved use by the Stockholm Convention (Löfstedt Gilljam et al. 2016).

There does not appear to be a comprehensive reference publically available to document the individual PFAS and the quantity of PFAS produced over the years. This is possibly because these data are proprietary, but also due to modifications to chemistries and products over the years (Lindstrom, Strynar, and Libelo 2011), complexity of the issue, and the general lack of publically available data (OECD 2018). That said, some estimates of production and emissions of select PFAS have been made based on the limited available data.

Prevedouros et al. (2006) estimated global emission of PFCAs at about 3,500–8,000 tons between the 1950s and 2002, with approximately 80% of emissions related to fluoropolymer manufacture (and use), based on overall annual production estimates of:

- APFO (ammonium salt of PFOA)-about 335–525 tons per year between 1951 and 2002
- APFN (ammonium salt of PFNA)-about 60–225 tons per year between 1975 and 2004
- POSF (building block for PFOS)-about 9,550 tons per year from 1960 to 2002.

Other production and emissions estimates for PFCAs are available from OECD (2015b), and for PFOS and PFOS precursors from Armitage et al. (2009), and Paul, Jones, and Sweetman (2009). OECD (2015b) calls for a new, comprehensive survey to evaluate both historical and ongoing emissions.

2.4.6 PFAS-Based Replacement Chemistry

With the emerging awareness of potential health and environmental impacts of some PFAS and related limitations on production of some PFAS, such as the SNURs (Section 2.4.2) and 2010/2015 PFOA Stewardship Program (Section 2.4.3), manufacturers began efforts to replace the use of long-chain PFAS chemistries with nonfluorinated chemicals, alternate technologies, and/or other, shorter chain PFAS (Wang, Cousins, et al. 2013). For example, decorative chrome plating typically now uses less toxic chromium III instead of chromium VI so that PFAS are not needed (Wang, Cousins, et al. 2013).

Some of the replacement chemicals are said to achieve the same performance effectiveness of some of their predecessors. A carpet manufacturer has found that performance of fluorine-free alternatives is “equivalent or superior to the fluorinated treatments” pg. 66, (CalEPA 2018). Conversely, a 2015 study concluded that there are no nonfluorinated alternatives that provide equivalent technical performance in textiles (Danish EPA 2015). PFAS-free AFFF has yet to be demonstrated to meet US Department of Defense performance specifications, but have been adopted by some other users (Section 3.8.1 and 3.10).

Several studies suggest some of the alternate PFAS chemistries may or may not be less hazardous than the long-chain predecessors, although publicly available information on most replacement chemicals is limited (Wang, Cousins, et al. 2015) (RIVM 2016); (OECD 2015b). Documentation regarding the USEPA’s review of hundreds of “shorter chain-length PFAS telomeric” substitutes is available under the TSCA New Chemicals Program (OECD 2013); (USEPA 2017i), and other documentation regarding replacement PFAS chemistries is available from the FluoroCouncil (2017). Draft toxicological evaluations have been provided for public comment by the USEPA for GenX chemicals and PFBS (USEPA 2018d) (USEPA 2018e). For further discussion of toxicity documentation for select PFAAs and replacement chemistries, see Section 7.

Although a full discussion of such PFAS chemistries is not possible here, it is important to be aware of the trend toward

shorter chain chemistries, as some of these PFAS increasingly may be detected in the environment. Some replacement PFAS have been detected in the environment and generated public concern and regulatory actions; however, information on significant environmental contamination by replacement PFAS is limited, and most are not detected by standard analytical methods (Wang, Cousins, et al. 2013). Some PFAS used as replacement chemicals, such as HFPO-DA and ADONA (used as replacements for APFO/PFOA in PTFE manufacture), and F53B (used as a replacement for PFOS in plating), have recently been added to USEPA Method 537.1 (Shoemaker and Tettenhorst 2018). Treatment processes used to remove these chemicals from waste streams may not be as effective as with longer chain PFAS (Sun et al. 2016).

Alternate PFAS chemistries are being used to replace long-chain PFAAs that have been phased out of production and/or use. In many cases, although similar legacy PFAAs were manufactured and used by many companies, these same companies have transitioned to the use of many different types of other PFAS as alternative chemicals. Many of these replacement PFAS are structurally similar to their long-chain predecessors, and are typically also manufactured using electrochemical fluorination (ECF) or fluorotelomerization (Wang, Cousins, et al. 2015) (CONCAWE 2016). Some of these fluorinated substitutes may degrade to form short-chain PFAAs. Some short-chain PFAAs, PFECAs, and related chemicals were manufactured as early as the 1980s, or earlier (Wang, Cousins, et al. 2015). Some PFAS used to replace long-chain PFAS are presented below (Hori et al. 2006; OECD 2007; Herzke, Olsson, and Posner 2012; Buck 2015; Wang, Cousins, et al. 2013; Wang et al. 2014; Wang, Cousins, et al. 2015; KEMI 2015b; Sun et al. 2016; Holmquist et al. 2016):

- short chain homologues of the long-chain PFAAs, including PBSF-based derivatives (for example, 4-carbon chain PFBS in lieu of POSF-based six-, eight-, and ten-carbon chain compounds) in many applications, including surface treatment
- perfluorohexane sulfonyl fluoride (PH_xSF, which can degrade to PFH_xS and is considered to be phased out in the United States) as an alternative to PFOS, primarily in China
- fluorotelomer-based products such as FTOH, for example, those with a six-carbon perfluorohexyl chain, including 6:2 fluorotelomer-based compounds in AFFF formulations and other six-carbon fluorotelomer-based products, side-chain fluorinated polymers, and PFPE products for surface treatment of food contact materials
- per- and poly-fluoroalkyl ether substances used as polymerization aids in manufacture of fluoropolymers, such as GenX chemicals (Section 2.2.3.5) and ADONA used as a replacement for APFO in the manufacture of PTFE, as well as other types of PFAS, such as cyclic or polymeric functionalized PFPEs as a replacement for APFN in the manufacture of polyvinylidene fluoride (PVDF)
- 6:2 fluorotelomer-based compounds, a PFBS-based compound, and fluorotelomer-based F-53 and F-53B (perfluoroalkyl ether potassium sulfonate) in lieu of PFOS in metal plating applications.

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2.5 PFAS Uses

PFAS have been produced on a commercial scale since the 1950s, and production continues today. The unique physical and chemical properties of PFAS impart oil, water, stain, and soil repellency, chemical and temperature resistance, friction reduction, and surfactant properties to a wide range of products.

Table 2-4 provides a general (not exhaustive) introduction to some of the uses of PFAS fluorochemistries that are, or have been, marketed or used (3M Company 1999a)) (Poulsen 2005) (OECD 2006) (Washington State Department of Ecology 2012) (OECD 2011) (OECD 2013) (Fujii, Harada, and Koizumi 2013) (OECD 2015b) (FluoroCouncil 2018) (Henry et al. 2018). The specific applications for all PFAS are not well documented in the public realm. For example, of the 2,000 PFAS identified in a 2015 study, only about half had an associated listed use (KEMI 2015b). Further discussion of select uses that may be associated with potentially significant environmental releases are provided in Section 2.6.

As discussed in Section 2.2.2.1, most polymer PFAS are considered to pose relatively less risk to human health and the environment than some nonpolymer PFAS. For this reason, Table 2-4 distinguishes between these two major classes of PFAS and where they are used in various industries and products. The major industries and applications summarized in the table are described in more detail in Section 2.6.1.

Table 2-4. Sample historic and current uses of PFAS

Industry/Application	PFAS Type	Documented Use and Examples of Some PFAS
Aviation and Aerospace	Polymer	Mechanical components made of fluoropolymers (such as PTFE and PFA tubing, piping, seals, gaskets, cables, and insulators)
	Nonpolymers	Hydraulic fluid additives made from PFSA salts (such as PFOS at about 0.1%) to prevent evaporation, fires, and corrosion
Automotive	Polymer	Mechanical components made of fluoropolymers, including wiring and cable, fuel delivery tubing, seals, bearings, gaskets and lubricants, and some polymer coatings on carpets
	Nonpolymers	Surface treatment for textiles, upholsteries, carpets, leather and exterior surfaces
Biocides (Herbicides and Pesticides)	Polymer	None reported
	Nonpolymers	Active ingredients such as short-chain sulfonamides in plant growth regulators and herbicides, and EtFOSA (sulfluramid) in ant and termite baits; inert enhancing ingredients in pesticides; PFPAs and PFPiAs as anti-foaming agents in solutions
Building and Construction	Polymer	Fluoropolymer membranes and coatings (such as PTFE, PVDF, and/or side-chain fluorinated polymers) in architectural materials (like fabrics, roofing membranes, metals, stone, tiles, concrete, radomes); adhesives, seals, caulks; additives in paints (for example, low- and no-VOC latex paints), varnishes, dyes, stains, sealants; surface treatment agent and laminates for conserving landmarks
	Nonpolymers	Additives in paints, coatings, and surface treatments (PASf- and fluorotelomer-based compounds, ammonium salt of PFHxA)
Cable and Wiring	Polymer	Coatings and jacketings made of fluoropolymers (such as PTFE and PVDF) for weathering, flame, and soil resistance, with cables used in many applications, including communication facilities, antennae, and computer networks
	Nonpolymers	None reported
Cosmetics/Personal Care Products	Polymer	Dental floss and micro powders used in creams and lotions.
	Nonpolymers	Cosmetics, shampoos, nail polish, eye makeup, denture cleaners

Industry/Application	PFAS Type	Documented Use and Examples of Some PFAS
Electronics	Polymer	Fluoropolymers (such as PVDF and PTFE) used in insulators, solder sleeves, printed circuit boards, cell phones, computers, speakers, and transducers
	Nonpolymers	Flame retardants for polycarbonate resin (such as the potassium salt of PFBS)
Energy	Polymer	Fluoropolymer films (such as FEP, PVDF) to cover solar panel collectors, electrolyte fuel cells, PTFE expansion joint materials for power plants
	Nonpolymers	Fuel cell and battery electrolyte (such as the lithium salt of PFAAs)
Firefighting/Safety	Polymer	Fluoropolymers used in firefighting equipment and protective clothing (such as those woven with PTFE). Other polymer coatings using side-chain fluorinated polymers)
	Nonpolymers	Coatings and materials used as water repellents and some Class B foam (may contain PFCAs, PFSAs, and fluorotelomer-based derivatives), vapor suppression for flammable liquids (for example, gasoline storage)
Food Processing	Polymer	Fluoropolymer fabrication materials (such as PTFE) (liners for trays, ovens, grills)
	Nonpolymers	May be used as coatings on food packaging
Household Products	Polymer	Nonstick coatings (fluoropolymers such as PTFE); aftermarket treatment for textiles, upholsteries, carpets, and leather (such as FT-based side-chain fluorinated polymers)
	Nonpolymers	Aftermarket treatment for textiles, upholsteries, carpets, and leather (such as PASFs); floor polishes (such as the ammonium salt of PFDA), coatings, and floor finishes (PFPA and PFPIAs) and cleaning agents and alkaline cleaners; automobile waxes; may include PFAAs, PASF- and fluorotelomer-based derivatives
Medical Products	Polymer	Fluoropolymers used in surgical patches, cardiovascular grafts, raw materials for human body implants (such as catheters, stents, needles, and other) given biocompatibility and extremely low coefficient of friction
	Nonpolymers	X-ray film, stain- and water-repellent protective medical fabrics (like surgical drapes and gowns) created from PASF- or fluorotelomer-based (meth)acrylate polymers and polyurethanes
Metal Plating	Polymer	None reported
	Nonpolymers	Wetting agent, mist suppression for harmful vapors, and surfactants (may include potassium, lithium, diethanolamine and ammonium salts of PFOS or 6:2 FTS)
Oil Production	Polymer	Lining of gas pipes
	Nonpolymers	Marketed for and potential instances of use in oil well production
Mining	Polymer	None reported
	Nonpolymers	Instances of surfactants used in ore mining flotation
Paper and Packaging	Polymer	Oil and grease and water repellent to paper, paperboard, molded pulp products (including food contact materials), and LDPE bags; examples include side-chain fluorinated polymers in which the PASF- or fluorotelomer-based alcohols or their acrylate or methacrylate esters are attached on side chains
	Nonpolymers	Phosphate ester salts (esterification of PASF or FT-based alcohols with phosphoric acid; PFPEs)
PFAS Production	Polymer	Not applicable
	Nonpolymers	Emulsion polymerization processing aids for fluoropolymers (such as PTFE, FEP, PFA, PVDF), (co)monomer of side-chain fluorinated polymers; (co)monomer of fluoropolymers and to make fluoroelastomers; may use salts of long-chain PFCAs (such as PFOA and PFNA), salts of short-chain PFCAs (such as PFHxA), or PFECAs

Industry/Application	PFAS Type	Documented Use and Examples of Some PFAS
Photolithography & Semiconductor	Polymer	Equipment raw materials (such as PFA) for molded wafer baskets to handle corrosive liquids and gases, use as fluids in mechanical vacuum pumps
	Nonpolymers	Photolithography (such as using PFOS) in manufacture of semiconductor chips
Textiles (Upholstery, Carpets), Leather, and Apparel	Polymer	Fluoropolymers (such as PTFE) are used in the construction of outdoor gear, clothing, and housewares; side-chain fluorinated polymers (such as PASF- or fluorotelomer-based (meth)acrylate polymers and -polyurethanes) may be used in oil- and water-repellent and stain release finishing and treatment coatings
	Nonpolymers	PFOA-based chromium treatment for paper and leather. Nonpolymer coatings used to treat textiles to provide oil- and water- repellent and stain release finishes

Information presented in this table captures potential instances of use but is not intended to indicate universal use. In addition, the table is not exhaustive of PFAS use in various industries.

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2.6 PFAS Releases to the Environment

This section summarizes sources of PFAS releases to the environment that have the potential for significant environmental impact, based on the type and magnitude of the release, and the types and concentrations of PFAS associated with that release. These sources are sites where PFAS could be, or are known to have been, released to the environment, even if the site is not the location where the PFAS were generated or used. Refer to Section 2.1 for a discussion of the relative significance of releases and source control, as not all of these facilities will have, or have been documented to have, PFAS releases, and not all releases are of the same magnitude.

These major sources are located both in the United States and abroad, and include:

- industrial facilities that produce PFAS or process PFAS, or facilities that use PFAS chemicals or products in manufacturing or other activities (Section 2.6.1)
- areas where fluorine-containing Class B firefighting foams are stored, used, or released (Section 2.6.2)
- waste management facilities, such as landfills (Section 2.6.3)
- wastewater treatment residuals and areas of biosolids production and application, with more significant impacts associated with industrial wastewater discharges (Section 2.6.4).

The fate and transport processes and distribution of PFAS in the environment are discussed in Section 5. Media-specific occurrence data are discussed in Section 6. Information about risk assessment, and human and ecological receptors is included in Section 9. Discussion of conceptual site model (CSM) components for each of the PFAS release categories listed above is included in Section 10.2.1.

2.6.1 Major Manufacturing and Industry Sources

Industrial source sites include primary and secondary manufacturing facilities. Primary manufacturing facilities are those where PFAS-containing products are synthesized and made into products or chemical feedstocks, or where PFAS are used as processing aids in fluoropolymer production. PFAS processing aids are not intended to be in the final product, but may be present at trace quantities (3M Company 2003) (Buck et al. 2011).

Secondary manufacturing facilities may use fluoropolymers and PFAS-based materials produced at primary manufacturing facilities as part of industrial processes, such as the application of coatings to finished products. In some industrial settings, PFAS are used for worker safety purposes, such as using PFOS-based materials to suppress harmful mists during electroplating activities (Section 2.6.1.3).

PFAS composition and release mechanisms will vary for each facility. The composition of PFAS released from industrial facilities depends on the type of PFAS produced or used by the facility.

The general PFAS release mechanisms and pathways at industrial facilities are illustrated in CSM Figure 2-16 and include wastewater and stormwater discharges; on- and off-site disposal of solid wastes; accidental releases such as leaks and spills; and stack and fugitive emissions. Stack emissions may result in aerial deposition of PFAS to soil and surface water (with subsequent leaching and infiltration to groundwater) related to the facility (Davis et al. 2007; Shin et al. 2011), as well as short- and long-range air transport of PFAS. Industrial facilities may also contain areas where fire training or fire response using AFFF has occurred, AFFF storage areas, and AFFF fire suppression systems inside buildings. Like many AFFF release sites, industrial sites may also have releases of co-contaminants (solvents, petroleum products, etc.) that could potentially influence fate and transport of PFAS.

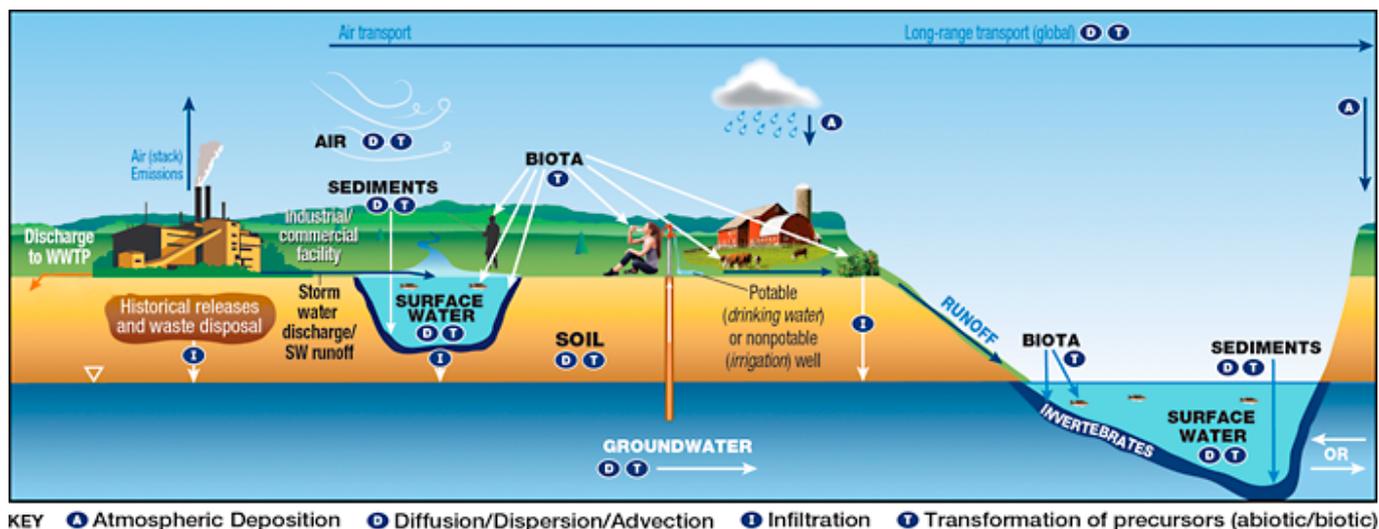


Figure 2-16. CSM for industrial sites.

Source: Adapted from figure by L. Trozzolo, TRC, used with permission.

The following subsections provide further details regarding potential sources of PFAS releases to the environment from PFAS use in manufacturing or industrial processes; these are not presented in order of the potential for significance of a release.

2.6.1.1 Building and Construction

Similar to other products, the chemical attributes of PFAS have led to advancements in building and construction materials. One particular application has been in composite wood and oriented strand board (OSB). Over the last 50 years, wood-based materials have used numerous additives for product strength and durability. A recent study performed on wood samples and OSB found primarily short-chain PFCAs and PFOA at concentrations ranging from 1.38 to 13.9 micrograms per kilogram ($\mu\text{g}/\text{kg}$) for PFCAs (Bečanová et al. 2016). Furthermore, wood fiber insulation has been shown to contain high amounts of PFHpA and other 5- to 8-carbon chain PFCAs (Bečanová et al 2016). Many manufacturers use urea- or phenol-formaldehyde due to their performance and low cost; however, the composition of the resins used by many manufacturers is proprietary.

Other materials, including certain types of building insulation (phenolic foam) have shown high amounts of PFOS. Additionally, PFAS (predominantly C8-C20 gamma-omega-perfluorotelomer thiols with acrylamide) have been used in the production of light weight concrete, concrete sandwich panels, and lightweight concrete blocks (Bečanová et al. 2016; Posner et al. 2013). The prevalence of these building materials in the construction of fire training areas, AFFF storage facilities, and other areas potentially exposed to PFAS led to potential issues with demolition waste. The porous nature of these materials (for example, concrete, brick) could lead to PFAS adsorption/absorption, representing a potential source of PFAS when disposed in landfills or recycling facilities (Australia Government DOD 2019).

PFAS, including fluoropolymers such as PTFE, are used in the manufacture of architectural fabrics, such as those used in the construction of roof domes, including large stadiums and transportation facilities (FluoroCouncil 2018).

PFOS-related chemicals have several uses in paint and varnishes. They can be used as wetting, leveling, and dispersing agents, and have also been used to improve gloss and antistatic properties. Additionally, they can be used as additives in dyestuff and ink. Furthermore, they can be used as pigment grinding aids or as agents to combat pigment flotation problems (KEMI 2004) (RPA 2004). Fluorosurfactants are commonly used in coatings application for substrate wetting, leveling, reduction of surface tension, oil repellency, and dirt pickup resistance (Danish EPA 2015; Posner et al. 2013).

Information received from different suppliers within the paint and varnish industry suggests that fluorinated surfactants in general are much more expensive alternatives compared to other surfactants. Therefore, fluorosurfactants are used only for special purposes in paint and varnishes, where it is necessary to gain such a low surface tension that no other (nonfluorinated) alternatives can achieve (Danish EPA 2015).

2.6.1.2 Cable and Wiring

In the 1950s the wire and cable industry began to use extruded grades of PTFE. This is a suspension polymerization process, which does not require surfactants, unlike dispersion polymerizations (for example, Teflon-coated pans). Melt extrusion is the process by which most fluoropolymers are applied to wires. For instance, FEP, PFA, and PVDF are heated to 260°C and

then melt extruded over wire to continuous lengths. The equipment used for melt-processable fluoropolymers requires temperature sensitivity of 427°F. PTFE is processed via paste extrusion for coating PTFE over wires due to its high melting point (ASTSWMO 2015) (Kotthoff et al. 2015) (Lau et al. 2007) (Lindstrom, Strynar, and Libelo 2011) (Oliaei et al. 2013) (Renner 2001) (Trudel et al. 2008). For more information on the safe handling of fluoropolymer resins during processing, see the Plastics Industry Association (2019) guidance document.

2.6.1.3 Metal Finishing and Plating

Electroplating is a process that uses electric current to apply a metal coating to the surface of an object. Metallic ions in an acidic electrolyte solution are used in the electrochemical deposition of metal coatings to the surface of the cathode (USEPA 1996a).

PFAS, particularly PFOS, have been used as mist suppressants that are added to metal plating and finishing baths to prevent air emissions of toxic metal fumes. In the United States, amendments to the National Emissions Standards for Hazardous Air Pollutants (NESHAP) under the Clean Air Act included a requirement to phase out the use of PFOS-based fume suppressants (a fume suppressant that contains 1% or greater PFOS by weight) in chromium electroplating by 2015 (USEPA 2012e). Some countries have phased out the use of PFOS in some electroplating operations, adopting the use of other fluorotelomers (for example, 6:2 FTS) as a substitute in hard chrome plating operations (Danish EPA 2015), (KEMI 2015b) or changing decorative chrome plating operations to employ the less toxic trivalent chromium.

Many different types of electroplating solutions can be used in plating activities, including hard and decorative chrome plating; chromic acid anodizing; nickel, cadmium, or lead plating; metal plating on plastics; and alkaline zinc plating. Chrome electroplating is the most significant contributor as it relates to PFAS use. In this process, PFAS are used as surfactants to reduce the surface tension of the electrolyte solution. Historically, PFOS was commonly used at a concentration of 5–10% to limit the development of bubbles and the emission of hexavalent chromium aerosols to workplace air, thereby reducing the potential hazard to workers posed by hexavalent chromium (USEPA 2009b) (OSHA 2013) (Danish EPA 2015).

Studies show use of PFAS in these settings can result in high concentration wastewater discharges (USEPA 2009b) and air emissions. Once the electrolyte solution can no longer be used, it may be treated to remove chromium and other metals, but PFOS and other PFAS may be present in effluent and deposited in sewage sludge (Danish EPA 2015). Investigations in Minnesota traced PFOS releases from one chrome plating operation to a wastewater treatment plant (WWTP) where elevated levels of PFOS were detected in the biosolids, effluent water, and fish in the receiving surface water (ATSDR 2008). Air emissions from another Minnesota chrome plater were found to have accumulated on the roof of the facility and from there contaminated stormwater and snow melting from the roof, which in turn contaminated the groundwater, a nearby surface water system, and fish (MPCA 2016).

2.6.1.4 Industrial Surfactants and Fluoropolymer Production

PFAS have been, and currently are, instrumental as surfactants in industrial and commercial production. It is noted that many specific surfactant uses of PFAS are not publically available or published (KEMI 2015b). Most well documented is the historical use of PFOA as a processing aid in the manufacturing of PTFE, where APFO is used to help mix together the chemicals needed to combine units of tetrafluoroethylene (TFE) to make PTFE. Similarly, APFN, the ammonium salt of perfluorononanoic acid (PFNA), has also been used in the production of PVDF. PVDF polymers that are produced with the aid of APFN are sold in solid phase, with notable residual APFN concentrations (100–200 ppm) (Prevedouros et al. 2006).

Since the voluntary phaseout of PFOA and related PFAS chemistries, replacement chemistries such as ADONA and the GenX process chemicals are now used in the production of fluoropolymers.

The PFAAs used as polymerization aids may occur as impurities/residuals in some fluoropolymer products; however, it is documented that PTFE does not degrade to significant levels of PFAAs during incineration (Aleksandrov et al. 2019) and fluoropolymers of low concern are shown to be stable (Henry et al. 2018).

PFAS are also used in the manufacturing of plastics and fluoropolymers, rubber, and compression mold release coatings. These have applications in tubing, piping, drums, molds, and resins (Poulsen 2005) (Prevedouros et al. 2006).

2.6.1.5 Paper Products and Packaging

Since the 1960s, PFAS have been used as grease-proofing agents on food contact materials (FCM) to prevent oil, grease, and moisture from foods from leaking through the packaging. This includes coated paper and cardboard such as pizza boxes, microwavable popcorn bags, parchment paper, fast food wrappers, paper cups, pet food bags, and other items (Rao and

Baker 1994) (Hekster, Laane, and De Voogt 2003) (Poulsen 2005) (Trudel et al. 2008) (Buck et al. 2011).

The U.S. Food and Drug Administration (FDA) currently approves more than 90 unique monomer and polymer PFAS in FCMs (USFDA 2016). In January 2016, the FDA rescinded approval for three families of long-chain PFAS used in FCMs, but these had been voluntarily removed from the market in 2011. N-MeFOSE and NEtFOSE were historically used to produce surface coatings for textiles and paper products (Zaggia and Ameduri 2012). PFAS currently used in FCM include polyfluorinated polyether-based polymers and shorter chain PFAAs (Wang, Cousins, et al. 2015) (Schaidler et al. 2017).

The most common PFAS detected in U.S. fast food wrappers include PFCAs (for example, PFOA and PFHxA), PFSAs (for example, PFBS), and fluorotelomer sulfonates (for example, 6:2 FTS) (Schaidler et al. 2017). Six of 20 FCM tested were found to contain detectable levels of PFOA even though in 2011 U.S. manufacturers had voluntarily agreed to stop distributing FCM that were manufactured using PFOA via an FDA initiative. The methodology was not sensitive enough to detect if the PFASs were intentionally added to the packaging material or if they were attributed to unintentional background levels (Schaidler et al. 2017). Refer also to Section 2.4.3 on the USEPA 2010/2015 PFOA Stewardship Program, which discusses the phaseout of PFOA and potential sources of PFOA that may remain in commercial and consumer products.

2.6.1.6 Photolithography/Semiconductor Industry

The semiconductor industry historically has used PFOS for their surface-active properties in the fabrication of imaging devices such as digital cameras, cell phones, printers, and scanners (Poulsen 2005). Studies have shown semiconductor waste streams containing the PFAAs PFBS, PFHxS, PFOS, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, and PFDoA (Lin, Panchangam, and Lo 2009). Similarly, in photolithography processes, PFOS has been used predominantly in applying top-layer antireflective coatings (TARCs), bottom antireflective coatings (BARCs), and etchants. Smaller quantities of PFOS and longer-chain PFAS have been used in wet etchants, film developers, cleaners, protective coatings, and color filters (SIA 2008), with ongoing uses permitted (Section 2.4).

2.6.1.7 Textiles, Leather, and Apparel (Including Carpet and Furniture)

Surface treatment of textiles, leather, carpet, and furniture upholstery with PFAS to make them stain, oil, and water repellent occurs both before (that is, at the factory) and after consumer acquisition for ongoing stain, oil, and water repellency (Prevedouros et al. 2006); (Ahrens 2011); (Herzke, Olsson, and Posner 2012). Aftermarket PFAS-containing stain-repellent products for carpets allow consumers to treat carpets and textiles at home (Renner 2001) (Hekster, Laane, and De Voogt 2003). Losses to the environment can be related to dry cleaning and laundering activities (Poulsen 2005) (3M Company 2000b).

Home textiles, including furniture and carpeting, as well as aftermarket PFAS surface treatment products, are also sources of long-chain perfluorinated chemical exposure (Guo et al. 2009). 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). According to California EPA (CalEPA) CalEPA (2018), pg. 12, "The PFAS polymers used in carpets, rugs, and other textiles can contain various amounts of mobile residual raw materials, impurities, or degradation products, including PFAAs and other PFAA precursors such as fluorotelomer alcohols (FTOHs) and perfluoroalkyl sulfonamide alcohols." Releases to the environment could occur from disposal of carpet cleaning wastewater (CalEPA 2018). Physical degradation of some consumer products (such as PFAS-treated textiles and carpets, as well as paper) may be a source of PFAS in house dust (Björklund, Thuresson, and de Wit 2009).

It should be noted that many treated home textiles and carpets are now manufactured with alternatives to long-chain PFAS; however, these products can have a long useful life, making it possible that items previously treated with long-chain PFAS are still in use (Brooke 2004). A 2009 study of over 100 consumer products conducted by the USEPA and Arcadis indicated that pretreated carpet, treated upholstery and textiles, as well as other floor treatments, are likely the largest source of PFAS receptor exposure in American homes (Guo et al. 2009).

Other studies have since shown nonpolymeric PFAS in leather samples and outdoor textiles to impart water, oil and stain resistance; applications include protective clothing, outerwear, footwear, umbrellas, tents, and sails (OECD 2013; Walters and Santillo 2006) (Kotthoff et al. 2015). Durable water repellent (DWR) is a fabric surface finish that creates a protective barrier. It is typically added at the factory, but is also available to consumers for apparel maintenance (Brooke 2004). The finishes/treatments are applied to materials in mills/tanneries and as aftermarket applications by professionals or do-it-yourself consumers as aqueous dispersions. In some aftermarket applications, they are applied as solutions in hydrocarbon-based or halogenated solvents (OECD 2013).

2.6.1.8 Other Potential Commercial or Domestic Sources of PFAS Releases to the Environment

There is the potential for everyday uses of PFAS to result in relatively smaller releases of PFAS to the environment. Of note, these may include, but are not limited to leaching from materials to media (for example, well construction and plumbing materials), discharges to on-site wastewater disposal systems from use of household products and cosmetics, discharges from car washing and waxing, and use of ski waxes (professional ski wax technicians may have significant inhalation exposures to PFAS (Nilsson et al. 2013). Snowmelt and surface waters near ski areas may have measurable PFAS impacts (Kwok et al. 2013).

2.6.2 Class B Fluorine-Containing Firefighting Foams

Some Class B firefighting foams designed for extinguishing flammable liquid hydrocarbon fires and vapor suppression may contain fluorine. These foams can be a major source of local PFAS release to the environment, with the CSM included in Figure 2-17.

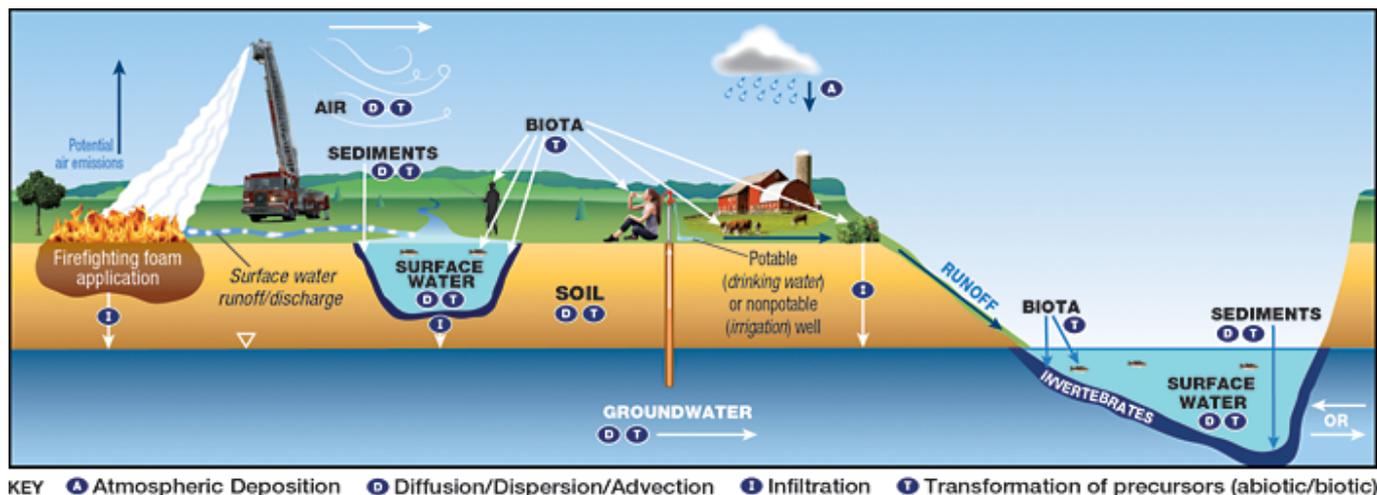


Figure 2-17. CSM for fire training areas.

Source: Adapted from figure by L. Trozzolo, TRC, used with permission.

Class B firefighting foams are commercial surfactant solutions that have been (and continue to be) stored and used for fire suppression, fire training, and flammable vapor suppression at military installations and civilian facilities and airports (Hu et al. 2016), as well as at petroleum refineries and bulk storage facilities, and chemical manufacturing plants and storage facilities (CONCAWE 2016). Additionally, local fire departments in communities have used and may maintain quantities of firefighting foam in their inventories for use in training and emergency response. Facilities that manufactured firefighting foams and landfills that received firefighting waste are also potential sources. Refer to Section 3 for more detailed information about firefighting foams.

2.6.3 Solid Waste Management Facilities

Environmental releases associated with the use of PFAS-containing products are primarily related to management of solid waste (for example, disposal of used items in a municipal solid waste (MSW) landfill or other legacy disposal areas). Other solid waste facilities, such as scrap yards and metal salvage facilities, might also be a potential source of release to the environment. Some PFAS are considered hazardous waste by some states (Section 8).

Landfills can be sources of PFAS because they are the ultimate repositories for PFAS-contaminated industrial waste, sewage sludge from wastewater treatment facilities, and waste from site mitigation, as well as for PFAS-bearing consumer wastes, such as goods treated with hydrophobic, stain-resistant coatings (Busch et al. 2010) (Eggen, Moeder, and Arukwe 2010). But the type and concentration of PFAS vary greatly among landfills, due to variations in the waste streams. Industrial waste can be a significant source of PFAS in landfills (as well as in wastewater and biosolids), particularly those that accept waste from facilities involved in the production or application of PFAS (Oliaei et al. 2013). Although MSW will contain PFAS due to its presence in so many consumer products, it generally is expected to have lower concentrations than landfills that accept industrial waste. Given the production timeline of PFAS, industrial, commercial, and consumer products and waste disposed since the 1950s are potential sources of PFAS release to the environment. As PFAS manufacturing processes change with time, the resulting type and composition of waste streams also change. PFAS production and use began several decades

before the enactment of federal and state regulations governing waste disposal; as a consequence, environmental and drinking water impacts from disposal of legacy PFAS industrial and consumer waste have been documented (Oliaei, Kriens, and Weber 2010) (Shin et al. 2011) (MPCA 2017).

Figure 2-18 illustrates common elements of CSMs associated with the potential release scenarios at waste management facilities.

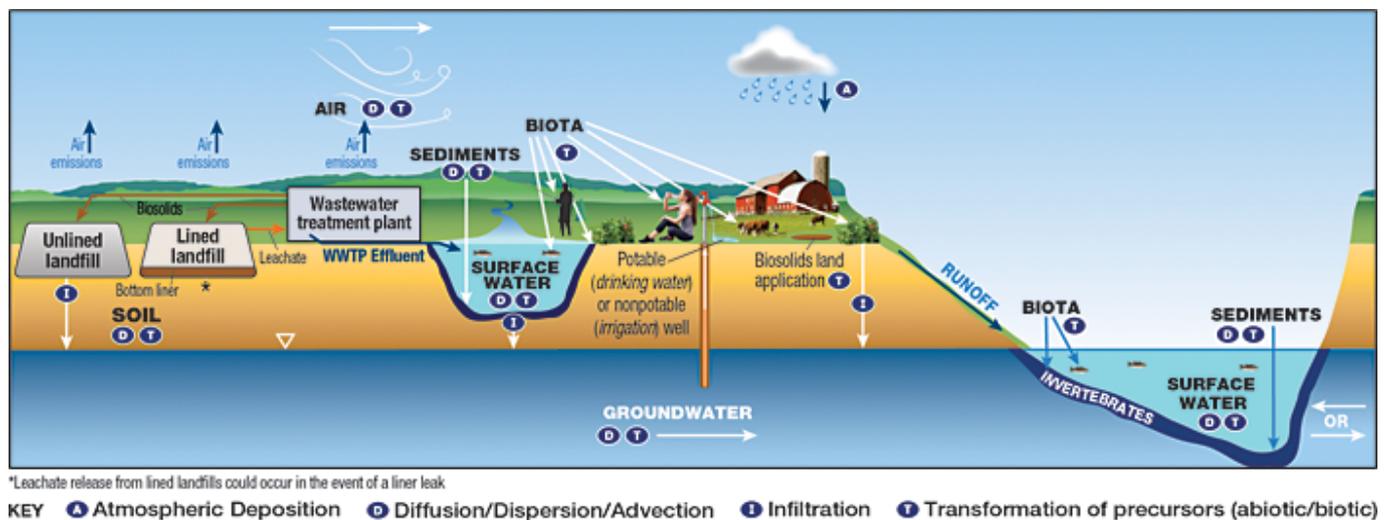


Figure 2-18. CSM for landfills and WWTPs.

Source: Adapted from figure by L. Trozzolo, TRC, used with permission.

2.6.3.1 Landfill Construction

Landfills are either lined or unlined (Figure 2-18). MSW 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). Although some states may have implemented construction standards at an earlier date, most landfills constructed before the 1990s were 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. Construction and demolition (C&D) landfills or nonmunicipal solid waste landfills are subject to the requirements specified in 40 CFR 257 Part A (and if they intend to accept very small quantity generator waste, they are also subject to 40 CFR 257 Part B). Minimum design criteria for landfill liners are not specified in 40 CFR 257. Therefore, new C&D and nonmunicipal solid waste landfills may be permitted and constructed (or new cells added to existing facilities) without synthetic liners. Some states may have more restrictive requirements. Therefore, unlined landfills (and legacy disposal areas not classified as landfills) have a higher potential of contributing PFAS to groundwater (Oliaei et al. 2013). Properly constructed and operated modern landfills provide one of the few available disposal/management options for PFAS-containing waste, including wastewater solids, remedial/treatment waste, and consumer products.

Landfills are currently required to use a daily cover or alternate daily cover. It is acceptable for alternative daily cover to include materials such as sludge, sludge-derived products, shredded automotive parts, spray-on foams, and other materials (Pohland 1993) that are possible sources of PFAS. 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).

Leachate from some MSW landfills has been shown to be a source of PFAS release to the environment (Busch et al. 2010) (Eggen, Moeder, and Arukwe 2010), although the fate and transport processes for PFAS through landfills into leachate are not well understood at this time. The processes for managing leachate have implications on the ultimate fate and transport of PFAS. Leachate collected from landfills is typically treated on site or transported to either a WWTP or evaporation ponds. If liners or leachate collection systems fail, PFAS may directly enter the environment. Modern landfills with properly constructed and operated liner and leachate collection systems should generally protect the underlying groundwater from PFAS releases. Leachate treatment by WWTPs is common prior to discharge to surface water or distribution for agricultural or commercial use (Lang 2016)). However, standard WWTP technologies are generally ineffective at reducing or eliminating PFAS (Hamid and Li 2016), (Ahrens, Hedlund, et al. 2016) (CRC CARE 2017b). As a result, the discharge of landfill leachate,

even if treated at WWTPs, can be a significant source of release of some PFAS to the environment (Ahrens et al. 2015) (CRC Care 2017).

2.6.3.2 Waste Age

Landfills containing sources of PFAS may continue to release PFAS to leachate 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). Although landfill leachate PFAS concentrations can be relatively high, landfill leachate discharged to WWTPs for treatment generally is considered a relatively minor source to the environment because the volume of leachate generated annually and sent to a WWTP for treatment is low compared to the flow volume in most WWTPs (Busch et al. 2010). However, legacy industrial waste landfills may constitute a major source of PFAS release to the environment (ATSDR 2008) (2012).

2.6.3.3 PFAS Composition

PFAS composition and concentration in leachates vary depending on waste age, climate, and waste composition (Allred et al. 2015) (Lang et al. 2017). Relative concentrations of PFAS in leachate and groundwater from landfills are different from 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). In one study, total PFAS concentrations were 5–30 times greater at landfills than at background reference sites (Ahrens et al. 2011). 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, Li, et al. 2012). Gas collection systems commonly employed at modern landfills should reduce possible PFAS emissions to air.

2.6.4 Wastewater Treatment and Wastewater Treatment Residuals and Biosolids

Consumer and industrial use of PFAS-containing materials, including disposal of landfill leachate and firefighting foam, may discharge PFAS-containing wastewater to municipal and industrial WWTPs (Lin, Panchangam, and Lo 2009; Ahrens et al. 2009) private septic systems, or other wastewater disposal systems.

2.6.4.1 Wastewater Treatment

WWTPs can provide the following pathways for PFAS to the environment (Figure 2-18):

- point source discharges of effluent
- leakage or unintended releases from surface impoundments and structures
- air emissions
- management and disposal of biosolids and other byproducts generated during the treatment process (Section 2.6.4.2).

The composition of PFAS in these media is a function of the different sources to the WWTP influent and the WWTP processes (Chen, Lo, and Lee 2012; Oliaei, D. Kriens, and Kessler 2006; Frömel 2016) (Schultz et al. 2006), including:

- type and concentration of PFAS received by the WWTP, particularly those that receive industrial wastewater discharges from industrial facilities manufacturing or using PFAS
- biological and chemical transformation of polyfluorinated substances (that is, precursor PFAS) to intermediate and terminal degradation products, such as PFAAs
- physical or chemical partitioning, or both.

Conventional sewage treatment methods used in WWTPs do not efficiently remove PFAAs (Ahrens et al. 2011) (Schultz et al. 2006). Even WWTPs with advanced treatment technologies (such as granular activated carbon (GAC), powdered activated carbon (PAC), or reverse osmosis (RO)) may not fully remove all PFAS if these systems were not designed with the intent to remove PFAS in addition to other targeted contaminants. Some PFAAs are frequently detected in WWTP effluent (for example, PFOA and PFBS), with concentrations of some PFAS ranging up to hundreds of ng/L. Ahrens et al. (2011) and Hamid and Li (2016) suggested that WWTP effluent is a major source of PFAAs to surface waters.

Evaluation of full-scale WWTPs has indicated that conventional primary (sedimentation and clarification) and secondary (aerobic biodegradation of organic matter) treatment processes can change PFAS concentrations and subgroups. For example, studies have shown increased concentrations of PFAAs in effluent, presumably from degradation of precursor PFAS (Schultz et al. 2006), and the possible creation of PFAAs from the oxidation of polyfluorinated precursors during the treatment process (Oliaei, D. Kriens, and Kessler 2006) (Frömel 2016; Houtz 2018).

PFAS may be concentrated in wastewater solids (for example, sewage sludge) generated throughout the wastewater treatment process (Schultz et al. 2006). PFAS may also be present in septage (solids removed from septic systems). Depending on waste management and disposal practices, land application or landfill disposal of wastewater solids, biosolids, or septage could potentially contaminate the environment.

Hu et al. (2016) suggested that the presence of WWTPs in an area could be predictive of the presence of PFOS and PFOA in drinking water. PFOS and PFOA are two of the most frequently detected PFAS in wastewater (Hamid and Li 2016). Using WWTP effluent-impacted surface water as a source of drinking water can, in turn, recycle the PFAS back to the WWTP, recirculating PFAS in the water cycle (Hamid and Li 2016).

At some WWTPs, studies have shown concentrations of PFAS in ambient air at WWTPs to be 1.5–15 times greater than background reference sites (Hamid and Li 2016). Hamid and Li (2016) noted that these elevated air concentrations of total PFAS include *polyfluoroalkyls* and that this has important implications considering the potential for their long-range transport and subsequent degradation to recalcitrant PFAAs. PFAS distribution (primarily PFAAs and FTOH, with higher concentrations of FTOH) changes based on the specific PFAS sources in the effluent and the type of treatment methods employed at the WWTP. Lagoon systems contain a greater fraction of PFAAs.

2.6.4.2 Biosolids Production and Application

PFAS (measured as PFCAs and PFSAs) have been found in domestic sewage sludge (Higgins et al. 2005), and PFAS occurrence in biosolids is reported to be prevalent and nationwide (Venkatesan and Halsden 2013). Given that more than half of the sewage sludge produced in the United States is applied to agricultural land as biosolids (USEPA 2017m), there is the potential for release of PFAS to the environment associated with biosolids production and application. PFAS are not known to be added to biosolids during processing or application.

PFAS may 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 to 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. PFAS concentrations can be elevated in surface and groundwater in the vicinity of agricultural fields that received PFAS-contaminated biosolids over an extended period of time (Washington et al. 2010). The Washington et al. study was completed in an area that received industrial wastewater discharges from several PFAS-related industrial dischargers. Other studies indicate that the potential PFAS releases from municipal biosolids (for example, those generated from facilities that do not receive PFAS-related industrial discharges), may still impact water quality, but at an apparent lower relative impact than at the industrial-influenced biosolids application sites (Gottschall et al. 2017).

The most abundant PFAS found in biosolids (PFOS and PFOA) are the same as those found in WWTP effluent, although biosolids may also contain other long-chain PFAS (Hamid and Li 2016). Although transformation polyfluorinated substances to PFAAs in land-applied biosolids 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).

Application of municipal biosolids as a soil amendment can result in a transfer of PFAS to soil (Sepulvado et al. 2011). These PFAS can then be available for uptake by some plants and soil organisms. There are indications that PFAAs can enter the food chain through the use of biosolids-amended soil (Lindstrom et al. 2011; Blaine et al. 2013; Blaine, Rich, Sedlacko, Hundal, et al. 2014) (Navarro et al. 2017). It is noted, however, that PFAAs present at one municipal biosolids application site were not found in grain grown in the application plot (Gottschall et al. 2017). Hamid and Li (2016) suggested that short-chain (< C7) PFAAs in biosolids subsequently used in land applications can lead to contamination of food (Section 5.6).

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3 Firefighting Foams

The PFAS Team developed a training module video with content related to this section, it is the Aqueous Film-Forming Foam video.

The purpose of this section is to assist aqueous film-forming foam (AFFF) users (first responders, regulators, environmental managers and environmental professionals) who manage AFFF releases. The section includes information about various aspects of using firefighting foams.

Section Number	Topic
3.1	Foam Formulations
3.2	Mechanisms for Release to the Environment
3.3	AFFF Procurement and Inventory
3.4	Foam Systems and Operations
3.5	Emergency Firefighting Operations
3.6	Immediate Investigative and Cleanup Actions
3.7	Treatment and Disposal Options
3.8	Firefighting Foam System Replacement
3.9	Federal, State and International Regulations and Guidance
3.10	Foam Research and Development

It should be noted that the priority of firefighters and first responders is to protect life and property. The information provided supports decision-making about firefighting using AFFF so that potential impacts to the environment can be minimized and mitigated once the fire emergency is ended, or at such time that sufficient resources are deployed to the scene to both handle the fire emergency and mitigate the environmental risks posed by AFFF use. Figure 3-1 illustrates the life cycle considerations of AFFF. The considerations are discussed in sections 3.3 to 3.8.



Figure 3-1. Life cycle considerations for AFFF.

Source: S. Thomas, Wood, PLC. Used with permission.

3.1 Foam Formulations

Class B firefighting foams are commercial surfactant solutions that are designed and used to combat Class B flammable fuel fires. Class B foams have been (and continue to be) stored and used for fire suppression, fire training, and flammable vapor suppression at military installations and civilian facilities and airports (Hu et al. 2016), as well as at petroleum refineries and bulk storage facilities and chemical manufacturing plants (CONCAWE 2016). Additionally, local community fire departments have used and may maintain quantities of firefighting foam in their inventories for use in training and emergency response. Facilities that manufactured firefighting foams and landfills that received firefighting waste are also potential sources.

All Class B foams are not the same. Although not usually categorized this way from a fire protection viewpoint, they can be divided into two broad categories from a PFAS perspective: fluorinated foams that contain PFAS and fluorine-free foams (F3) that do not contain PFAS. Figure 3-2 highlights the two broad categories of Class B foams and their subcategories.

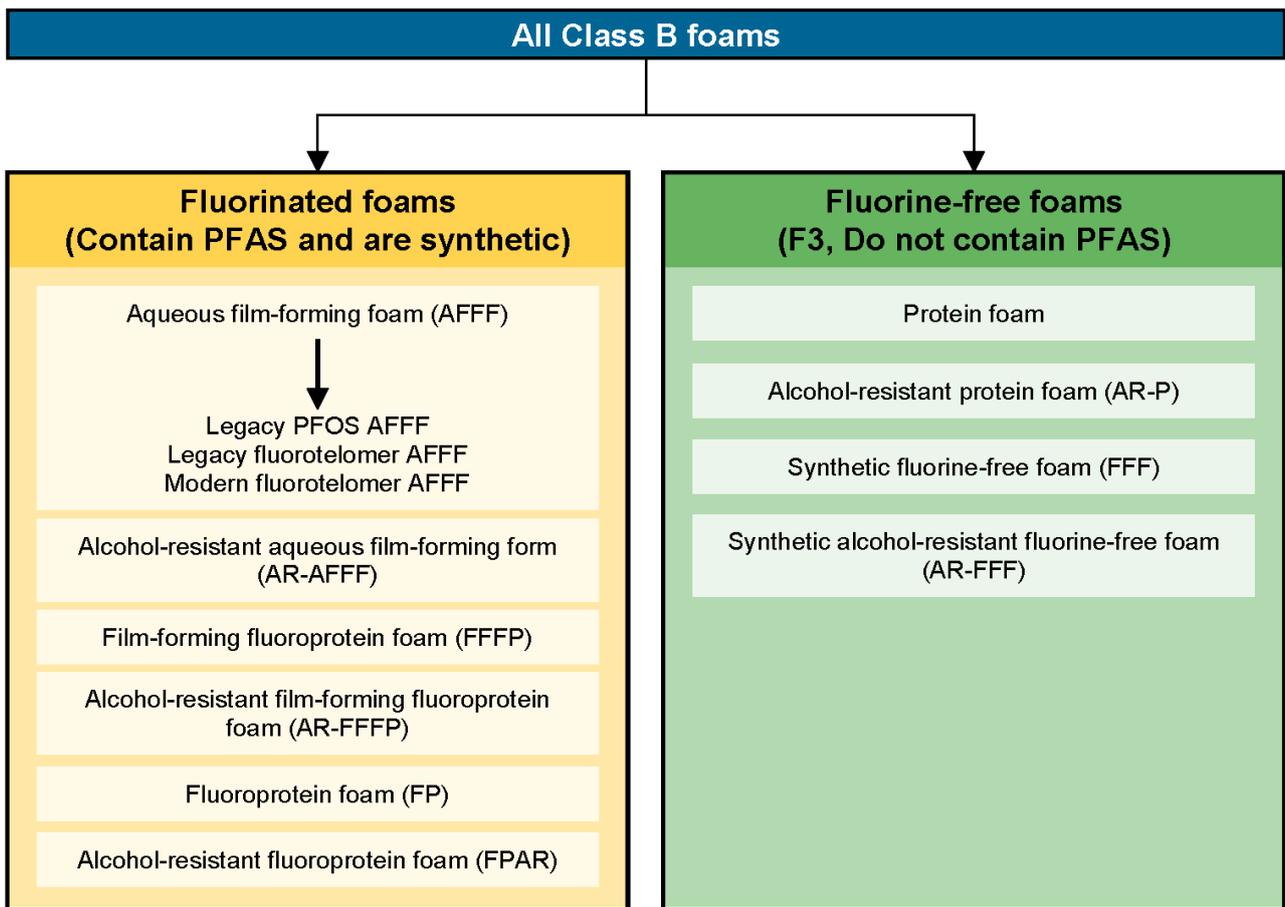


Figure 3-2. Types of Class B foams

Source: S. Thomas, Wood, PLC. Used with permission.

All Class B foams have the potential to create an adverse environmental impact if released uncontrolled to the environment, particularly if the foam reaches drinking water sources, groundwater, surface water, or other natural waters. For all Class B foams, including F3, there is a potential for acute aquatic toxicity and excessive biological and chemical oxygen demand, as well as nutrient loading, depending on where the discharge occurs.

This section is focused on AFFF because it is the most widely used and available type of Class B foam. AFFF is a highly effective type of Class B foam that is especially effective on large liquid fuel fires. AFFF is of particular concern because it contains PFAS. As discussed elsewhere in this document, many PFAS are highly persistent and mobile in the environment and are not removed by traditional drinking water treatment methods typically used by public water suppliers.

The fluorosurfactants in AFFF formulations can be produced either using the ECF process or the fluorotelomerization process. Both ECF-derived and telomer-derived AFFF contain diverse mixtures of PFAS (Barzen-Hanson et al. 2017). The ECF process results in a PFAS mixture dominated by PFAAs—both PFSA and PFCA homologues, while the fluorotelomerization process exclusively produces AFFF formulations consisting of polyfluorinated compounds (Houtz et al. 2013). ECF-based AFFF formulations were voluntarily phased out of production in the United States in approximately 2002 (Section 2.4.1). Despite the phaseout, however, ongoing permitted use of legacy AFFF can still result in long-chain PFAA contamination. Several organizations (for example, U.S. Department of Defense) commenced replacement of legacy PFOS AFFF with modern fluorotelomer AFFF, but some legacy AFFF remains in service or stockpiled at other facilities (Section 3.7.1).

Fluorotelomer foams have been in use since the 1970s and became the predominant foam after 2001, when the major manufacturer (3M) of long-chain ECF-based foams (legacy PFOS foam) discontinued production. Fluorotelomerization-derived AFFF is still manufactured and used in the United States but has been reformulated to limit, if not eliminate, long-chain PFAS; these foams are now referred to as modern fluorotelomer foams. Studies 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 with increased use of telomer-based AFFF (CONCAWE 2016; Anderson et al. 2016).

To further classify AFFF products in terms of current usage and environmental considerations, they can be divided into three categories, including legacy PFOS AFFF, legacy fluorotelomer AFFF, and modern fluorotelomer AFFF (as shown in Figure 3-2).

- Legacy PFOS AFFF was manufactured in the United States from the late 1960s until 2002 exclusively by 3M and sold under the brand name “Lightwater” (USDOD 2014a). 3M did license some companies overseas to use their products and formulations. Legacy PFOS AFFFs contain PFOS and perfluoroalkane sulfonates (PFASs) such as perfluorohexane sulfonate (PFHxS) (Backe, Day, and Field 2013). Although phased out of production in 2002, legacy PFOS AFFFs are the dominant source of PFAS at AFFF-impacted sites (CONCAWE 2016). Furthermore, because of its long shelf life, stock of legacy PFOS AFFF could exist at any given fire department today.
- Legacy fluorotelomer AFFF were manufactured and sold in the United States from the 1970s until 2016 and encompass all other brands of AFFF besides 3M Lightwater or their licensed products (Schultz et al. 2006). Although they are not made with PFOA, they contain polyfluorinated precursors (Backe, Day, and Field 2013) (Place and Field 2012) that are known to degrade to PFCAs, including PFOA (Weiner et al. 2013) (Harding-Marjanovic et al. 2015).

Modern fluorotelomer AFFF was developed in response to the USEPA 2010/2015 voluntary PFOA Stewardship Program (USEPA 2018a). Most foam manufacturers have now transitioned to the production of only short-chain (C6) fluorotelomer-based fluorosurfactants. These modern fluorotelomer AFFFs, or “C6 foams,” do not contain or break down in the environment to PFOS or PFOA and are currently considered to be less toxic and have reduced bioaccumulative potential compared to long-chain (C8) fluorosurfactants. But under particular environmental conditions, breakdown products of C6 foams can include PFHxA, PFPeA, and 5:3 FTCA (Kempisty, Xing, and Racz 2018). Modern fluorotelomer AFFF may contain trace levels of PFOA as an unintended manufacturing impurity or byproduct.

Fluorotelomer foams, short-chain fluorotelomer foams, and C6 foams are analogous and will be referred to as “modern fluorotelomer foams.” When discussing legacy PFOS or C8 foams, the term “legacy foams” will include both legacy PFOS AFFF and legacy fluorotelomer AFFF.

Legacy foams were first introduced by the naval firefighting services in 1964 (Gipe and Peterson 1972). The U.S. Naval Research Laboratory (NRL) began research on the development of firefighting foams in the 1960s. This led to advancements in fire suppression performance and increased firefighting safety (US Naval Research Laboratory 2017). In 1969, the U.S. Department of Defense (USDOD) issued military specification MIL-F-24385, which dictates the performance of all AFFF (with performance standards referred to as “Mil-Spec”). AFFFs shown to perform to MIL-F-24385 requirements are listed on the U.S. military’s AFFF Qualified Product Listing (QPL). The first date AFFF was placed on this list was May 15, 1970 (MIL-F-24385 QPL/QPD History of Type 6 AFFF). DOD maintains the online qualified products database (QPD) that lists all AFFF agents that have been tested and qualified by the NRL to meet the Mil-Spec, currently referenced as MIL-PRF-24385, (USDOD 2018b). On July 1, 2006, the Federal Aviation Administration (FAA) required that commercial airports certified under 14 CFR Part 139 purchase only AFFF that is Mil-Spec compliant (FAA 2006, 2016; 14 CFR 139.317). Recently, the FAA Reauthorization Act modified that requirement. More information can be found in Section 3.9.3.1.

Different types of AFFF were produced to meet firefighting specifications, such as Mil-Spec, rather than formulated to contain a specified mixture of PFAS. Firefighting foams are a complex mixture of both known and unidentified PFAS. 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 variable (Backe, Day, and Field 2013). However, due to the production methods, any given AFFF formulation contains complex mixtures of PFAS, many of which can be identified only by nontargeted analytical methods (Barzen-Hanson et al. 2017).

AFFF is typically formed by combining hydrocarbon surfactants, organic solvents, fluorosurfactants, polymers, and other additives (Kempisty, Xing, and Racz 2018). AFFF concentrates are commercially available in both 3% and 6%. Figure 3-3 illustrates the typical composition of a 3% AFFF concentrate; water/diluent makes up more than 60% of the concentrate, up to 20% is solvents, and as much as 18% is surfactants, of which less than 2% is fluorosurfactants. When the concentrate is mixed with water, the resulting solution achieves the interfacial tension characteristics needed to produce an aqueous film that spreads across the surface of a hydrocarbon fuel to extinguish the flame or reduce the hydrocarbon vapors.

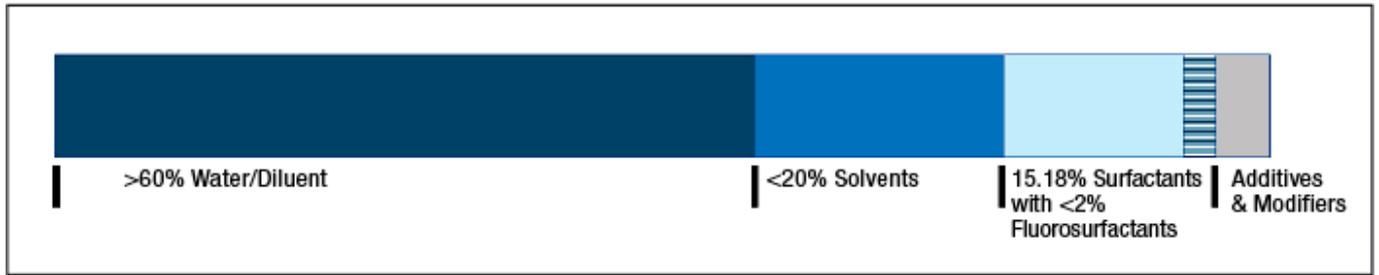


Figure 3-3. Typical composition of 3% AFFF concentrate.

Source: S. Thomas, Wood, PLC. Adapted from Kempisty, Xing, and Racz 2018.

3.2 Mechanisms for Release to the Environment

Firefighting foam is applied by mixing foam concentrate and water to make the firefighting foam solution, which typically contains less than a fraction of a percent of fluorinated surfactants once in mixture. When applied to a fire, the foam solution is aerated at the nozzle, yielding finished firefighting foam. Thousands of gallons of foam solution may be applied during a given event. Figure 3-4 illustrates the use of firefighting foam, how it may be released to the environment, and potentially affected media. Once released to the environment, AFFF can contaminate soil, surface water, and groundwater.

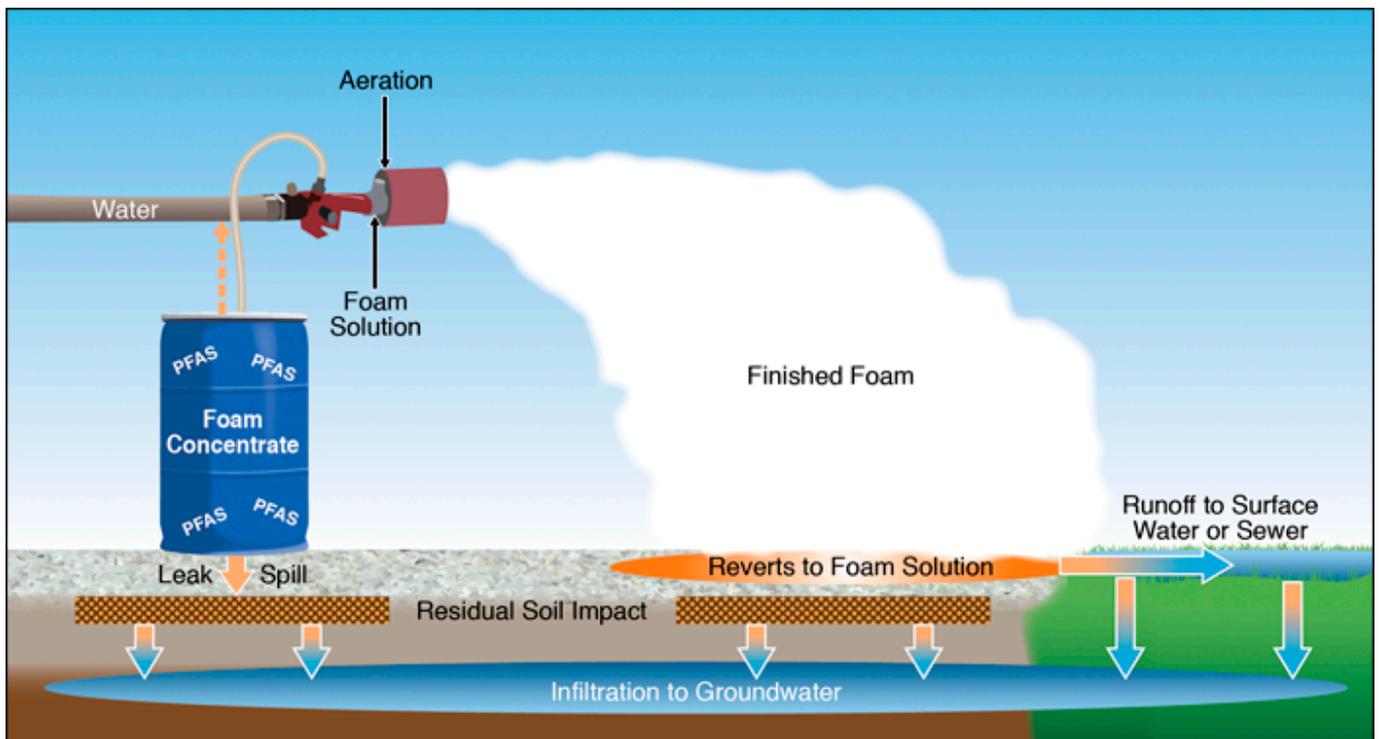


Figure 3-4. Release of firefighting foam.

Source: Adapted from figure by J. Hale, Kleinfelder. Used with permission.

Firefighting foams are released into the environment through various practices and mechanisms (Anderson et al. 2016) (Hale 2016) (Thalheimer 2017) such as:

- low-volume releases of foam concentrate during storage, transfer, or operational requirements that mandate periodic equipment calibration
- moderate-volume discharge of foam solution for apparatus testing and episodic discharge of AFFF-containing fire suppression systems within large aircraft hangars and buildings
- occasional, high-volume, broadcast discharge of foam solution for firefighting and fire suppression/prevention for emergency response
- periodic, high-volume, broadcast discharge for fire training
- accidental leaks from foam distribution piping between storage and pumping locations, and from storage tanks

and railcars.

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), see Section 5.2.5. 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 (McKenzie et al. 2016; McGuire et al. 2014). For additional detail on fate and transport of PFAS from AFFF releases see Section 5.

The USDOD has undertaken an evaluation of potential firefighting foam contamination at its facilities nationwide (Anderson et al. 2016). Similar efforts have been undertaken by some states. For example, the Minnesota Pollution Control Agency (MPCA) conducted a statewide survey of firefighting foam use at training sites. Working with the State Fire Chiefs Association, the MPCA identified more than two dozen locations where Class B foams were likely used in firefighting training (Antea Group 2011).

Figure 2-17 illustrates common elements of CSMs associated with the potential AFFF release scenarios at fire training areas.

3.3 AFFF Procurement and Inventory

This section discusses procurement and inventory of AFFF, including suggestions for storing inventory to minimize the potential for accidental releases.

3.3.1 Foam Selection and Requirements

Multiple manufacturers in the United States and abroad produce AFFF concentrate in 1%, 3%, or 6% concentrations. Most AFFF sold or in stock in the United States is either 1) listed by Underwriters Laboratory (UL) based on conformance with UL Standard 162, "Foam Equipment and Liquid Concentrates," or 2) tested by NRL and granted qualification by U.S. Naval Sea Systems Command in accordance with the Mil-Spec. Only AFFF meeting the Mil-Spec is used in military applications and at FAA-regulated airports.

Military and FAA AFFF applications subject to Mil-Spec account for more than 75% of AFFF used in the United States (Airport Cooperative Research Program ACRP (2017)). Hence, the production of AFFFs has historically been driven by firefighting specifications, such as Mil-Spec, which requires a specific percentage concentration of PFAS. Current Mil-Spec AFFFs contain $\leq 1\%$ (approx. 0.5–0.6%) fluorosurfactants after the concentrate is mixed with water to create the final foam solution used to extinguish or prevent high-hazard flammable liquid fires; however, the exact AFFF PFAS mixtures are highly variable. Non-Mil-Spec Class B foams can vary from fluorine-free to having concentrations of PFAS similar to Mil-Spec AFFF. Furthermore, where fire risk allows it, users who are not subject to Mil-Spec requirements are less likely to use foam formulations that contain PFAS given the environmental implications and increasing prevalence of F3. However, the knowledge of environmental implications of PFAS was historically lacking and is still not widely understood by first responders, and there are many historical examples of AFFF use by municipal fire departments during fire response activities.

3.3.2 AFFF Storage and Handling

AFFF concentrate is available from the manufacturers in containers ranging from 5-gallon buckets to 5,000-gallon tanker trucks. The most common method of shipping is in 5-gallon buckets, 55-gallon drums, or 265-gallon intermediate bulk containers. Shipping containers are typically not double walled but made of plastic, steel, or steel reinforced plastic tote construction to resist damage/puncture. Per National Fire Protection Association (NFPA) 11, Section 4.3.2.3, bulk liquid storage tanks should be fabricated from or be lined with materials compatible with the concentrate, designed to minimize evaporation of foam concentrate, and stored within the listed temperature limitations (NFPA 2016b).

In fire suppression systems, the AFFF concentrate is typically stored in either an atmospheric (non-pressurized) tank or a bladder tank (pressurized). Atmospheric tanks are single- or double- walled tanks and can supply proportioning foam concentrate pumps or venturi-based proportioners that feed the suppression system. Atmospheric tank piping arrangements may include recirculation from downstream of the pump back to the tank. The bladder tanks contain a bladder filled with foam concentrate that is squeezed by water between the shell of the tank and the bladder. As long as the bladder integrity

is maintained, the foam concentrate does not mix with the shell water.

Safety data sheets are provided by all manufacturers for each specific type of AFFF. Labels on shipping containers conform to U.S. Department of Transportation (USDOT) standards. AFFF and AFFF-impacted materials (soils and absorption materials), including concentrate being disposed, rinsate, and foam supply system materials, are not currently considered to be hazardous materials under federal regulations. Some individual states have passed legislation to include PFOS, PFOA, and other PFAS on their hazardous substances list and otherwise restrict the sale and use of AFFF (for example, (Washington Senate 2018) (New York State 2017). Regulations are discussed further in Section 3.9.

Best practice is to treat foam concentrate with caution and to ensure containment until proper disposal. AFFF materials should be labeled to clearly indicate the contents of the container. It is important that all containers are kept clean so that any signs of leakage can be easily and quickly identified during container inspections, with the labeling pointed outward for easier reading.

3.4 Foam Systems and Operations

Class B firefighting foams are employed globally to fight flammable liquids fires where risk of damage to property or human life is high. These products are particularly prevalent in airport settings. This section describes common AFFF system operations, including system testing and training. Additionally, information is provided in Section 3.8 for organizations that want to replace legacy PFOS AFFF systems with modern fluorotelomer AFFF or F3.

3.4.1 Fixed System Testing

Fixed fire suppression systems that utilize any of the foam types and application methods are permanent designs and should incorporate the containment, collection, and runoff components in the event of system discharge into the design. Examples include flammable liquid warehouse, waste treatment facility, and aircraft hangar fire suppression systems. New systems should be designed to include foam containment and collection mechanisms such that foam releases that occur during testing or activation are not released to the environment, or the AFFF can be captured for disposal. AFFF design standards require minimum durations for foam system discharge to meet the suppression/control requirements and in some cases require specific volumes of concentrates and foam solution to be contained in on-site storage tanks. Fixed AFFF proportioning systems that are connected to city water mains should be fitted with backflow preventers to protect the city water mains from potential AFFF contamination.

Codes, standards, and authorities having jurisdiction over fixed system testing, such as NFPA Standards 16 (NFPA 2019) and 25 (NFPA 2017), can require that the equipment produce a foam/foam solution that can be tested and compared to laboratory standards. System testing generates a small amount of foam that should be contained or controlled by the design to the best extent possible for proper disposal. Foam can be wetted with fog nozzles/mist to knock down the foam and dilute it. Gentle squeegee and sweeping are required to keep the solution from aspirating during cleanup and dilution. Alternatives, such as testing with water (without foam) or testing with fluorine-free training foam or surrogate liquids having similar physical properties, may be considered to minimize disposal issues. Check applicable regulatory requirements for testing to determine frequency and type of testing required, as well as what is specifically mandated for foam type before any alternatives are considered to ensure compliance with appropriate laws.

3.4.2 Mobile Firefighting Equipment Testing

Firefighting equipment requires inspection, calibration, and testing to ensure reliability and performance to specifications. In accordance with fire protection standards (for example, NFPA Standard 412, (NFPA 2020) and manufacturer's recommendations, the testing of mobile firefighting equipment should be conducted routinely and documented.

Multiple pieces of equipment can be tested or inspected simultaneously. Mobile equipment, including but not limited to mobile foam extinguishers, firefighting vehicles, and marine craft, can be collected, tested, and cleaned and foam concentrate samples can be collected in a single location to minimize potential impacts. It is recommended that testing of mobile firefighting equipment is executed at purpose-built facilities specifically designed to capture and contain all generated foam and wastewater for treatment, reuse, or disposal.

Conditions during equipment testing should include secondary containment measures to ensure foam solutions can be captured and managed and environmental impact minimized. Alternatives to traditional testing methods may be considered, such as:

- using water or surrogate solutions for training
- testing equipment indoors
- spraying into drums or other containers
- testing within lined pits or spill containment equipment
- testing with closed-loop AFFF testing systems to minimize and eliminate discharge (for example, FAA CertAlert 19-01 (FAA 2019)).

Other controls include not testing during adverse weather conditions, not testing where the facility is not deemed fit for purpose, conducting a risk assessment of the activity, and minimizing foam wastewater volume generated whenever possible. As with fixed fire suppression systems, mobile equipment that complies with NFPA Standard 412 requires that the equipment produce a foam/foam solution that can be tested and compared to laboratory-analyzed solutions (NFPA 2020).

3.4.3 Training Exercises

Facilities should have specifically designed areas and structures to conduct training exercises involving flammable liquid fires and foam systems. The fire training areas (FTAs) should be arranged to contain/control the training site for the safety of the persons being trained. Control of training fires as well as applied foam and/or foam solutions is maintained by the facility design. The FTA should also be designed for collection/recovery of unburned fuels as well as the foam solution and fire water following the completion of training exercises. Conducting outside exercises during windy weather conditions should be avoided, as the foam solutions can be difficult to contain due to natural aspiration and windblown transport.

Past training exercises at airports and military installations employed large quantities of foam/foam solutions. To prevent further releases to groundwater, USDOD issued a policy in January 2016 requiring prevention of uncontrolled land-based AFFF releases during maintenance, testing, and training activities. Current USDOD policies prohibit using AFFF with PFOS for testing, maintenance, or training exercises with the exception of shipboard activities.

Consider minimizing the volume of foam used to the greatest extent possible. If permitted by the applicable regulatory requirements for training, consider entirely discontinuing the practice of using expired legacy AFFF and modern fluorotelomer AFFF as training foam. Whenever possible, seek fluorine-free alternatives for training events; consider training with water or training foam where practicable, not Class B foam, and certainly not with Class B foam containing PFAS. Any wastewater or foam generated from training activities should be kept to a minimum and foam spraying should be restricted to target areas only (not sprayed over wide areas). Preplanning responses that deploy AFFF can identify weaknesses in both AFFF use strategies and in fuel and fire water runoff and containment. This can also identify the need for calling mutual aid early to assist with containment tactics.

3.5 Emergency Firefighting Operations

Fire response planning in advance can identify various options for firefighting and contingency planning for fire wastewater capture. Where possible and as setup allows, consider containing and recovering AFFF used for emergencies for disposal. Use mutual aid resources to assist with containing the fuel and fire water runoff should your department not have the resources available to fight the fire emergency and contain the runoff (Section 3.4). Although federal law currently does not prohibit the use of existing stocks of legacy AFFF, any discharge of foam containing PFAS to public waters can be considered a release of a “pollutant or contaminant” under the Comprehensive Environmental Response Compensation and Liability Act (CERCLA), 42 U.S. Code § 9601, and therefore may be subject to remediation requirements.

Emergency scenarios vary case by case. Industrial plant fire brigades and responding emergency crews utilize portable foam generators or monitor nozzles to apply foam to pooled flammable liquids (potential fires) or existing fires. In cases where the fire involves a fixed system, it is critical that an arrangement for containment/control of runoff is included in the design. The following are examples of how preplanning can better inform the use and containment of AFFF at an industrial facility:

Consideration should be given to parts of facilities not protected by the fixed foam system that could be subject to AFFF application in the event of an emergency incident and opportunity for containment of foam.

- Industrial processes have many components, and only portions of the process are protected by the fixed foam systems. For example, a scrubber, or filter found within industrial smokestacks, may be part of the process that

is not protected by the foam system and may be outside the discharge area where design considerations have been made for containment/control. Emergency response units may be required to apply foam/water to the location of the scrubber, outside the planning boundaries, in the event the fire that originated in the process was conveyed to the scrubber unit.

- At oil refineries, F3 may be used for small incidents and fluorinated foam reserved for the large tank fires. Fluorine-free and new generation C6 foams have been tested in large-scale tests (involving up to 40 m foam travel requirements) and could be considered suitable for application to fires involving some tank sizes and the associated dike area fires. But firefighting foam use is rapidly evolving, and as such, those responsible for tank application foam selection should refer to the latest test results from any recognized independent source (for example, LASTFIRE) to determine whether F3 could meet the performance requirements.
- On some remote industrial sites, where no immediate threat to life or property exists, and given the additional resources necessary to manage the wastewater produced, the best response may be to let the fire burn instead of applying AFFF.

3.5.1 Personal Protective Equipment

The use of personal protective equipment (PPE) is highly recommended when exposure to AFFF, as well as other firefighting foams, is anticipated. A critical aspect of PPE is ensuring the proper use of the equipment. The equipment should be used correctly, maintained, and decontaminated routinely (Queensland Government 2018).

During the application or immediate cleanup of AFFF foam, the use of a self-contained breathing apparatus or positive pressure-supplied air respirator is recommended to avoid respiratory exposure. Dermal exposure should also be avoided, as skin contact can result in irritation and dryness. When responding to fires, first responders should wear appropriate turnout gear, or proximity gear per their specific department requirements.

PPE cleanup after using AFFF (as well as other foams) is discussed in the next section.

3.5.1.1 Decontamination

Although PPE will prevent initial exposure to AFFF, contamination of the PPE itself can present health risks. Decontamination of the PPE and personal hygiene are crucial preventative measures in reducing or avoiding exposure to AFFF, as well as in avoiding cross-contamination.

When handling AFFF concentrate or foam, it is imperative to avoid hand-to-mouth contact. After the use or cleanup of AFFF, responders should wash hands and use other decontamination procedures to remove any residual AFFF from the skin. Responders should remove contaminated clothing and launder before reuse.

PPE should be placed in a bag and container after exposure to AFFF as well as other foams. In 2014, NFPA released its latest edition of NFPA 1851: Selection, Care and Maintenance of Protective Ensembles for Structural Firefighting and Proximity Firefighting. This standard provides guidance for proper care of firefighting protective gear as well as health hazards associated with improper maintenance or contamination of protective equipment (NFPA 2014). The standard outlines different decontamination measures for turnout gear as well as proximity gear.

Turnout gear is the general PPE for firefighting. It should be machine washed in warm water in the normal cycle. Turnout gear should be spot treated with warm water, a soft brush, and mild detergent prior to being machine washed. When hand washing and spot treating PPE, wear protective gloves—either latex or PVC—to avoid skin contact with any residual AFFF. No fabric softener or bleach should be used. The turnout gear should never be washed in home washing machines, as this practice has the potential to contaminate personal clothing. Advanced cleaning is suggested at least on a yearly basis (Avsec 2015).

Although PPE decontamination prior to reuse is important, it is equally important to recognize when decontamination is not possible. In this case, the gear should be discarded in accordance with local, state, and federal regulations.

When decontaminating or laundering PPE, the disposition of the waste stream should be considered. The potential for environmental impacts due to laundering in washing machines is not well defined, but the potential does exist. Regulatory agencies should consider including decontamination procedures when working with firefighters, refinery safety personnel, and other potential first responders to develop BMPs.

3.5.2 Initial Mitigation Efforts for Firefighting Foam

Initial mitigation efforts following a release of firefighting foam include source control, containment tactics, and recovery tactics. Each is further described in this section.

Discharges of AFFF can occur during firefighting operations, system testing, equipment malfunctions, or incidental releases. In addition to foam, a large amount of water is often applied when attempting to suppress a fire. Due to the highly miscible nature of AFFF, the main objective of the initial mitigation efforts should be to reduce the footprint of contamination by limiting the spread of foam and fire water. This is often done through various containment and recovery tactics while making sure that the release has been abated and response personnel are safe.

Specific department or facility fire wastewater management considerations may be outlined in a fire response plan, which should include information such as resources available within the facility or department fire protection jurisdiction to contain and recover fire water, protect sensitive areas (for example, public and private water systems, storm drains, surface water, critical wildlife habitat), and address safety considerations when conducting water management tactics. By using the fire response plan, first responders familiar with the content can increase the potential for a successful response while reducing or eliminating any imminent or substantial threat to human health, safety, welfare, or the environment.

3.5.2.1 Source Control

In addition to AFFF application for emergency response, accidental discharge of AFFF can occur from faulty or malfunctioning equipment such as hard-lined fire suppression systems in aircraft hangars or equipment used to apply or contain foam (for example, fire engines or storage tanks). The first step in any response is to stop the accidental discharge or release at the source by disabling or shutting off the system, if possible, and then temporarily or permanently repairing the malfunctioning equipment. By controlling the source, the impact to the environment is minimized.

3.5.2.2 Containment Tactics

Due to AFFF's miscible nature, as well as the large amount of water often applied in combination with the foam, containment tactics that prevent or minimize surface water runoff are critical during and after emergency response activities. Proper containment tactics may also reduce the footprint of the affected area to make the containment and cleanup easier. Depending on resources available to response personnel and conditions of the release, tactics such as ditching, berming, diking, damming, and blocking storm drains, culverts, or other surface inlets can help to contain runoff. When using these tactics, it is important to ensure that any digging activity will not result in breaking through a confining layer that would allow contaminated water to move more quickly into the subsurface and specifically to groundwater. Several response organizations have tactics manuals available online for review, including the Spill Tactics for Alaska Responders (STAR) Manual (AK DEC 2014) and Alaska Clean Seas Tactics Manual (Alaska Clean Seas 2017). Most manuals are targeted at tactics proposed to be conducted after a release of oil or other petroleum products, but most of these tactics will also apply to AFFF releases. General guidance, similar to this section, on containment tactics to be conducted after a foam discharge has been provided by several other organizations, including the Firefighting Foam Coalition (FFFC 2016, 2018) and the Queensland Department of Environment and Science (Queensland Government 2018).

As stated previously in this section, preplanning can greatly assist with prioritizing sensitive areas or locations that need protection during the mitigation or response effort after an AFFF discharge, as well as the resources necessary to succeed with this strategy. The containment tactics used and resources required will differ among sites. Preparedness can be increased by identifying potentially sensitive areas. Also, designing infrastructure such as aircraft hangars with foam-applying fire suppression systems so that the discharged foam is automatically directed to storage tanks or containment structures can minimize the need for any cleanup. The DOD has provided guidance via Engineer Technical Letters (USACE 2018) that address containment/disposal system design for AFFF discharges from open systems (such as nozzle and deluge sprinkler systems) and closed systems (in which individual sprinkler heads are activated only by heat of a fire).

Because no single set of containment tactics is going to be applicable to all facilities or departments where a foam discharge occurs, it is important for each user to conduct preplanning to identify solutions that fit its facilities, objectives, and specific response scenarios.

3.5.2.3 Initial Recovery Tactics

Recovery tactics can differ depending on the amount of AFFF released, as well as whether the AFFF is discharged during firefighting operations or accidentally (for example, from malfunctioning equipment). Collection of large volumes of AFFF concentrate or the 1%, 3%, or 6% AFFF mixture combined with water could require the use of mechanical devices such as

pumps or vacuum trucks, while absorbent material might suffice to clean up after a smaller release. The AFFF and water mixture has a low flammability and a high flash point, so there is no need to use intrinsically safe pumps or mechanical devices unless other, more flammable compounds are present in the fire water being recovered.

It may be beneficial to remove affected AFFF saturated materials such as soil and vegetation to reduce or eliminate surface or subsurface migration of potential contaminants. Removal of contaminated media may reduce or eliminate the need for additional investigation and cleanup in the future; however, focus during the initial mitigation effort should be on the more easily recoverable media such as affected waters or slurries. Initiating recovery tactics as soon as possible after a release of AFFF will greatly reduce the footprint of PFAS-contaminated materials and lower the cost of the total mitigation effort.

3.6 Immediate Investigative and Cleanup Actions

A series of immediate investigative actions can be taken after the use of AFFF at the site of a fire to determine the level, nature, and extent of the contamination. First responders should collect information regarding the volume of AFFF discharged, its concentration, active ingredients, and discharge location information.

Information about actions to be taken after the immediate actions is included in Section 10, Site Characterization; Section 11, Sampling and Analytical Methods; and Section 12, Treatment Technologies.

Traditional field-screening methods used for other types of contaminants (for example, PID field screening for petroleum) are not effective for PFAS due to their unique chemistry, generally low volatility, and lack of development of colorimetric or reactive chemistry technologies. Some efforts have been made to develop mobile analytical laboratories, which are covered in Section 10.3.1.2 of this document.

3.6.1 Visual Site Delineation

Visual site delineation refers to outlining the affected area of contamination based on visual clues, such as a visible foam and wet ground, as a guide. The extent of foam should be marked using survey tape, lathe, and pin flags placed to identify locations of AFFF contamination. This technique of determining the initial expanse of the contamination is simple to perform directly after a discharge and can be useful for reference in future testing on the site. In addition, photographs of the site taken during or immediately after the incident can be used to determine the extent of AFFF impacts.

3.6.2 The Shake Test

The shake test is an informal qualitative field-screening method that provides a visual analysis of the site contamination. The shake test can apply to both water and soil-water solutions. In the shake test, a small sample (10–25 mL) is collected on site by the field personnel and shaken. After it is shaken, if there is foaming in the sample, it should be noted and then submitted for analysis (Transport Canada 2017). Photographs of the samples may be helpful. The presence of foam implies the sample is contaminated with AFFF. This test is a good indicator for high concentration contamination. It may not be able to detect lower concentrations of contaminants, so lab testing may still be required.

3.6.3 Initial Investigative Sampling

Investigative sampling is used to determine the nature and extent of contamination, including concentrations at and surrounding release areas. Initial investigative sampling can help to determine whether additional characterization is necessary, in addition to informing the need for and extent of interim or permanent remedial actions. Combining the information gained from investigative and confirmation sampling with information from a CSM will inform project managers as to whether further site characterization and remediation or mitigation efforts are needed. See Section 5 (Environmental Fate and Transport Processes), Section 10 (Site Characterization) and Section 12 (Treatment Technologies) for additional information on the actions that may be needed following initial response.

3.6.4 Interim Removal

Following the information gathering described above, or possibly prior to initial investigative sampling, additional source control can be achieved through removal of soils that are expected to be highly contaminated. During an initial removal action intended to target PFAS hot spots, soil excavation can be guided by shake tests (Section 3.6.2). An interim removal is not necessarily designed or expected to remove all contamination but can help to reduce the migration of PFAS into other media, including groundwater and surface water. To determine how to dispose of the soil, see Section 12 (Treatment Technologies).

3.6.5 Confirmation Samples

Once removal actions take place, confirmation samples are taken to confirm that an excavation or interim removal successfully removed the soil contamination that exceeds applicable regulatory or risk-based levels. If confirmation sampling determines that soil contamination still exists at levels of concern, additional removal actions or other types of remediation or mitigation may be required. The type, number, and distribution of confirmation samples is determined on a site-specific basis according to local regulatory guidance.

3.7 Treatment and Disposal

BMPs suggest that all AFFF foam concentrate volume be fully accounted for at each storage location, from fire trucks to suppression systems to storage containers. Weights of other AFFF system components requiring disposal should be similarly observed. Disposal certificates for materials bound for removal should indicate volumes of AFFF concentrate or solution or weights of system components or debris, as applicable. Total volumes or weights generated for disposal should match that indicated on disposal certificates.

3.7.1 AFFF Concentrate

The disposal of AFFF concentrate is dependent on the product type and the ingredients present in the product to be disposed. Several methods are currently offered as means for disposal of AFFF concentrate. AFFF concentrate has been disposed of using incineration in the United States (FFFC 2016). The effectiveness of incineration, and the temperature and time conditions required to achieve complete PFAS destruction are currently not well understood (USEPA 2020e). In some cases, disposal via burial of a stabilized concentrate at a hazardous waste management facility has been used. Manufacturers' product literature should be consulted for information regarding the specific foam concentrate to be disposed. Stakeholder concerns regarding AFFF waste disposal practices are presented in Section 13.1.11.

AFFF concentrate bound for disposal should be properly documented in compliance with state and federal transportation regulations (as discussed in Section 3.3.2) and shipped to the selected disposal facility under a proper manifest. After the concentrate product has been disposed of, a certificate of disposal should be generated by the disposal facility, transmitted to the product owner, and retained by the disposal facility. This certificate of disposal should be transmitted to the state regulatory agency for review and maintained on file by the product owner.

DOD is currently replacing legacy foam concentrates with modern fluorotelomer foams at many installations across the United States. Legacy foams are being removed from active use as part of this replacement project and the removed product was being disposed of through incineration.

3.7.2 Fire - and Flush Water Containing AFFF

Fire water produced during training or emergency response, as well as flush water produced during the rinsing of firefighting systems and equipment, is managed and disposed of as a generated waste because these waters contain dilute concentrations of PFAS. Practitioners may consult with local regulatory agency personnel ideally prior to the generation of fire- and flush water so that there is a good understanding of local laws and regulations governing disposal. Standard practices for foam containment and cleanup should be developed prior to use such that response teams have the needed equipment and training before an event occurs. Some fire water disposal options are focused on reducing the volume of wastewater through concentration and disposal of the generated concentrate via incineration, landfilling, stabilization, or other mechanisms. See section 3.7.1 for comments related to these disposal methods. Widely used treatment methods, as presented in Section 12 are as follows:

- granular activated carbon treatment
- discharge to and treatment at a wastewater treatment plant
- pumping AFFF-impacted fire water into watertight, secure containment basins and allowing the water phase to evaporate, leaving behind a solid or semi-solid material containing the AFFF concentrate. The remaining material is then disposed of at a certified waste management facility (USDOD 1997). This method is an option only in some localities and where climatic conditions are favorable.

3.8 Firefighting Foam System Replacement

The AFFF application design is specific for each foam and use. Changing between foam types or application objectives could

require a complete system review and, potentially, redesign and modification of system components to meet the new objectives or material and performance requirements. When objectives or requirements are changed, each subject system should be evaluated and modified individually to ensure that operational objectives are met.

Procurement at U.S. airports is primarily driven by regulatory performance requirements, notably the DOD Mil-Spec, MIL-PRF-24385, as well as FAA requirements (ACRP 2017). DOD recommends complete replacement of the required AFFF concentrate supply and rinsing of the storage and discharge system prior to refilling with a different concentrate product (USDOD 2017). This not only prevents any unforeseen incompatibility issues, but also greatly reduces possible cross-contamination and the uncertainty of AFFF formulations (PFAS profile/content).

Applicable replacement products standards include NFPA Standards 11 (NFPA 2016b) and 16 (NFPA 2019) for foam water sprinkler and foam water spray systems and NFPA Standards 1901 (NFPA 2016a) and 412 (NFPA 2020) for equipment.

3.8.1 Replacement Products

Replacing foams and foam systems generally follows four steps:

1. Assess and understand the specific hazards and application objectives.
2. Ensure that foam product to be adopted is listed and approved for use on the specific assets that are being protected and the hazards that that are being mitigated.
3. Ensure that the foam product storage system and the foam/water application system meet product storage (for example, materials compatibility and storage temperature), proportioning, and application requirements.
4. Ensure that the selected foam product(s) meet applicable requirements (such as Mil-Spec, Underwriters Laboratories (UL), or Factory Mutual compliance). These organizations audit manufacturers to ensure compliance with their standards.

Where two or more foam products meet applicable performance requirements, the foam with the best environmental performance should be selected. Alternatives currently available as replacement products for legacy AFFF include products discussed in the following sections.

3.8.1.1 Fluorine-Free Foams (F3)

Most foam manufacturers now produce Class B F3s. Performance of these foams should be evaluated carefully as future purchasing decisions are made. As of September 2019, F3s are not yet approved for use on Class B fires at federal- and FAA-regulated facilities that require Mil-Spec-compliant AFFF. But a mandate within the FAA Reauthorization Act of 2018 (enacted October 5, 2018) directs the FAA to stop requiring the use of fluorinated foam no later than 3 years from the date of enactment (October 4, 2021), so F3 use is anticipated at FAA-regulated facilities in the near future.

There continues to be robust discussion regarding the replacement of AFFF products with F3 formulations. For example, the organization IPEN has published a document titled *Fluorine-Free Firefighting Foams (3F): Viable Alternatives to Fluorinated Aqueous Film-Forming Foams (AFFF)*, which states that F3 products are as effective in combating Class B fires as AFFF and concludes that because of the lower environmental impact of F3 products, the use of AFFF should be discontinued (IPEN 2018). The Fire Fighting Foam Coalition (FFFC) produced a three-page document responding to the IPEN paper, which discusses technical details regarding differences in foam performance for certain types of Class B fires and performance standards (as opposed to composition standards) that continue to necessitate the use of AFFF or other fluorochemical products for certain hazards. Additional challenges to the replacement of AFFF with F3 foams are also described in the FFFC document (FFFC 2018).

3.8.1.2 Modern Fluorotelomer Foams

If it is determined that the performance of a fluorinated Class B foam is required for a specific hazard (for example, the federal regulation requiring AFFF use for military applications, at FAA-regulated airports, and/or other high hazard Class B fires and potential incidents), users should purchase modern fluorotelomer foams. Most foam manufacturers have transitioned to the production of only short-chain (C6) fluorosurfactants, so it is likely that any AFFF bought today meets that requirement. But foams made with only short-chain (C6) PFAS may still contain trace quantities (parts per billion) of PFOA and PFOA precursors as byproducts of the manufacturing process. This should be confirmed with the supplier.

Although there are currently mandated specifications requiring the use of fluorinated foams at airports and military installations, users should be aware that compounds in modern fluorotelomer foams are regulated by several states and are known to have probable effects on human health (Section 7.1). Use of these foams may be restricted to emergency

situations only and not for use in firefighting training activities. Local and state regulations may require reporting of their release, including emergency use. Section 3.9 discusses the current state of regulations on AFFF use.

3.8.2 System Decontamination and Sampling During Foam Replacement

The replacement of Mil-Spec legacy foam with the modern foams requires review of system components, particularly the proportioning system, to ensure that appropriate system performance will be maintained. During foam replacement, a thorough clean-out of storage tanks and associated pipework is highly recommended prior to filling with replacement foam concentrate. There is potential for PFOS and PFOA contamination from legacy AFFF, as described in Section 3.1, and from PFOA and other PFAS from fluorotelomer foams. For nonmilitary applications, legacy AFFF and replacement modern foams may not be compatible. In these cases, the foam manufacturers should be consulted when a foam change is required and current best practices for foam replacement, system decontamination, and verification sampling should be considered.

Currently, there are no regulatory guidelines or requirements pertaining to the clean-out of AFFF firefighting systems when foam concentrates containing legacy foams are replaced with alternative foams; however, local and state governments and other organizations continue to develop policy and guidance on replacing foams. DOD (and other foam users) requires their contractors to perform a triple rinsing step after the legacy AFFF is removed from a system. The rinse water is containerized and managed as a waste material as presented in Section 3.3.2. After the rinse water is removed, the modern fluorotelomer AFFF concentrate is added to the system and the system is function tested and placed back into service. Specific department or facility fire wastewater management considerations may be outlined in the facility or installation spill response plan, which should include information and resources available within the facility or on the installation to contain and recover AFFF-containing fire water to protect the environment. Organizations should check with local and state regulatory agencies regarding local policies and guidance for foam change-out. Sampling of rinsate to ensure that residual contamination has been removed may be considered before adding replacement foams, and sampling of replacement foams that have gone through the system may provide the best assurance that PFAS will not continue to be released when the systems are used.

3.9 Federal, State, and International Regulations and Guidance

3.9.1 Overview

This section summarizes representative information on the regulation of PFAS-containing firefighting foams (AFFF). Although federal law currently does not prohibit the use of existing stocks of legacy AFFF, any discharge of foam containing PFAS to public waters can be considered a release of a “pollutant or contaminant” under CERCLA, 42 U.S. Code § 9601, and therefore subject to remediation requirements. In February 2019, the USEPA announced in its PFAS Action Plan that the agency is beginning to evaluate designating PFOA and PFOS as “hazardous substances” through one of the available statutory mechanisms, including potentially CERCLA Section 102 (USEPA 2019h).

As of September 2019, AFFF use is explicitly regulated by some states, such as the State of Washington and the State of New York (Table 3-1); however, other states regulate PFOA, PFOS or their salts, and other PFAS in AFFF as hazardous substances or hazardous waste. These regulations effectively limit the storage and/or environmental release of legacy AFFF (both legacy PFOS AFFF and legacy fluorotelomer AFFF), as well as potentially triggering cleanup actions. Similar bills, banning the use of AFFF for testing and training, have been passed in other states such as Arizona, Colorado, Georgia, Kentucky, and Minnesota.

Examples of hazardous substance and hazardous waste regulations, as well as other federal, state, and international guidance pertaining to AFFF, are presented below. For more information pertaining to the regulation of PFAS, see Section 8. This section addresses only regulations related to AFFF.

Table 3-1. Representative state AFFF regulatory and legislative activity

State	Regulation or Bill	Initial Effective Date	What is Regulated?	Specific Requirement	Reference
New York	6NYCRR Part 597	March 2017	PFOS, PFOA, and Class B foams	PFOS and PFOA are hazardous substances. Storage and registration requirements for class B foams if those foams contain at least 1% by volume of PFOS and PFOA (acid and salt) and prohibit the release of 1 pound or more of each into the environment during use. If a release exceeds the 1-pound threshold, it is considered a hazardous waste spill and must be reported. Clean-up may be required under the state's superfund or brownfields program (NYDEC 2017). New York's Chemical and Bulk Storage regulations may also trigger further registration and storage requirements for foams that contain one of the four PFAS designated as hazardous substances (NY CRR Parts 596-599).	(NY DEC 2017a)
Washington	WAC 296-24-33001	July 2020	Class B foams	Class B firefighting foams cannot be used or discharged for training purposes, and manufacturers of firefighting personal protective equipment must provide written notification to purchasers if the equipment contains PFAS. Beginning July 1, 2020, manufacturers of class B firefighting foams may no longer manufacture, sell, or distribute for sale PFAS-containing class B firefighting foams except for the following uses: applications where the use of a PFAS-containing firefighting foam is required by federal law, including but not limited to the requirements of 14 CFR 139.317 (such as military and FAA-certified airports). Other exceptions include: Petroleum Terminals (as defined in RCW 82.23A.010), Oil Refineries, Chemical Plants (WAC 296-24-33001)	(Washington State Legislature 2018c)
Virginia	House Bill 2762ER	January 2020	PFAS-containing AFFF	Virginia Department of Fire Programs and the Virginia Fire Services Board begin assisting municipal fire departments to transition to fluorine-free foams, where possible. Effective the same date, the bill bans the discharge or use of PFAS-containing AFFF foams for testing or training unless the facility has implemented containment, treatment, and disposal measures to prevent release to the environment.	State of Virginia, 2019

3.9.2 Take-Back Programs

Several states have implemented “take-back” programs for AFFF. For example, in May 2018, the Massachusetts Department of Environmental Protection (MA DEP), in partnership with the Massachusetts Department of Fire Services, implemented a take-back program to assist fire departments in the proper disposal of legacy firefighting foams that could impact water resources (MA DEP 2018a). MA DEP provided funding to assist local fire departments in identifying these foams in their stockpiles and for MA DEP to dispose of them. Any AFFF manufactured before 2003 is eligible under the take-back program. Vermont also announced a take-back program (VT DEC 2018a). Users should contact their state regulatory agency for information on available take-back programs.

3.9.3 Federal Guidance

As of publication, F3s do not meet the performance requirements of the Mil-spec and therefore are not used at federal- and FAA-regulated facilities. A mandate within the FAA Reauthorization Act of 2018 (enacted October 5, 2018) directs the FAA to stop requiring the use of fluorinated foam no later than 3 years from the date of enactment (October 4, 2021), so F3 use is anticipated at FAA-regulated facilities in the near future (FAA 2018). The National Defense Authorization Act of fiscal Year 2020 (signed into law Dec 20, 2019) requires the DOD to phase out its use of AFFF at all military installations by Oct. 1, 2024, with limited exceptions, and immediately stop military training exercises with AFFF. The secretary of the Navy must publish specifications for PFAS-free firefighting foam at all military installations and ensure that the foam is available for use by Oct. 1, 2023.

3.9.4 International Guidance on AFFF

Internationally, there are many governmental agencies that have developed guidance or operational policy for AFFF. Some examples are briefly presented in Table 3-2.

Table 3-2. Representative international AFFF regulatory and guidance activity

Country	Initial Effective Date	What is Regulated?	Specific Requirement	Reference
Canada	January 2018	PFOS, PFOA, long-chain PFCAs	Canada prohibits the manufacture, use, sale, or import of a number of PFAS-containing chemicals and products, such as AFFF, that have these chemicals. Canada allows certain exemptions, including the use of AFFF that contains residual levels of PFOS at a maximum concentration of 10 ppm; the use and import of AFFF contaminated with PFOS in military equipment returning from a foreign military operation; and the import, use, sale, and offer for sale of AFFF that contains PFOA and/or LC-PFCAs used in firefighting.	(ECCC 2017)
Germany	May 2013	AFFF	The German Federal Environment Agency released a Guide for the Environmentally Responsible Use of Fluorinated Firefighting Foams. The guidance discusses what AFFFs are, when it is necessary for use, why it endangers humans and the environment, and the consequences of use.	(German Federal Environment Agency 2013)
Australia	July 2016	Firefighting foam	The Queensland Department of Environment and Heritage Protection issued an Operational Policy on the Environmental Management of Firefighting Foam. The objective of the policy was to define the requirements and expectations for the handling, transport, storage, use, release, waste treatment, disposal, and environmental protection measures of AFFF.	(Australia Government DOD 2007)

3.10 Foam Research and Development

Current modern AFFF fluorosurfactant alternatives are largely short-chain C6 telomer-based fluorosurfactants. The fluorosurfactants do persist in the environment, and they have the potential to create breakdown products that are also persistent. Although numerous fluorine-free alternatives are already on the market, there is still a need to develop novel firefighting foams that provide the desired firefighting performance while not being harmful to human health and the environment. Research is currently being conducted to further evaluate modern fluorotelomer and fluorine-free alternatives. Research is discussed below.

3.10.1 Research on Current AFFF

Research is being conducted to provide a better understanding of AFFF in the environment and to develop novel technologies to clean up or remove AFFF at contaminated sites. Due to the ability of these legacy AFFF to spread quickly and prevent re-ignition of fuel fires, combined with the fact the USEPA did not require manufacturers to remove their long-chain inventory as part of the 2010/2015 PFOA Stewardship Program, some legacy stockpiles are still being used today (Barclift 2013).

Since 2017, the Strategic Environmental Research and Development Program (SERDP) has been funding research intended to identify and test F3s that meet the performance requirements defined in MIL-PRF-24385. New formulations must be compatible with existing AFFF and supporting equipment. Projects include evaluation of persistence and aquatic toxicity of the alternative materials and will provide human health and environmental impact assessments on the ingredients, formulations, and byproducts being studied. Table 3-3 summarizes the AFFF alternatives studies supported by SERDP-Environmental Security Technology Certification Program (ESTCP).

Table 3-3. Summary of the AFFF alternatives studies supported by SERDP-ESTCP

Lead Investigator	Objectives	Expedited Completion	Project Link
Dr. Joseph Tsang, Naval Air Warfare Center Weapons Division	Proof-of-concept for the development of the next generation of fluorine-free firefighting foam formulations as a replacement for existing aqueous film-forming foam (AFFF). The novel foam systems produced in this research are derived from polysaccharide copolymers and nanoparticles that are sustainable, nontoxic, and water-soluble (or water-dispersible), and will be applied using existing military firefighting equipment.	Aug-18	https://serdp-estcp.org/Program-Areas/Weapons-Systems-and-Platforms/Waste-Reduction-and-Treatment-in-DoD-Operations/WP-2737/WP-2737

Lead Investigator	Objectives	Expedited Completion	Project Link
Dr. John Payne, National Foam	<p>Improve understanding of the physical and chemical processes that underlie firefighting foams, and how the components of a foam formulation can deliver the properties required for good fire-extinguishing performance while minimizing environmental burdens.</p> <p>Statistical method will be employed to develop a fluorine-free surfactant formulation that meets the performance requirements defined in MIL-F-24385. A life cycle assessment will compare the environmental impact of each foam type and identify routes to improving environmental performance.</p>	Sept-19	https://serdp-estcp.org/Program-Areas/Weapons-Systems-and-Platforms/Waste-Reduction-and-Treatment-in-DoD-Operations/WP-2738/WP-2738
Dr. Ramagopal Ananth, U.S. Naval Research Laboratory	<p>Develop a fluorine-free firefighting surfactant formulation that meets the performance requirements of MIL-F-24385F and is an environmentally friendly drop-in replacement for the current environmentally hazardous AFFF.</p>	Dec-20	https://serdp-estcp.org/Program-Areas/Weapons-Systems-and-Platforms/Waste-Reduction-and-Treatment-in-DoD-Operations/WP-2739/WP-2739

The results and full reports of these and future projects will be available at the SERDP-ESTCP website (<https://serdp-estcp.org/>).

Examples of other ongoing research includes:

- Petroleum Environmental Research Forum (PERF), 2016. Firefighting Foam Human Health and Environmental Risks at O&G (Oil and Gas) Operations. This project aims to capture the state of knowledge of the fate, transport, and effects of C8 PFAS AFFF alternatives and identify limitations of and data gaps in the current studies or data sets to inform risk assessment and risk-based decision-making.
- European Chemicals Agency, 2020. Assessment of Alternatives to PFAS-Containing Fire-Fighting Foams and the Socio-Economic Impacts of Substitution.
- European Commission, 2020. The Use of PFAS and Fluorine-Free Alternatives in Fire-Fighting Foams.
- The Fiscal Year 2020 National Defense Authorization Act (NDAA), passed in December 2019, included \$49M in research funding for AFFF and F3 activities.

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4 Physical and Chemical Properties

The PFAS Team developed a training module video with content related to this section, it is the Naming Conventions and Physical and Chemical Properties video.

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.

Section Number	Topic
4.1	Challenges and Limitations Related to PFAS Physical and Chemical Properties
4.2	Physical Properties
4.3	Chemical Properties

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 (ρ) 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/cm³ and 974 mg/L (Table 4-1), respectively, would be predicted to behave similarly to carbon tetrachloride (with a density of 1.59 g/cm³ 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 FTSAs 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, FTSAs, 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 PFASs 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_p)

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_h)

The Henry's law constant (K_h), as well as the air-water partition coefficient (K_{aw}), 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, FTSAs, FASEs, and FASAs (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 PFASs are for the acid form and are therefore not relevant because PFCAs and PFASs 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 $K_{oc,r}$ including site-specific $K_{oc,r}$ 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) ¹
Low polarizability	Electron cloud density not easily impacted by the electric fields of other molecules	Weak intermolecular interactions	Hydrophobic and lipophobic surfactant properties ²
		Low surface energy	
Small size ³	Atomic radius of covalently bonded fluorine is 0.72 Å	Shields carbon	Chemical stability (low reactivity)

¹When paired with an acid functional group such as a carboxylic or sulfonic acid
²When paired with a functional group that is hydrophilic (for example, a carboxylate)
³Smallest 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, $\text{pH} < 3$).

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⁻] is the concentration of the anion, and [H⁺] is the concentration of the hydrogen ion at equilibrium.

The dissociation constant is also commonly expressed as its negative logarithm, $\text{p}K_a$, where:

$$\text{p}K_a = -\log_{10}(K_a)$$

Higher $\text{p}K_a$ values indicate that an acid will dissociate less in water at a given pH than will an acid with a lower $\text{p}K_a$. When the pH of a solution equals the $\text{p}K_a$, 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 $\text{p}K_a$ 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 $\text{p}K_a$ 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.

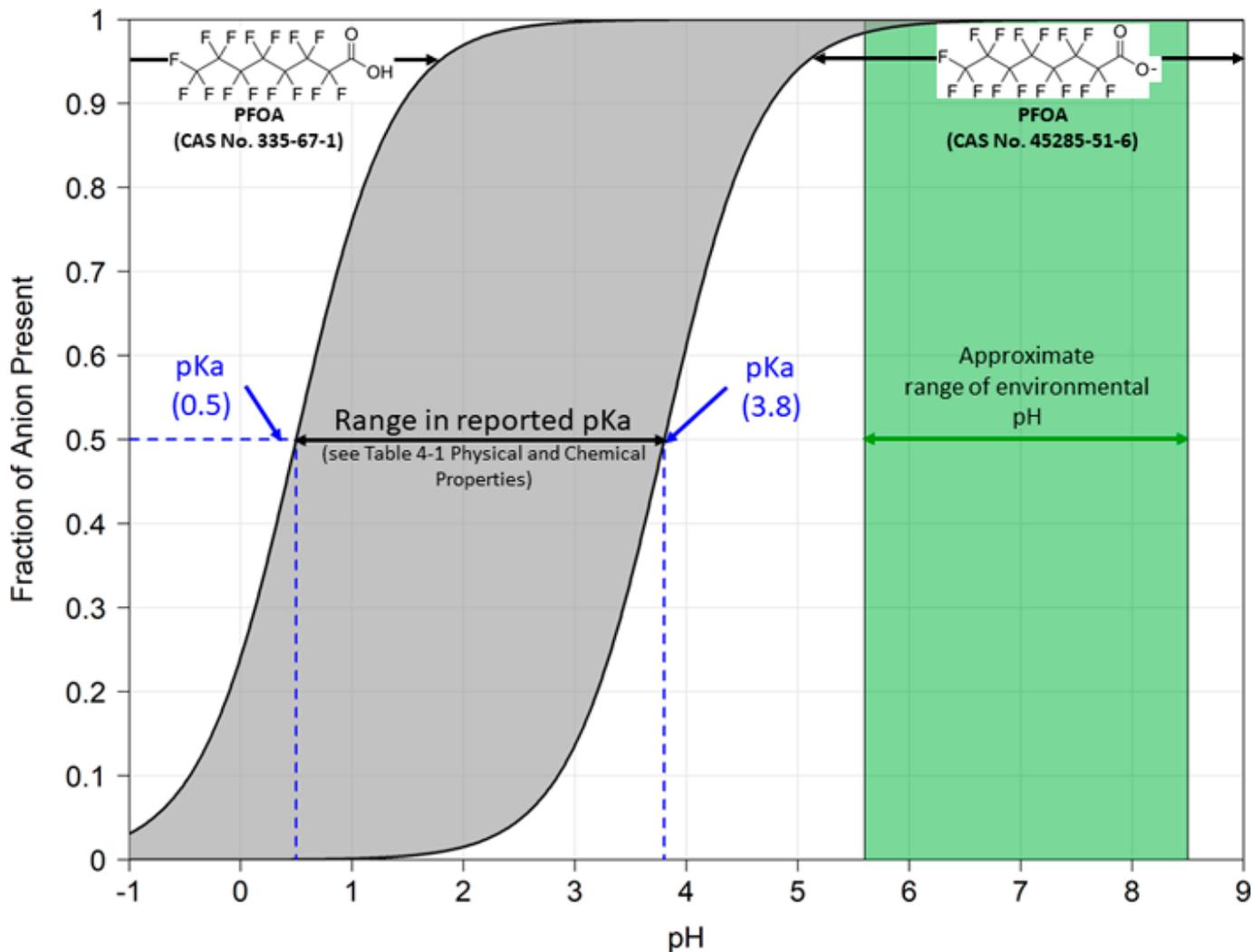


Figure 4-1. Titration curve for PFOA—relation of pKa to environmental pH.

Source: E. DiFilippo, S.S. Papadopoulos & 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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5 Environmental Fate and Transport Processes

The PFAS Team developed a training module video with content related to this section, it is the Fate and Transport video.

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

Section Number	Topic
5.1	Fate and Transport Introduction
5.2	Phase Partitioning
5.3	Media-Specific Migration Processes
5.4	Transformations
5.5	PFAS Uptake into Aquatic Organisms
5.6	PFAS Uptake into Plants

5.1 Fate and Transport Introduction

5.1.1 Overview of PFAS Fate and Transport

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

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

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

5.1.2 Factors Affecting PFAS Fate and Transport

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

- **PFAS characteristics:** Critical factors include the chain length, the ionic state of the compound (for example, the charge(s) carried by the molecule at a typical environmental pH), the type of functional group(s), and the extent of fluorination (for example, perfluorinated versus polyfluorinated compounds). These properties strongly influence the type and extent of PFAS partitioning and transformation that can be expected to occur. A description of these physical-chemical properties is provided in Section 4.

- **site characteristics:** Site characteristics generally define the nature of the source but also have an effect on PFAS-media interactions. Potentially relevant characteristics include soil type (including properties such as permeability, surface charge, organic carbon content, exchange capacity, mineralogy, water content), depth to groundwater, oxidation-reduction conditions, precipitation/infiltration rates, surface water and groundwater flow rates, prevailing atmospheric conditions, and the presence of co-contaminants.

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

5.1.3 Section Organization

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

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

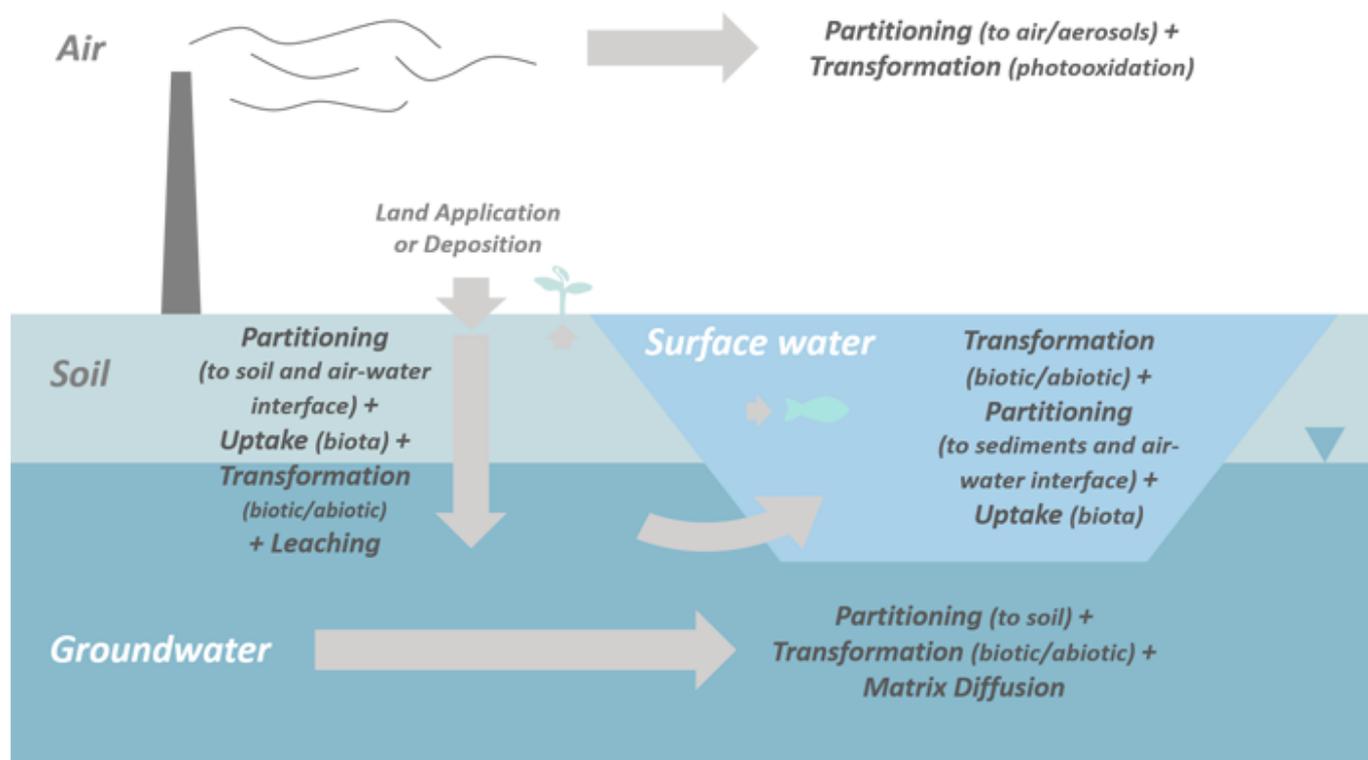


Figure 5-1. Fate and transport processes relevant for PFAS.

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

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

these precursors to PFAAs has been shown to occur in a variety of environmental media and can result in unexpected temporal and spatial trends in PFAS occurrence. The susceptibility of individual PFAS to transformation processes can also influence how each will bioconcentrate and bioaccumulate within various biotic species.

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

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

5.2 Phase Partitioning

5.2.1 Introduction

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

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

5.2.2 Considerations for PFAS Partitioning

5.2.2.1 Pure Phase PFAS

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

5.2.2.2 PFAS Forms Micelles and Foam

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

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

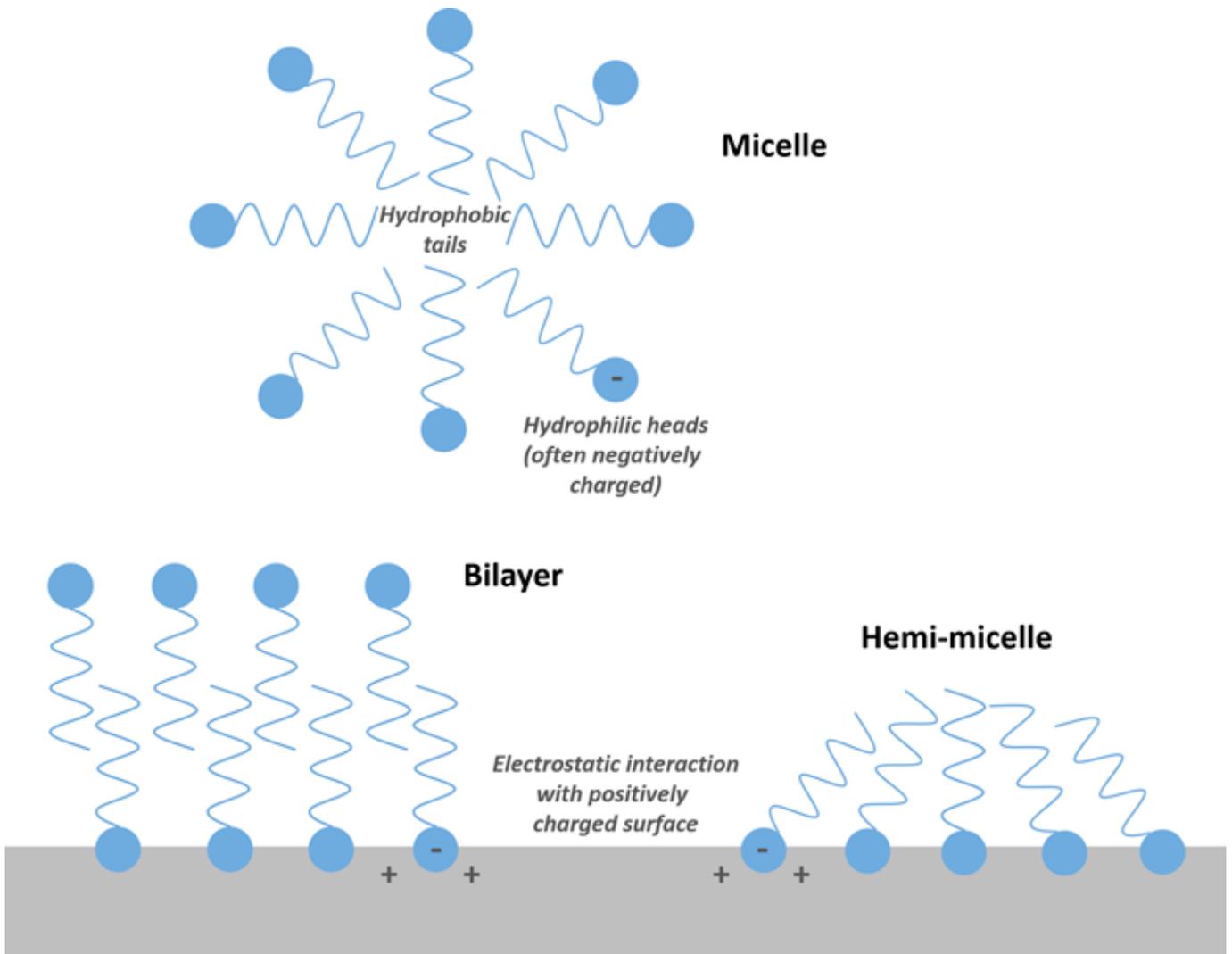


Figure 5-2. Illustration of the formation of PFAS micelles, hemimicelles, and bilayers. Also shown is an example of aggregation at a positively charged surface. Note that the opposite effect (electrostatic repulsion of PFAS) can occur if the surface is negatively charged.

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

5.2.3 Partitioning to Solid Phases

PFAS can partition to a number of different solid-phase materials, including soils and sediments (Higgins and Luthy 2006) and membranes (Fitzgerald et al. 2018). PFAS may also partition to mobile colloids, resulting in facilitated transport (Brusseau et al. 2019). The partitioning of PFAS to solid-phase minerals is the most widely studied and is thought to occur through two primary processes: 1) sorption to organic carbon via hydrophobic interactions, and 2) electrostatic interactions (Higgins and Luthy 2006). The relative contribution of each process can vary depending on surface chemistry and other geochemical factors.

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

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

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

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

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

The contribution of electrostatic interactions to partitioning is highly dependent on soil type and soil solution chemistry. Most soils contain both fixed-charge and variably charged surfaces, such that the net charge on the soil, as well as charge of functional groups of individual PFAS, can be strongly influenced by pH. For example, the net negative charge on most clay minerals can result in electrostatic interactions with cationic functional groups that are present on some PFAS; however, many PFAS, such as PFOA and PFOS, are anionic at environmentally relevant pH, such that electrostatic repulsion in soils dominated by negatively charged minerals would enhance the mobility of anionic PFAS relative to cationic and zwitterionic PFAS. Changes in pH potentially impact these electrostatic processes by altering surface charges (or possibly the ionic nature of the PFAS). As a result, decreases in pH have been shown to enhance sorption by anionic PFAS such as PFOS and other PFAAs (Higgins and Luthy 2006), although the buffering capacity of some soils (for example, carbonates) may mitigate these impacts. Furthermore, increased levels of polyvalent cations such as Ca^{2+} can lead to increased partitioning to soil (Higgins and Luthy 2006; McKenzie et al. 2015). The effects of these various electrostatic interactions can be complex in an environmental setting and may hinder or facilitate transport of PFAS following a release.

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

5.2.4 Partitioning to Air

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

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

5.2.4.1 Partitioning to Air/Water Interfaces

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

through electrostatic repulsion.

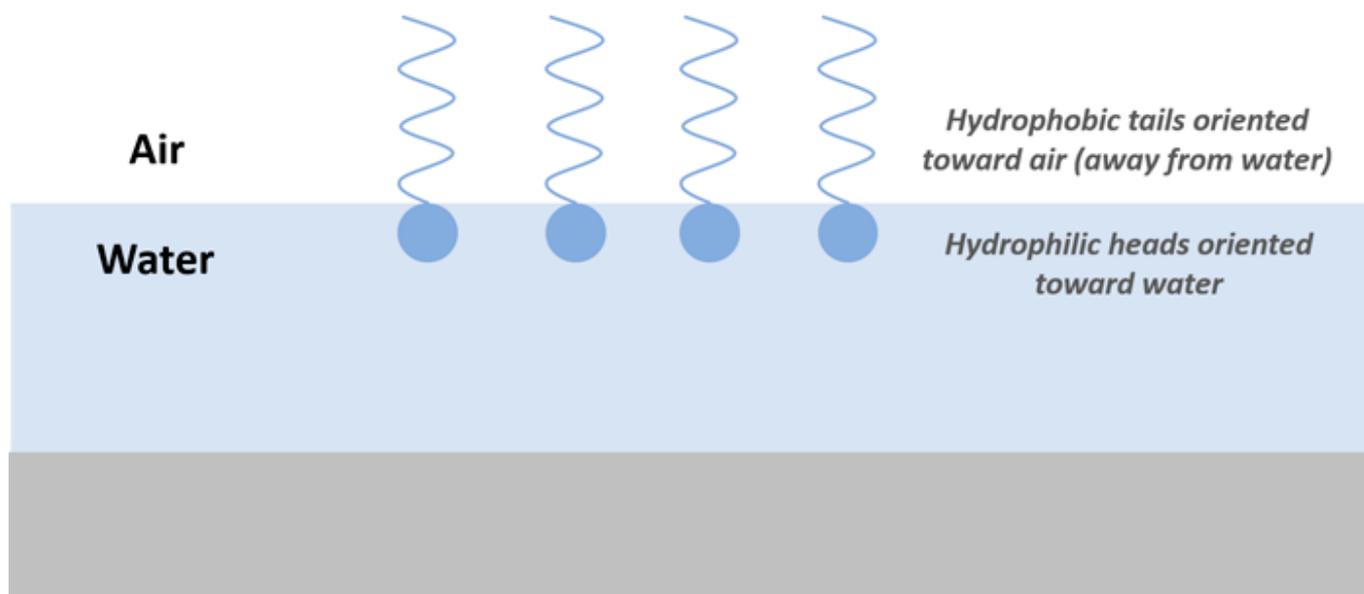


Figure 5-3. Example of expected orientation and accumulation of PFAS at air-water interface.

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

5.2.5 Partitioning into NAPL Co-Contaminants

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

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

5.3 Media-Specific Migration Processes

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

5.3.1 Diffusion In and Out of Lower Permeability Materials

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

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

5.3.2 PFAS Transport via Air

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

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

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

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

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

Atmospheric deposition can occur as dry or wet deposition, both of which are relevant for PFAS (Barton, Kaiser and Russell 2007, 2010; Dreyer et al. 2010; Taniyasu et al. 2013). During dry deposition, PFAS that are preferentially associated with liquid or particle phases in air (aerosols) can be naturally deposited onto surfaces via settling, diffusion, or other processes. When precipitation contributes to washout of these PFAS-containing aerosols, the process is known as wet deposition. Wet and dry deposition are the major mechanisms for removal of PFAS from the atmosphere and can occur from the scavenging of particle-bound PFAS or partitioning of gaseous PFAS from water droplets (Dreyer et al. 2010; Barton, Kaiser and Russell 2007; (Hurley et al. 2004). Deposition is considered a sink term for the atmosphere because mass is removed and the potential for longer range atmospheric transport is reduced. However, this same process thus represents a potential source of PFAS to terrestrial and aquatic environments. Once settled, PFAS adsorbed onto soils or other surfaces (including indoor surfaces) can be resuspended when particulate matter is disturbed by wind or other physical means. See Section 6.1 for further discussion of atmospheric deposition of PFAS.

Short-range atmospheric transport and deposition can result in PFAS contamination in terrestrial and aquatic systems near points of significant emissions, impacting soil, groundwater, and other media of concern (Davis et al. 2007). Evidence of

releases has been observed in areas where hydrologic transport could not plausibly explain the presence of PFAS in groundwater, with the extent of contamination reaching several miles from sources and in distribution patterns independent of regional hydrology (Frisbee et al. 2009; Post 2013; Post, Cohn, and Cooper 2012; NYS DOH 2016b; NH DES 2017; VT DEC 2016b). Releases of ionic PFAS from factories are likely tied to particulate matter (Barton et al. 2006), which settle to the ground in dry weather and are also wet-scavenged by precipitation (Slinn 1984; Sehmel 1984).

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

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

5.3.3 Leaching

PFAS present in unsaturated soils are subject to downward leaching during precipitation, flooding, or irrigation events that promote dissolution of soil-bound contaminant mass (Sepulvado et al. 2011) (Ahrens and Bundshuh 2014). This process can result in PFAS transport from surface soils to groundwater and surface water, because releases often involve surface applications (for example, AFFF and biosolids) or atmospheric deposition. Leaching is also potentially relevant for plant uptake and transport of PFAS contained in landfill waste without adequate leachate control (Benskin, Muir, et al. 2012; Yan et al. 2015; Lang et al. 2017). Leaching potential is a function of media properties (for example, pH, redox conditions, and increased partitioning with organic carbon in soil), PFAS structural properties (for example, ionic charge and chain length), and site conditions that influence the degree of flushing (for example, precipitation rates and depth to groundwater) (Gellrich, Stahl, and Knepper 2012; Anderson, Adamson, and Stroo 2019).

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

5.4 Transformations

5.4.1 Introduction

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

chain PFAAs. Although available studies on both biotic and abiotic transformation of polyfluorinated PFAS primarily consist of controlled laboratory experiments (discussed below), an increasing number of field studies have also been published demonstrating the relevance of precursors at a variety of sites with different source scenarios (for example, (Weber et al. 2017) (Dassuncao et al. 2017)).

5.4.2 PFAA Precursors

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

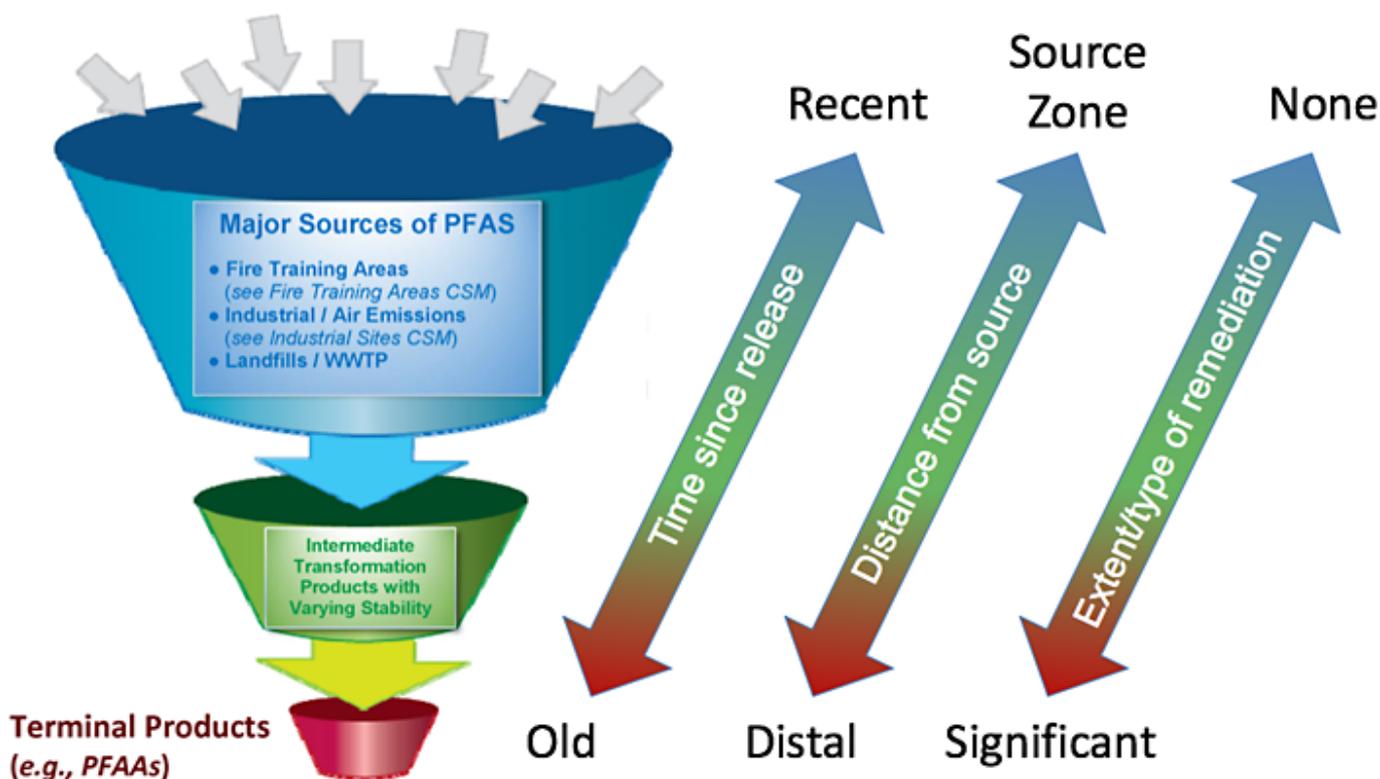


Figure 5-4. Illustration of precursor transformation resulting in the formation of PFAAs.

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

5.4.3 Atmospheric Transformations

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

Widely measured PFCAs precursors in the atmosphere include primarily FTOHs (Thackray and E Selin 2017) (Young and Mabury 2010) (Martin et al. 2002). Wang, Xie, et al. (2015) collected marine atmospheric samples during an expedition

research cruise that spanned the Southern Ocean, Atlantic Ocean, and Arctic Ocean; samples were analyzed for several precursors, including FTOHs, FTAs, FOSAs, and FOSEs. The researchers found that FTOHs were the predominant species.

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

Atmospheric transformation of precursors to PFCAs is a multistep process, and the PFCA product yield is a function of several factors, including ratio of nitros oxides (NO_x) and peroxy radicals (RO_2) species. High NO_x levels result in lower long-chain PFCA yields, thus long-chain PFCA yields are typically higher in remote regions (Young and Mabury 2010). Thackray and E Selin (2017) calculated theoretical maximum yields for formation of PFOA and PFNA from 8:2 FTOH that were highly variable, ranging from far less than 1% to 40% (PFOA) or 80% (PFNA), depending on local photochemical conditions.

5.4.4 In Situ Transformations

5.4.4.1 Abiotic Pathways

Abiotic processes shown to cause transformations of precursors in soil and water under ambient environmental conditions include hydrolysis, photolysis, and oxidation. Hydrolysis of some precursors, followed by subsequent biotransformation, can produce PFSAs. An important example is the production of PFOS from perfluorooctane sulfonyl fluoride (POSF) (Martin et al. 2010). Other hydrolysis reactions produce PFCAs. In particular, Washington and Jenkins (2015) showed that the hydrolysis of fluorotelomer-derived polymeric precursors forms monomeric precursors of PFOA and other PFCAs with half-lives of 50–90 years at neutral pH. Also, oxidation of precursors by hydroxyl radicals can occur in natural waters, with the fluorotelomer-derived precursors being oxidized more rapidly than electrochemical fluorination (ECF)-derived precursors (Gauthier and Mabury 2005; Plumlee, McNeill, and Reinhard 2009). Shorter chain PFCAs as well as PFSAs such as perfluorobutane sulfonate (PFBS) also can be produced by oxidation reactions between hydroxyl radicals and sulfonamido derivatives (D'Eon et al. 2006). Finally, in some cases, abiotic precursor transformations may not initially produce any PFAA (for example, the formation of various polyfluorinated sulfonamido intermediate compounds from ECF-derived precursors), though eventual formation of PFAAs may still be possible.

5.4.4.2 Aerobic Biological Pathways

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

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

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

In detail, most commonly studied in microcosm experiments have been the 6:2 and 8:2 FTOHs in soil, sludge, or aqueous matrices. Although observed degradation rates and intermediates are variable among these studies, \leq C8 PFCAs have been consistently observed as terminal transformation products (Dinglasan et al. 2004; Wang, Szostek, Buck, et al. 2005; Wang, Szostek, Folsom, et al. 2005; Liu et al. 2007; Saez, de Voogt, and Parsons 2008; Wang et al. 2009). However, a pure culture experiment with *P. chrysosporium* (a white-rot fungus) reported much lower PFCA yields with alternate pathways (Tseng et al. 2014). Other telomer-derived polyfluorinated PFAS investigated include the 6:2 fluorotelomer mercapto alkylamido sulfonate (Weiner et al. 2013), the 6:2 fluorotelomer sulfonate (Wang et al. 2011), the 4:2, 6:2, and 8:2 fluorotelomer

thioether amido sulfonates (Harding-Marjanovic et al. 2015), the perfluorooctane amido quaternary ammonium salt (Mejia-Avendaño et al. 2016), the 6:2 fluorotelomer sulfonamide alkylamine, and the 6:2 fluorotelomer sulfonamide alkylbetaine (D'Agostino and Mabury 2017). All demonstrate the formation of PFCAs with variable rates and inferred pathways. Aerobic biotransformation of various ECF-derived polyfluorinated PFAS has also been demonstrated in several studies. Studied PFSA precursors include N-ethyl perfluorooctane sulfonamido ethanol (Rhoads et al. 2008; Zhao et al. 2016; Zhang et al. 2017), N-ethyl perfluorooctane sulfonamide (Mejia Avendaño and Liu 2015), and perfluorooctane sulfonamide quaternary ammonium salt (Mejia-Avendaño et al. 2016). All demonstrate formation of PFASs with variable rates and inferred pathways.

5.4.4.3 Anaerobic Biological Pathways

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

Defluorination of PFOA and PFOS was observed during anaerobic oxidation of ammonium under iron reducing conditions (Huang and Jaffé 2019).

5.4.5 Polymer Transformation

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

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

Polymer transformation research has indicated the following.

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

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

Russell et al. (2008); Russell et al. (2010) investigated the biodegradation potential of two types of side-chain fluoropolymers, fluorotelomer-based acrylate polymer and urethane polymer in soils for 2 years. Based on the experimental

data for PFOA, the estimated half-life of acrylate polymer was 1,200–1,700 years and urethane polymer was 28–241 years (geometric mean of 102 years). However, the polymer used in this study contained high residuals. Later, Washington et al. (2009) studied the biodegradation potential of fluorotelomer-based polyacrylate, which contained low residuals, and based on the experimental data for PFOA, the acrylate polymer half-life was estimated at 870–1,400 years. Further, based on the assumption that degradation is surface-mediated, the authors also modeled and estimated the half-life for finely grained polymers, which are typical of commercial products. They did this by normalizing to the estimated surface area of the polymer and derived a half-life of 10–17 years, which suggests fine-grained, side-chain fluoropolymer products may be a potentially significant source of PFCA to the environment. Washington et al. (2015) studied the biodegradability of commercial acrylate polymer for 376 days in soils using exhaustive extractions (Washington et al. 2014) and estimated half-lives ranging from 33 to 112 years. In this study, it was also observed that the acrylate polymer can undergo OH-mediated hydrolysis in pH 10 water and it degrades 10-fold faster than in the neutral treatment. This is the only abiotic transformation of side-chain fluorinated polymer reported in the literature, so the mechanism of abiotic degradation needs further investigation. Another research group, Rankin et al. (2014) studied the biodegradation of laboratory-synthesized fluorotelomer-based acrylate polymer in soil, plant, and biosolids for 5.5 months. Degradation rates were faster in plants and biosolids than in soils. Even in this study, a broad range of estimated half-lives of 8–111 years was reported. The modeling assumptions used in different studies lead to variability in reported half-lives (Russell et al. 2008; Russell et al. 2010; Washington et al. 2009; Washington et al. 2010; Washington et al. 2015; Washington et al. 2018).

5.4.6 Practical Implications

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

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

5.5 PFAS Uptake into Aquatic Organisms

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

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

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

- Bioconcentration factor (BCF)—the direct uptake of PFAS by an organism from the water column (through the gills), measured as the ratio of the concentration in an organism to the concentration in water (typically measured in the laboratory, units typically in L/kg)
- Bioaccumulation factor (BAF)—the amount of PFAS taken up from bioconcentration plus the contribution of PFAS in the diet of the organism (can be measured in the laboratory or field, typically unitless);

- Biomagnification factor (BMF)—an increase in tissue concentration as one moves up the food chain based on a predator/prey relationship (always measured in the field, typically unitless), often defined as the concentration of chemical in an organism divided by the concentration of chemical in its food.

There are hundreds of publications addressing partitioning of PFAS into biota by all three mechanisms and the subject is too broad to cover in this document. To assist in understanding this process, a sampling of data from some of the more visible review papers, along with references, is provided in Table 5-1 (as a separate Excel file). This table includes values for both invertebrates and fish. It is also important to add that due to both the historical precedence and domination of most media by PFOA/PFOS, most research evaluating PFAS uptake to aquatic organisms has focused on these two compounds.

5.5.1 Bioconcentration

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

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

5.5.2 Bioaccumulation

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

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

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

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

- Bioconcentration and bioaccumulation of perfluorinated acids are directly related to the length of each compound's fluorinated carbon chain.
- Fluorinated sulfonates are more bioaccumulative than carboxylates of the same carbon chain length.
- Fluorinated carboxylates with seven carbons or fewer (perfluorooctanoate and shorter PFCAs) are not considered bioaccumulative according to promulgated persistent, bioaccumulative, and toxic (PBT) criteria of 1,000–5,000 L/kg.
- PFCAs with seven fluorinated carbons or fewer have low biomagnification potential in food webs.
- More research is necessary to characterize the bioaccumulation potential of carboxylates with longer fluorinated carbon chains (> 7 fluorinated carbons), as carboxylates with longer carbon chains may exhibit partitioning behavior similar to or greater than PFOS.

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

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

5.5.3 Biomagnification

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

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

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

A study by Houde et al. (2006) looked at PFOS and C8-C14 perfluorinated carboxylates in the bottlenose dolphin at two marine sites (Sarasota Bay, FL, and Charleston, SC). Based on estimated TMFs, those authors concluded that PFOS and C8-C11 PFCAs biomagnified in this marine food web (Table 5-1, also cited by (Franklin 2016)). Interestingly, for PFCAs, PFOA had the highest TMF, with values progressively decreasing as chain length increased. Conder et al. (2008) reported similar results for perfluorinated acids, with BMF values ranging from 0.1 to 20 (geometric mean of 2). They concluded and Lescord et al. (2015) affirmed that PFCAs with less than seven carbons, and PFSAs with less than six carbons, do not biomagnify and that the bioaccumulation of PFCAs can be directly related to fluorinated carbon chain length (just as the bioaccumulation of persistent lipophilic compounds can be related to hydrophobicity). Conder et al. (2008) also noted that the biomagnification of PFCAs in aquatic food webs is lower than that of most persistent lipophilic compounds, with PFOS being the only perfluorinated acid consistently exhibiting the potential for biomagnification. Finally, Butt et al. (2008) observed biomagnification factors for PFAS in “ringed seal-polar bear” food webs of the Canadian Arctic. Biomagnification factors were greater than one for C8-C14 PFCAs, as well as for PFOS and PFOSA. Like Houde et al. (2006), they observed a decrease in BMF as the carbon chain number increased.

5.6 PFAS Uptake into Plants

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

5.6.1 Bioconcentration/Bioaccumulation

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

Blaine et al. (2013) studied the uptake of PFAAs by greenhouse lettuce and tomato grown in soils prepared to mimic an industrially impacted biosolids-amended soil, a municipal biosolids-amended soil, and a control soil (but incorporated contaminated biosolids equivalent to 10 times higher than the agronomic rates allowed for Class B biosolids), a municipal biosolids-amended soil, and a control soil. BCFs for many PFAAs were well above unity, with PFBA having the highest BCF in lettuce (56.8) and PFPeA the highest in tomato (17.1) in the industrially impacted biosolids-amended soil. BAFs for PFCAs and PFSAs were, in general, slightly higher in the industrially impacted soil than in the municipal soil (~0.3–0.8 log units). The BCFs for PFAAs in greenhouse lettuce decreased approximately 0.3 log units per -CF₂ group (one carbon, two fluorine groups in a molecule). They also conducted a limited field study, in which they measured PFAA levels in lettuce and tomato grown in field soil amended with only a single application of biosolids (at the agronomic rate for nitrogen). The PFAA levels were predominantly below the limit of quantitation (LOQ). In addition, corn stover, corn grains, and soil were collected from several full-scale biosolids-amended farm fields. At these fields, all PFAAs were below the LOQ in the corn grains and only

trace amounts of PFBA and PFPeA were detected in the corn stover. The Blaine et al. (2013) study confirms that the bioconcentration of PFAAs from biosolids-amended soils depends strongly on PFAA concentrations, soil properties, type of crop, and analyte. BCFs developed in Blaine et al. (2013) Blaine et al. (2013) can be seen in Table 5-2.

Gobelius, Lewis, and Ahrens (2017) studied the uptake of 26 PFAS in plants (trees) at an AFFF (fire training) site with contaminated soil and groundwater. Samples from groundwater and different plant species (birch, spruce, cherry, ash, elder, beechfern, and wild strawberry) and tissues (that is, roots, trunk/cores, twigs, leaves/needles) were collected. Foliage had the highest BCFs of all tissues, ranging from 0 to 14,000 and accumulated the highest number of PFAS (8 out of 26), with birch sap showing BCF values up to 41 for 6:2 FTSA. The highest mean BCFs were found for 6:2 FTSA (472; n = 52), PFOS (28; n = 36), PFHxS (10; n = 42), and PFOA (5; n = 24), which might correspond to the AFFF composition used at the site. For PFOA, the mean BCFs (\pm s.d.) were 18 ± 15 for spruce, followed by birch (1.2 ± 1.5) and cherry (0.25 ± 0.043). The authors concluded that PFAS were detected in all plant species, and the distribution followed the order of “shoots to roots”—that is, leaves > twigs/stems > trunk > roots. They cited other authors who have shown that “this order has proven applicable to all samples and species.” Hence, PFAS tend to accumulate in the vegetative portions rather than in the plant storage tissues.

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6 Media-Specific Occurrence

The long period of time during which PFAS have been produced and the many sources of PFAS release to the environment have resulted in low-level contamination of most environmental media worldwide. The concentrations of these human-caused ambient or “background” concentrations may vary widely, based on proximity to industrial areas, patterns of air and water dispersion, and many other factors. As a result, any claims regarding “universal” values for background levels of PFAS should be viewed skeptically. This section provides a relative understanding of PFAS concentrations in various environmental media but does not represent an exhaustive literature review. Note that media-specific occurrences of PFAS are constantly being added in the literature and on state, federal, and other countries’ PFAS websites.

The following sections include figures summarizing the observed concentrations of PFAS that have been reported in the literature. Important details concerning each study used in developing the figures are included in the tables in Section 17.1. As discussed under PFAS Releases to the Environment (Section 2.6), the presence of PFAS in environmental media and ecological receptors has been traced to air emissions; direct discharges to soil, groundwater, and surface water; and leakage from landfills. Sections on Phase Partitioning (Section 5.2) and Media-Specific Migration Processes (Section 5.3) illustrate that PFAS occurrence in the air, aqueous, and solid phases is highly interrelated. Subsequent sections on Human Health Effects (Section 7.1) and Ecological Toxicology (Section 7.2) suggest that PFAS risks to human health may result from exposure via drinking water, groundwater, soils, food, and other media types. Further, ecological impacts are observed on a global scale. This suggests that a complete assessment of PFAS sources and exposure risks, including fate and transport processes that may drive future exposure concerns, requires understanding of PFAS occurrence across multiple phases. This section focuses on occurrence in air, soil and sediment, groundwater, surface water, and biota.

PFAS occurrence in several media types is an active area of research. As discussed in Section 11, sampling and analytical methods are still being optimized and standardized; thus, it is difficult to compare results between studies and conclusions may change over time. PFAS concentrations presented below for different media often indicate maximum values; mean or median values are often well below the maximum values reported for different studies. The processes that influence media-specific PFAS concentrations are illustrated in CSMs shown in Figure 2-16, Figure 2-17 and Figure 2-18.

Section Number	Topic
6.1	Air
6.2	Soil and Sediment
6.3	Groundwater
6.4	Surface Water
6.5	Biota

6.1 Air

Certain PFAS are found in ambient air, with elevated concentrations observed or expected in urban areas nearest to major emission sources described in Section 2.6, such as industrial facilities that produce PFAS or use PFAS chemicals or products in manufacturing; areas where Class B firefighting foams containing fluorine are used or released; waste management facilities, including landfills and wastewater treatment plants; and areas of biosolids production and application (Barton et al. 2006; Ahrens et al. 2011; Liu et al. 2015). Reported concentrations for ionic species such as PFOA and PFOS typically fall within a range of about 1-20 pg/m³ (picograms/cubic meter), although concentrations of PFOA as high as 900,000 pg/m³ have been observed near large manufacturing facilities, including in Parkersburg, West Virginia (Barton (Barton et al. 2006). Concentrations of volatile PFAS such as FTOHs can be in the hundreds of pg/m³ in outdoor air (Figure 6-1A and Table 17-1A).

PFAS have also been observed in indoor air and dust in homes, offices, and other indoor environments (Figure 6-1B and

Table 17-1B). Indoor air concentrations of certain PFAS can be higher than outdoor air concentrations due to the presence of indoor sources (Fromme et al. 2015; Fraser et al. 2012; Goosey and Harrad 2012; Shoeib et al. 2011; Kaiser et al. 2010; Langer, Dreyer, and Ebinghaus 2010; Strynar and Lindstrom 2008; Shoeib et al. 2004). Examples of indoor sources of potential PFAS exposure include stain- and water-resistant coatings used on a number of consumer products, such as carpets, upholstery, clothing, grease-resistant paper, food packaging, and nonstick cookware and ingredients in cleaning products, personal care products, cosmetics, paints, varnishes, and sealants (ATSDR 2019c; Liu et al. 2015; Liu et al. 2014) (Gewurtz et al. 2009; Guo et al. 2009). PFAS concentrations in indoor air have been reported in the range of about 1–440 pg/m^3 for PFOA and PFOS. Concentrations of volatile PFAS such as FTOHs have been reported on the order of 10,000–50,000 pg/m^3 in schools, homes, and offices. Concentrations of FTOHs have been observed in excess of 300,000 pg/m^3 inside commercial buildings (Fromme et al. 2010).

As discussed in Section 5.3.2, 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 2016b; NH DES 2017; VT DEC 2016b). Releases of ionic PFAS from factories are likely tied to particulate matter (Barton et al. 2006), which settle to the ground in dry weather and are also wet-scavenged by precipitation as discussed in Section 5.3.2. Models indicate that deposition depends on amount of PFAS emissions, local topography, particle size, weather patterns, and release characteristics such as smokestack height, effluent flow rate, 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 contaminants.

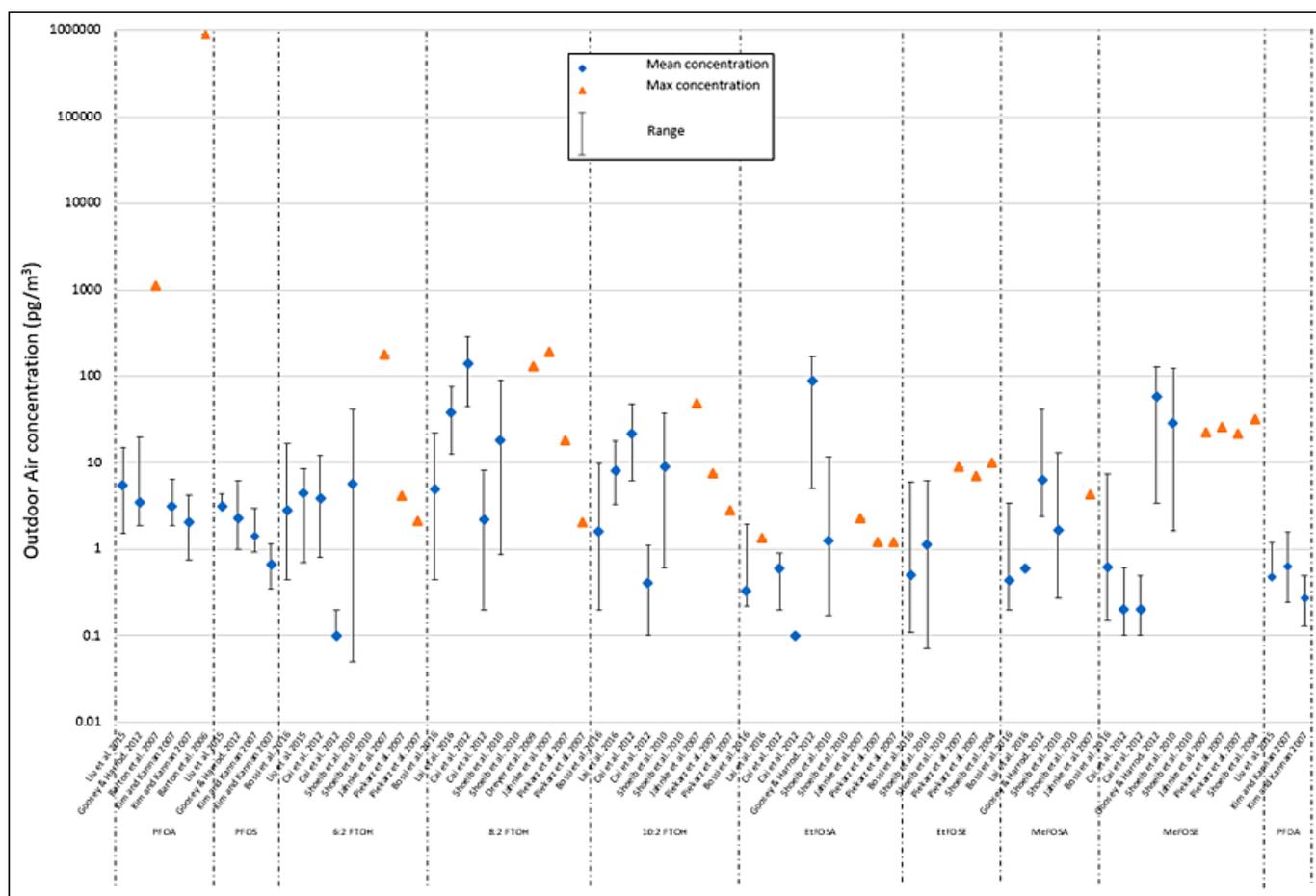


Figure 6-1A. Observed PFAS concentrations in outdoor air.

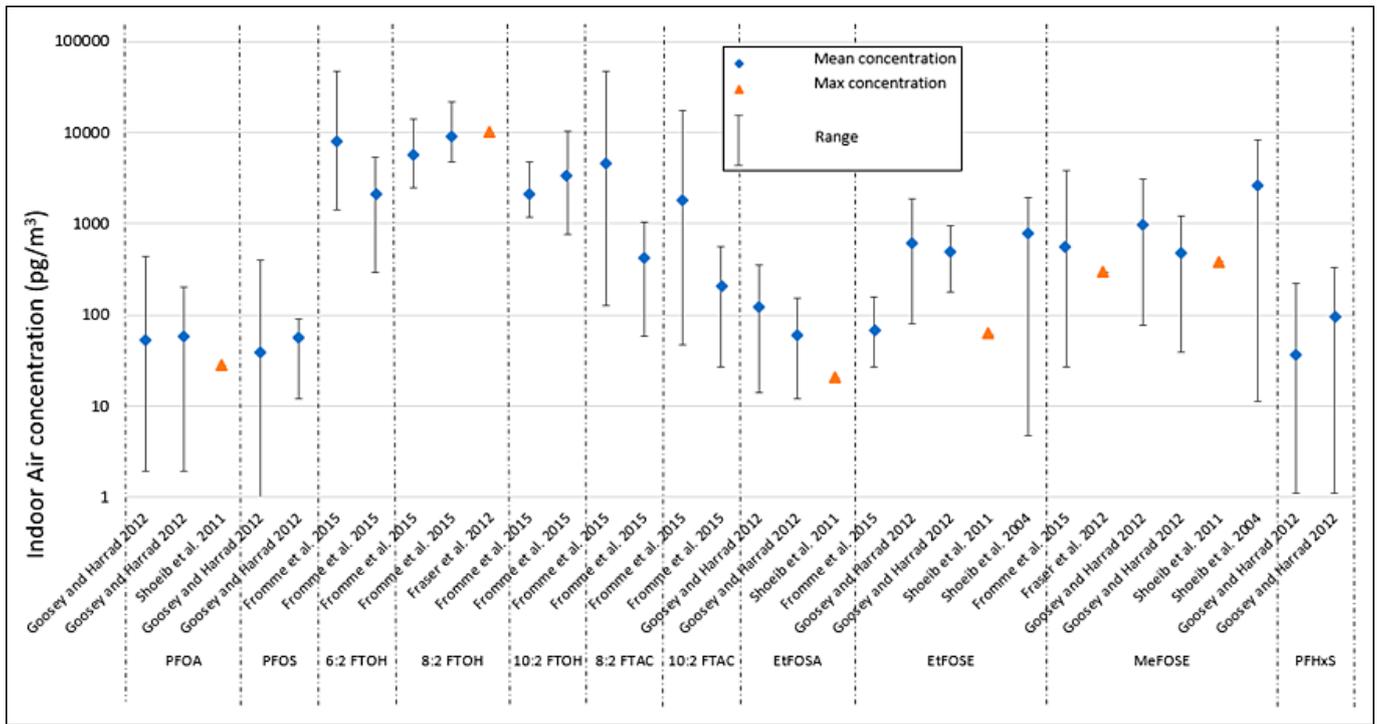


Figure 6-1B. Observed PFAS concentrations in indoor air.

6.2 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. Soil and sediment may act as secondary sources of PFAS via leaching to groundwater and runoff to surface water through leaching and percolation processes, respectively. PFAS distribution in soil is complex, reflecting several site-specific factors such as total organic carbon (TOC), particle surface charges, and phase interfaces (Section 5.2.3). Properties of individual PFAS, such as alkyl 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 soils and sediments (Zhu et al. 2019; Rankin et al. 2016; Strynar et al. 2012).

Atmospheric transport and deposition of PFAS occur on regional and global scales. PFAS concentrations in soil have been observed across a wide range of locations, which suggests that detection of a PFAS in soil does not always imply a local source (Table 17-2 and Section 5.3.2).

Other environmental sources of PFAS to soil include direct application (for example, AFFF and industrial discharge) or soil amendment with PFAS-affected media, such as biosolids (Figure 6-2 and Table 17-2). Individual PFAS concentrations may be above $1,000 \mu\text{g}/\text{kg}$ at AFFF sites. In comparison to AFFF sites, published data on soil PFAS concentrations in industrial settings are limited (Table 17-2). PFAS soil concentrations at industrial sites may be highly variable, depending on the nature of PFAS release and proximity to the source. Concentrations at sites with applied biosolids or sludge will vary depending upon application rates, frequency, duration, and concentration of PFAS in the applied material.

PFAS discharge to surface waters has also affected sediments. Detected concentrations for surface sediments in lakes and rivers reported in the literature generally range up to approximately $100 \mu\text{g}/\text{kg}$, and concentrations and relative distributions of PFAS are variable depending upon types of sources and distance from point sources (Table 17-2). At least one study showed that PFAS concentrations correlate to parameters such as TOC, nitrogen, and phosphorus in sediment (Qi et al. 2016). Dated sediment cores have been used to evaluate deposition of lead, mercury, and other contaminants through time. A recent study of Great Lakes cores (Codling et al. 2018) suggested that the same techniques will also be applicable to PFAS deposition trends. Reported values for ΣPFAS in cores ranged from nondetect to $46.6 \mu\text{g}/\text{kg}$, and concentrations typically increase with time in the cores. Sediment core analysis may be effective for estimating deposition rates only for a subset of PFAS. Long-chain PFAS exhibit greater sorption to sediment, with concentration at a given depth interval representing deposition during that time period. Short-chain PFAS showed less sorption and were more mobile in the sediment column, and therefore were not effective indicators of PFAS deposition rates. This suggests that as more short-chain PFAS are used

as replacements for PFAS applications, sediment cores will have less utility for evaluating trends in deposition rates.

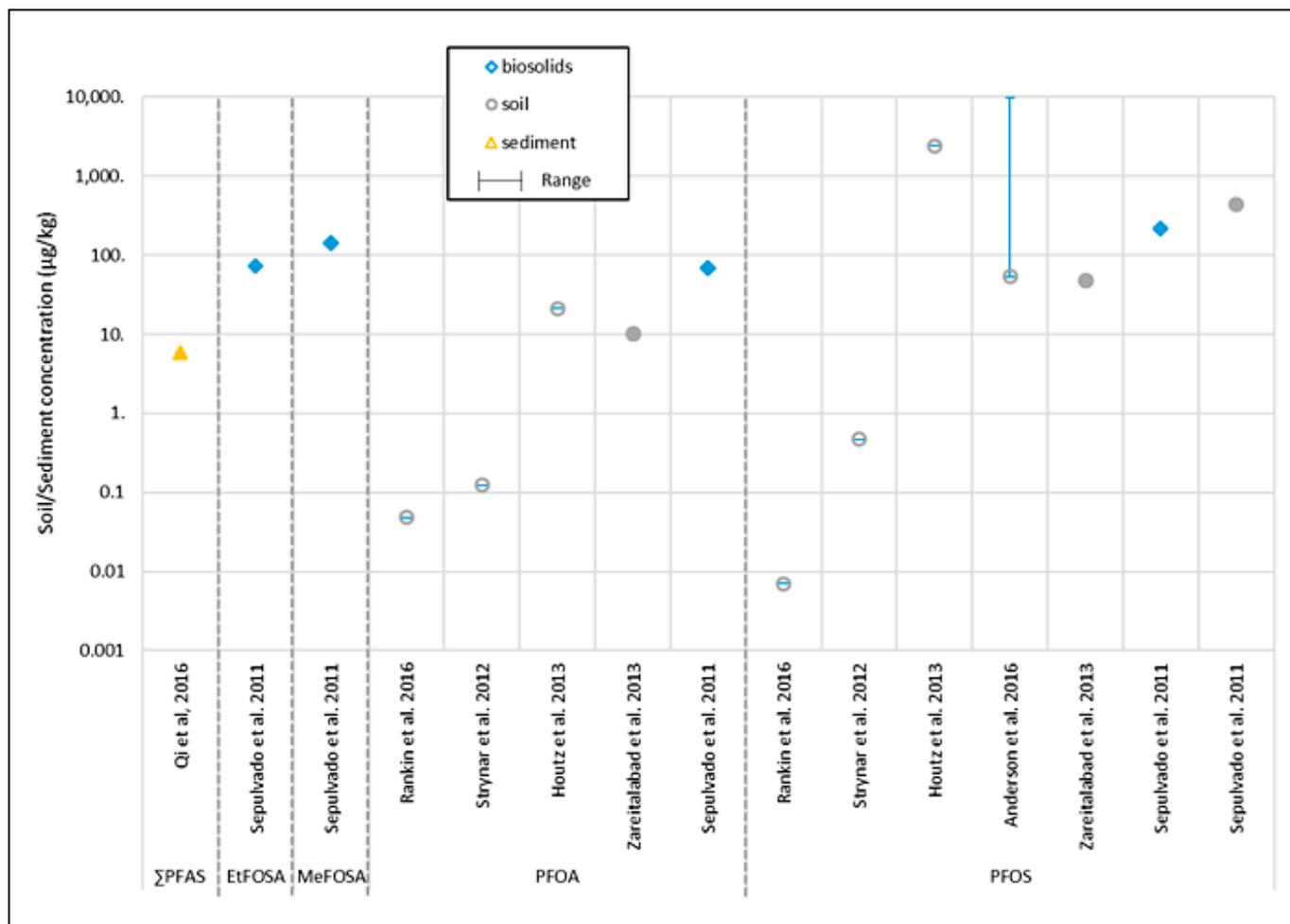


Figure 6-2. Observed PFAS concentrations in soils and sediment.

6.3 Groundwater

USEPA has assembled an extensive data set of the occurrence of six PFAAs in public drinking water. This data set is the result of required monitoring of approximately 4,900 public water systems (all large systems serving more than 10,000 people, plus a subset of smaller systems) for six PFAAs in finished 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 originated from groundwater wells (n = 22,624), surface water (n = 12,733), and mixed sources (n = 792) (USEPA 2017o). A summary of the UCMR3 occurrence data, including analytical reports, is included in Section 8.2.2.2. One or more PFAAs 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). In addition, 59 out of 4,905 public water systems (PWSs) reported PFOA and PFOS at concentrations that exceed the USEPA health advisory of 0.07 µg/L (ATSDR 2018a); these systems represent 1.3% of all of the PWSs that monitored under UCMR3. 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). Individual states are collecting information on PFAS occurrence in smaller public water supplies such as schools and mobile home parks that do not meet the threshold to comply with the Unregulated Contaminant Monitoring Rule, so were not sampled during UCMR3, and for which data are often publicly available, for example, in New Hampshire at NH DES (2020).

Groundwater occurrence data collected as part of domestic and international studies have also characterized the range of PFAS concentrations associated with AFFF release sites, industrial facilities, and landfills; examples of these study results are provided in Figure 6-3 and Table 17-3.

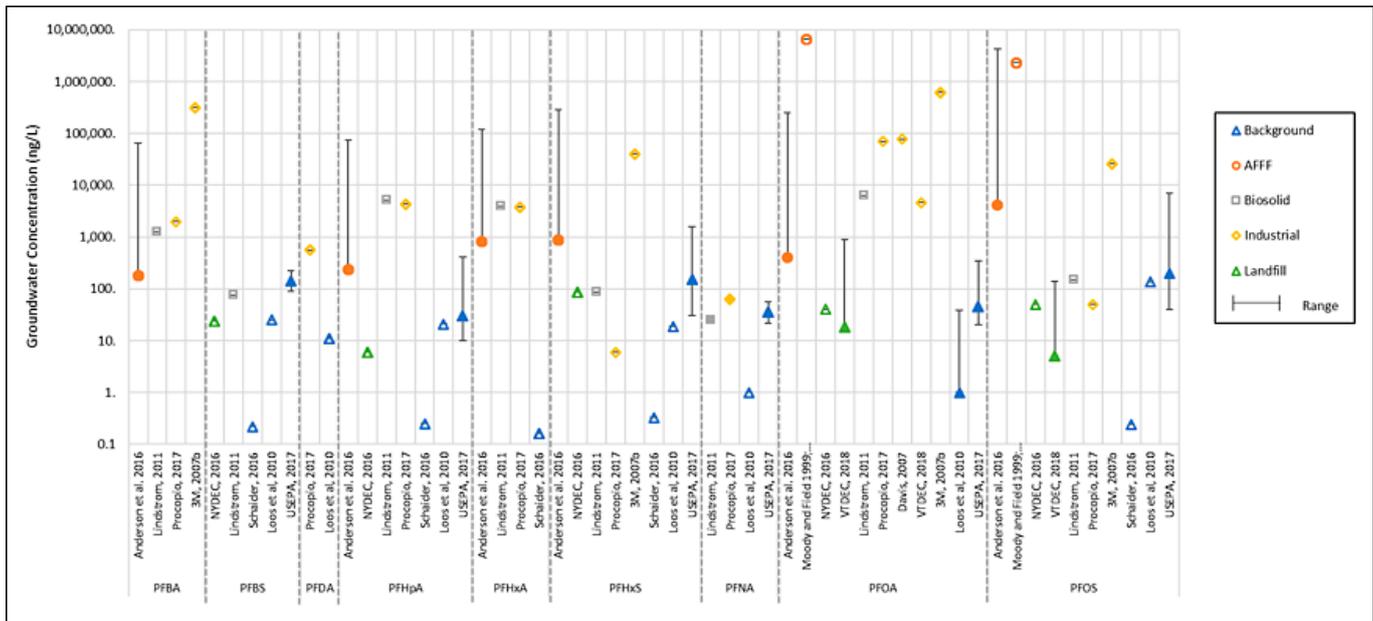


Figure 6-3. Observed PFAS concentrations in groundwater.

6.4 Surface Water

Freshwater, marine water, and stormwater PFAS concentrations usually depend on proximity to the point of release and source concentrations. In addition to releases associated with identified sources, stormwater runoff from nonpoint sources may contribute significant loads of PFAS to surface water (Wilkinson et al. 2017; Zushi and Masunaga 2009). The sorption of PFAS to suspended solids may affect surface water PFAS concentrations. Suspended microplastics may also influence PFAS in surface water (Llorca et al. 2018). Figure 6-4 and Table 17-4 present examples of observed PFOS and PFOA surface water 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, a recent study found perfluoro-2-propoxypropanoic acid (PFPrOPra also known as the GenX chemical HFPO-DA) in untreated water drawn from the Cape Fear River in North Carolina at concentrations up to 560 ng/L, and GenX was just one of many non-alkyl acid PFAS identified (Sun et al. 2016). Surface water occurrence is also an important source of drinking water supply impacts (USEPA 2018f; Post et al. 2013).

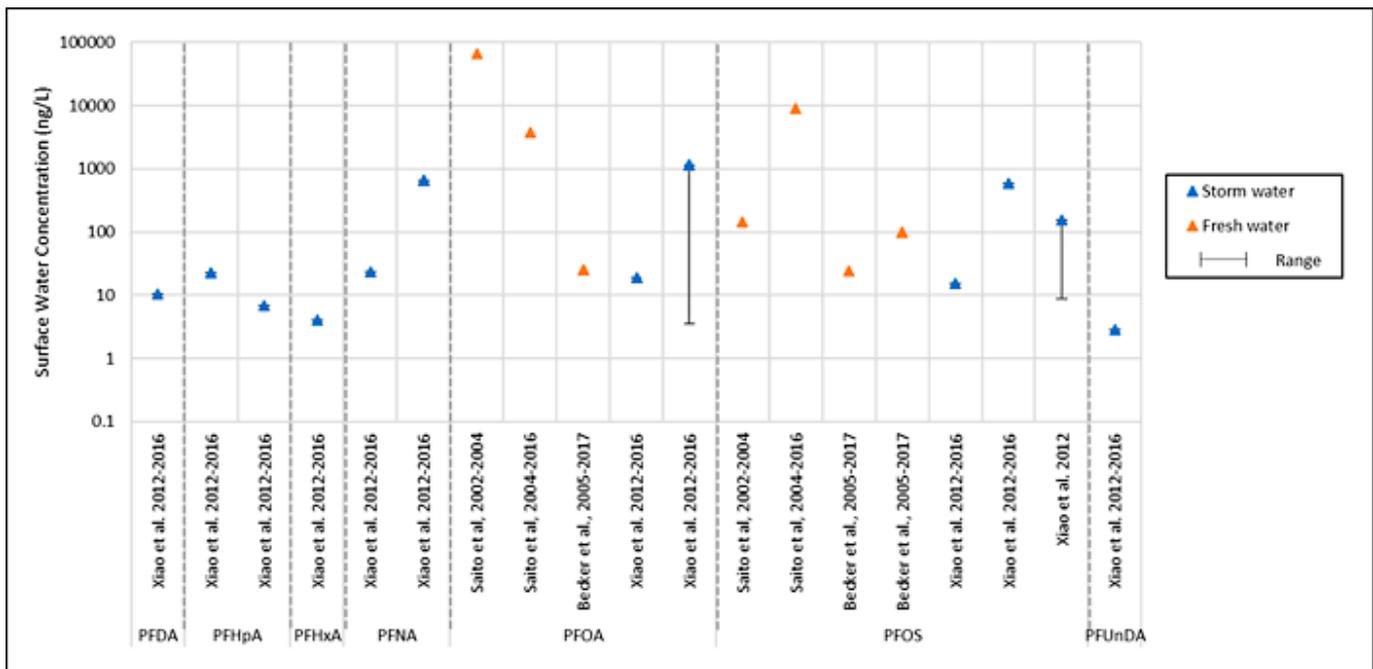


Figure 6-4. Observed PFAS concentrations in surface water.

6.5 Biota

Because PFAS are distributed globally and have a propensity to bioconcentrate, they have been found to be ubiquitous in fish, wildlife, and humans. 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 (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.

6.5.1 Plants

Studies show evidence of uptake and accumulation of 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 (Section 5.6). 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; Blaine, Rich, Sedlacko, Hundal, et al. 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. 2015) or near known PFAS sources (Shan et al. 2014). Based on bioconcentration factors discussed in Section 5.6, concentrations in plants will generally reflect the same concentrations in soil and, for trees with deep roots, groundwater (Gobelius, Lewis, and Ahrens 2017).

6.5.2 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 with similar concentrations 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 Bundshuh 2014). Studies present a PFAS range of approximately 0.1–10 mg/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 (< 2–4.3 mg/kg) with a 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 mg/kg (Martin et al. 2004). The PFAS concentrations in invertebrates were greater than in fish from this lake.

In soil invertebrates, current research indicates that 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 biosolids-amended soils, the mean PFAS BAFs in earthworms have been found to range from 2.2 (PFOA) to 198 (PFDoA) g dry weight (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).

6.5.3 Fish

Accumulation of PFAS in fish is well documented, particularly for PFOS, longer chained PFCAs (with eight or more carbons), and perfluorodecane sulfonate (PFDS) (Houde et al. 2011; Martin et al. 2013; Conder et al. 2008). 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).

In fish, PFOS tends to partition to tissues of high 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. Concentrations of PFOS and other PFAAs tend to be higher in whole fish samples compared with fillets given that a major fraction of PFAAs is found in the carcasses of fish rather than fillets (Fliedner et al. 2018). PFAA concentrations sometimes increase with fish size; however, the relationship with fish size is not consistent as observed for other contaminants such as mercury (Babut (Babut et al. 2017; Gewurtz et al. 2014).

Fish data for PFOS collected near known sources (for example, AFFF sites) from some key studies are summarized in Figure 6-5 and Table 17-5.

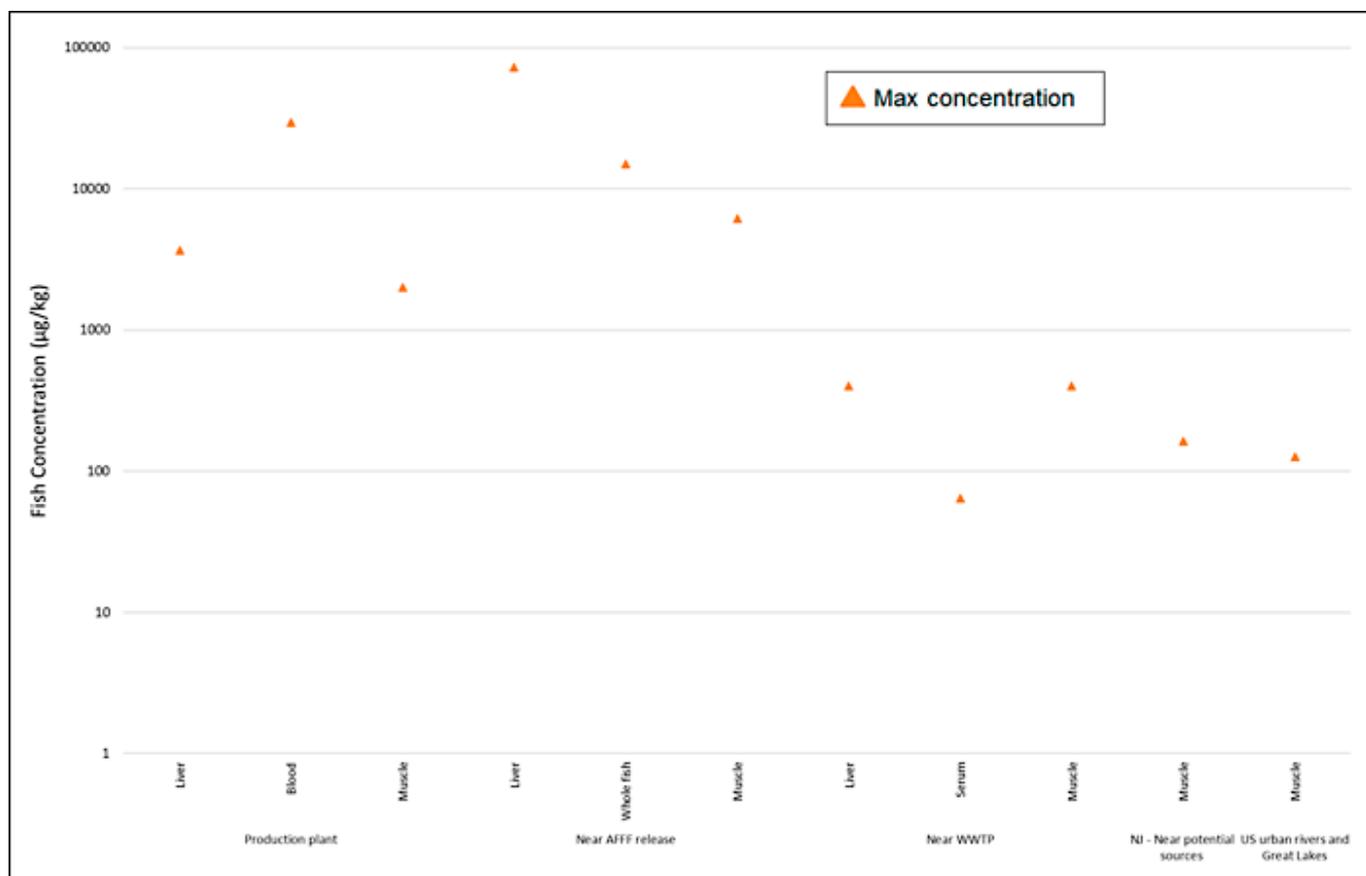


Figure 6-5. Observed PFAS concentrations in fish.

6.5.4 Vertebrates

Most research addressing PFAS concentrations in vertebrates focuses on temporal trends in animals at the top of the food chain, such as piscivorous birds (for example, seagulls) and mammals (for example, dolphins, seals). The concentrations are often reported in protein-rich organs known to concentrate PFAS. For example, to evaluate temporal trends between 2002 and 2014, levels of PFAS were measured in liver samples of Indo-Pacific humpback dolphins and finless porpoises (136–15,300 and 30.5–2,720 ng/g dw, respectively) (Gui et al. 2019). Livers of Beluga whales in the Arctic were the only organ sampled to better understand the relative bioaccumulation of persistent organic compounds (Reiner et al. 2011). These data using top marine predators as “sentinels” of PFAS are important in terms of assessing whether concentration trends are increasing or decreasing in the global environment.

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7 Human and Ecological Health Effects of select PFAS

The PFAS Team developed a training module video with content related to this section, it is the Human and Ecological Effects video.

This section discusses both the information related to assessing health effects of PFAS in humans (Section 7.1) and the adverse effects on ecological (nonhuman) species (Section 7.2). Section 7.1 provides information on human biomonitoring and exposure, toxicokinetics, toxicology in mammalian species, and human epidemiology for long-chain and short-chain PFAAs and the fluorinated ether carboxylates (FECAs) commonly known as the GenX chemical HFPO-DA and ADONA. The section is supplemented by additional material on each of these topics, which is included as Section 17.2. Section 7.2 is organized to include ecological toxicology information on invertebrates (aquatic, benthic, terrestrial), vertebrates (fish, birds, reptiles, amphibians, mammals), and plants. PFAS ecotoxicology data summary tables have been developed as separate Excel spreadsheets.

For further information on the scientific names and carbon chain length of PFAAs addressed in these sections, see Section 2.2 of this document. Use of the human health effects information in guidance values is discussed in Section 8.3 and in site risk assessment in Section 9.1.

Section Number	Topic
7.1	Human Health Effects
7.2	Ecological Toxicology

7.1 Human Health Effects

The PFAS discussed in this section and in Section 17.2 include perfluorocarboxylic acids (PFCAs) with 4-14 carbons and perfluorosulfonic acids (PFSAs) with four or more carbons. Also covered are two FECAs: ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoate (also known as perfluoro-2-propoxypropanoic acid, PFPrOPrA and as the GenX chemical hexafluoropropylene oxide [HFPO] dimer acid; and 4,8-dioxa-3H-perfluorononanoate, commonly known as ADONA. These FECAs are replacements for PFOA as processing aids in certain fluoropolymer production. They are included because they are of current interest and health effects data are available. There is little or no publicly available health effects information for most of the many other PFAS used in commerce (Section 2.5), including precursors that can be converted to PFAAs in the environment and in the human body.

The best studied PFAAs are PFOS and PFOA, although considerable information is available for some other PFAS, including PFNA, PFHxS, PFBA, PFBS, and the GenX chemical HFPO-DA. Laboratory animal toxicology studies and human epidemiological studies suggest health effects that may occur as a result of long-term exposure to PFOA and PFOS at environmentally relevant levels. Figure 7-1 summarizes current health effects information, the references for which are discussed in this section. The other PFAS mentioned above cause generally similar effects in animal studies, with toxicity generally occurring at higher doses for the short-chain PFAAs than for long-chain PFAAs. These health effects, discussed in more detail in Sections 7.1.3, and 7.1.4 are the basis for current guidance values and regulations for PFOA, PFOS, and several other PFAS. These are available in a separate Excel file published regularly by ITRC on the fact sheets page.

<ul style="list-style-type: none"> • Animal <ul style="list-style-type: none"> <input type="checkbox"/> Liver effects <input type="checkbox"/> Immunological effects <input type="checkbox"/> Developmental effects <input type="checkbox"/> Endocrine effects (thyroid) <input type="checkbox"/> Reproductive effects <input type="checkbox"/> Hematological (blood) effects <input type="checkbox"/> Neurobehavioral effects <input type="checkbox"/> Tumors (liver, testicular*, pancreatic*) <p>* PFOA Only</p>	<ul style="list-style-type: none"> • Human (possible links) <ul style="list-style-type: none"> <input type="checkbox"/> Liver effects (serum enzymes/bilirubin, cholesterol) <input type="checkbox"/> Immunological effects (decreased vaccination response, asthma) <input type="checkbox"/> Developmental effects (birth weight) <input type="checkbox"/> Endocrine effects (thyroid disease) <input type="checkbox"/> Reproductive effects (decreased fertility) <input type="checkbox"/> Cardiovascular effects (pregnancy induced hypertension) <input type="checkbox"/> Cancer* (testicular, kidney)
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Figure 7-1. Some health effects of PFOA and/or PFOS identified from published studies (not exhaustive).

USEPA has completed draft toxicity assessments for the GenX chemicals and PFBS (USEPA 2018e, d), and USEPA announced in December 2018 that five additional PFAAs (PFNA, PFBA, PFHxA, PFHxS, PFDA) will be reviewed for toxicity assessment through the Integrated Risk Information System (IRIS), but no timeline has been established (USEPA 2019e).

Much of the information presented here is recent, and new studies continue to become available. Additionally, it should be noted that it was not possible to include all relevant citations, particularly for those compounds with large health effects data sets. Further information on the topics in this section can be found in databases such as the National Library of Medicine’s PubMed (a database containing citations to relevant peer-reviewed publications), and in reviews such as Kirk (2018) and Lau (2012), and in several chapters of the Agency for Toxic Substances and Disease Registry (ATSDR) draft toxicological profile (ATSDR 2018e), DeWitt (2015), and NICNAS (2018) for PFAS in general; Australian Department of Health Expert Panel, which is a review of systematic reviews since 2013 and key national and international reports since 2015:

- PFOA: Australia Government DOH (2018); USEPA (2016h, 2016d) and NJDWQI (2017c) NJDWQI (2017a)
- PFOS: USEPA (2016g, 2016c) MDH (2019a), and NJDWQI (2018b)
- PFNA: NJDWQI (2015)
- PFBS: MDH (2017c) and USEPA (2018e) (draft)
- PFBA and PFHxS: MDH (2018a, 2019b)
- GenX chemicals: RIVM (2016), Chemours (posted online by (NC DEQ 2018)), and (USEPA 2018g) draft
- Short-chain PFAAs: Buck (2015) and Danish EPA (2015)
- FECAs: Buck (2015)

Human biomonitoring and sources of exposure are addressed in Section 7.1.1. Information on serum levels of long-chain PFAAs from communities with contaminated drinking water is presented in Table 17-6. The unique toxicokinetic properties of PFAS are discussed in Section 7.1.2. Table 17-7 summarizes available data on PFAS elimination half-lives in humans and experimental animals. The numerous reviews of potential epidemiological associations of health endpoints with PFAAs are discussed in Section 7.1.3. Toxicology studies in mammalian species are summarized in Section 7.1.4, and more detailed toxicology information is presented in Section 17.2.5 and Table 17-8 (provided as a separate Excel file).

Finally, data gaps and research needs are discussed in Section 7.1.5.

7.1.1 Human Biomonitoring and Sources of Exposure

Numerous human biomonitoring studies (such as (CDC 2018, 2019; Olsen et al. 2017)) have demonstrated that certain PFAS, particularly long-chain PFAAs, are present in the blood serum of almost all U.S. residents. Long-chain PFAAs, with half-lives of one to several years, are slowly excreted in humans. Therefore, serum levels are indicators of long-term exposure to long-chain PFAAs and do not fluctuate greatly with short-term variations in exposure. Serum PFAA concentrations originate from direct exposure to the compounds and from metabolism of precursor compounds to PFAAs within the body (reviewed in Kudo (2015)). The largest U.S. general population biomonitoring studies are from the National Health and Nutrition Examination

Survey (NHANES), a nationally representative survey conducted by the Centers for Disease Control and Prevention (CDC), which began monitoring for PFAS in 1999–2000 (Figure 7-2). As can be seen in Figure 7-2, serum PFAS levels in the general population have declined over time, most notably for PFOS. The most recent NHANES monitoring data (2015–2016) include seven PFAAs (PFOA, PFOS, PFNA, PFHxS, PFDA, PFUnDA, PFDaA) and one other PFAS (MeFOSAA); four additional PFAS (PFBS, PFHpA, PFOSA, EtPFOSA) that were infrequently detected in earlier rounds of NHANES were not monitored in 2015–2016 (CDC 2019). Other adult U.S. general population biomonitoring data come from four studies of blood donors in 2000–2015 (Olsen et al. 2017) and the California Environmental Contaminant Biomonitoring Program (CA OEHHA 2011).

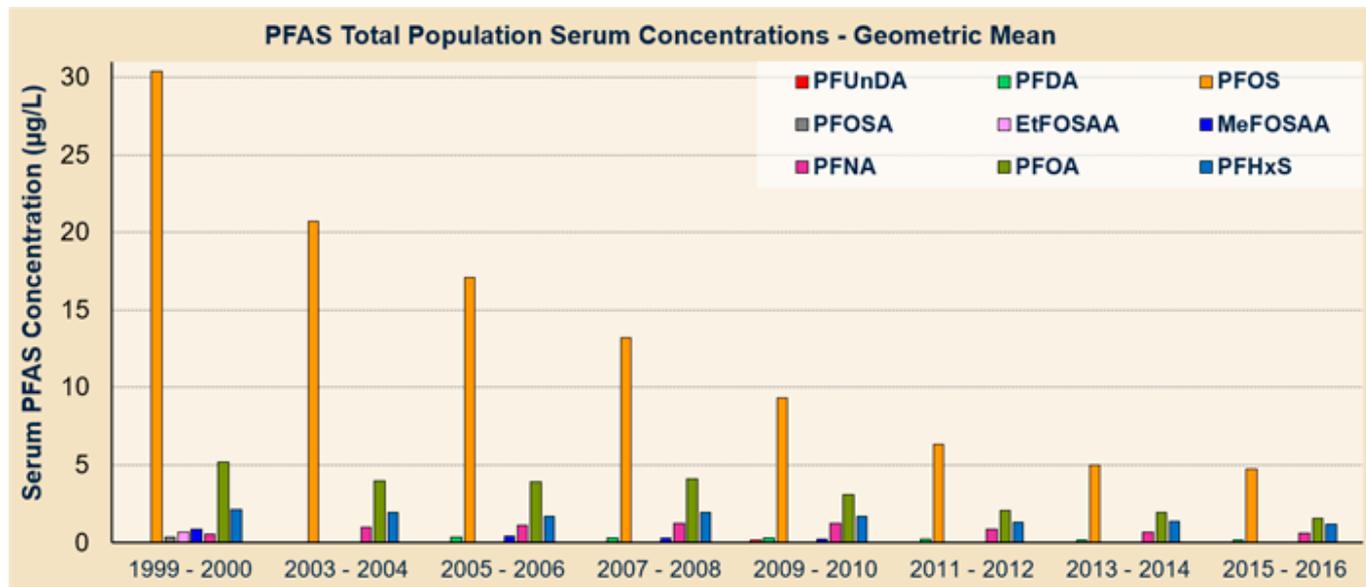


Figure 7-2. Geometric mean serum concentrations (ng/ml) of selected PFAAs (NHANES, 1999-2016).

In the general population, where there is no specific source of PFAS contamination and PFAA concentrations in drinking water and serum are in the typical “background” range, the primary sources of exposure to PFAAs and their precursors appear to be food and food packaging, and consumer products (particularly nonpolymer aftermarket treatments and coatings; Section 2.5), and house dust formed from such consumer products (Trudel et al. 2008; Fromme et al. 2009; Vestergren and Cousins 2009; Beesoon et al. 2012; Gebbink, Berger, and Cousins 2015). PFAS have been detected in air (ATSDR 2018e), and inhalation is therefore an additional potential exposure pathway. Serum levels of PFOS and PFOA documented by NHANES data appear to indicate that the phaseout of production and use of these chemicals in most products has resulted in decreased PFOS and PFOA exposures for the general population from these sources. As this occurs, the relative contribution from drinking water to these PFAAs will increase (where they are present in the drinking water).

In communities near sources of PFAS contamination, exposures that are higher than those in the general population can result from ingestion of contaminated drinking water or consumption of fish from contaminated waters. As PFAS concentrations in drinking water increase, the contribution of drinking water to the total body burden increases and typically dominates an individual’s exposure. Information on serum levels of long-chain PFAAs from communities with contaminated drinking water in several U.S. states and other nations is found in Table 17-6. Finally, occupational exposures to workers can be higher than exposures from environmental media.

Specific considerations and exposure routes relevant to PFAS exposures in the fetus, breast-fed and formula-fed infants, and young children are discussed in Section 17.2. Also see Section 17.2.2 for additional discussion of human biomonitoring and sources of human exposure.

7.1.2 Toxicokinetics

PFAAs have unique toxicokinetic properties as compared to other types of persistent organic pollutants (POPs). Unlike most other bioaccumulative organic compounds (for example, dioxins, PCBs), PFAAs do not have a high affinity for adipose tissue (that is, fat). In contrast, PFAAs are water soluble, have an affinity for proteins, and generally distribute primarily to the liver, blood serum, and kidney (Bischel et al. 2011; Lau 2012, 2015; Kato 2015). PFAAs, GenX chemicals, and ADONA are not metabolized (meaning they do not break down to other PFAS). However, some PFAS that are PFAA precursors can be metabolized to PFAAs within the body.

In general, short-chain PFAS are excreted more rapidly than longer chain PFAS in humans and other mammalian species. The excretion rates for specific PFAS can vary substantially between species, and in some cases between males and females of the same species. Table 17-7 summarizes available data on PFAS elimination half-lives in humans and experimental animals. Half-lives in laboratory animals (rodents and nonhuman primates) generally range from hours to several months for long-chain PFAS, and hours to several days for short-chain PFAS. Human half-lives for PFAS are longer than in other mammalian species, with estimates of several years for long-chain PFAAs and several days to one month for shorter chain PFAAs such as PFBA, PFHxA, and PFBS. Because of the much longer human half-lives, animal-to-human comparisons must account for the much higher internal dose (for example, blood serum level) in humans than in animals from the same administered dose.

Toxicokinetics relevant to developmental exposures to PFAAs are important because developmental effects are considered to be sensitive endpoints for toxicity of long-chain PFAAs, and some human studies have found associations of long-chain PFAAs with decreased fetal growth. PFAAs cross the placenta (reviewed in Lau (2012) and Kudo (2015)) and are present in breast milk (Luebker, Case, et al. 2005; White et al. 2009) (Kato 2015), and long-chain PFAAs have been found in cord blood (for example, (Wang et al. 2019) and amniotic fluid (Stein et al. 2012; Zhang, Sun, et al. 2013). In human infants, exposures from breast milk result in substantial increases in long-chain PFAA serum levels during the first months after birth (Fromme et al. 2010; Mogensen et al. 2015). Exposures to infants from formula prepared with PFAS-contaminated water are also higher than in older individuals due to their higher rate of fluid consumption (USEPA 2011a).

Toxicokinetic factors called clearance factors, which indicate bioaccumulative potential, can be used to relate external doses (mg/kg/day) of PFOA and PFOS to steady-state serum levels (ng/L). When combined with average water ingestion rates (USEPA 2011a), these factors can be used to predict that the expected average increases in the levels of PFOA or PFOS in blood serum from long-term drinking water exposure are 100-fold or greater than the concentration in the drinking water (Bartell 2017; NJDWQI 2017a; Post, Gleason, and Cooper 2017).

Finally, toxicokinetics in rodents (Loveless et al. 2006; De Silva et al. 2009) and humans (Zhang, Beesoon, et al. 2013; Gao et al. 2015; Beesoon et al. 2011) may differ among isomers of the same PFAA.

See Section 17.2.3 for additional discussion of PFAS excretion and excretion rates, toxicokinetics relative to developmental exposure, the relationship of human exposure to serum levels, and isomer-specific toxicokinetics.

7.1.3 Human Epidemiology Studies

The epidemiological database for long-chain PFAAs is more extensive than for many other environmental contaminants. Based on publications available through the National Library of Medicine's PubMed database, well over 100 human studies have examined associations (that is, statistical relationships) between PFAS, primarily long-chain PFAAs, and a wide variety of diseases and health endpoints (NJDWQI 2018a). Some effects, such as changes in serum lipids, liver biomarkers, uric acid levels, thyroid endpoints, vaccine response, and fetal growth, have been evaluated in multiple studies and populations, while only one or a few studies were located for many other effects.

These studies can be categorized based on the type of population evaluated: general population, communities with contaminated drinking water, or occupationally exposed workers. Almost all of these studies were published within the past 10 years, with the exception of a small number of occupational studies from a few years prior to that time.

Although discussion of individual epidemiological studies is beyond the scope of this section and the corresponding appendix section, evidence for associations and/or causality for some PFAAs and certain health effects (for example, increased cholesterol, increased liver enzymes, decreased vaccine response, thyroid disease, and for PFOA, some types of cancer) has been evaluated by various academic researchers and government agencies. The conclusions of some of these evaluations are discussed briefly below, with additional detail provided in Section 17.2.4.

For some health endpoints, there is general consensus for consistent evidence for association with one or more long-chain PFAAs, while conclusions differ among evaluations by different groups of scientists for other endpoints. For additional endpoints, data are too limited to make a conclusion, results are inconsistent, or there is no evidence for an association. The general reviews cited in Section 17.2.4 include detailed discussions of epidemiological data for PFOA, PFOS, and PFNA. In-depth reviews for other individual PFAAs (for example, PFHxS, PFDA, PFUnA) are not available.

As shown in Table 7-1, associations in human epidemiological studies of PFAAs (primarily PFOA and PFOS) for some endpoints (for example, increased liver enzymes, decreased fetal growth, decreased vaccine response) are consistent with animal toxicology studies (Section 7.1.4). For serum lipids (for example, cholesterol), conflicting observations (increases in humans versus decreases in rodents) may be impacted by differences in the fat content in the diets of humans versus

laboratory animals and/or large differences in the exposure levels in human versus animal studies (Tan et al. 2013; Rebholz et al. 2016).

Associations of some health endpoints with certain PFAAs are generally, although not totally, consistent, and some evaluations have concluded that the data for certain effects support multiple criteria for causality. However, risk-based toxicity factors (Reference Doses for noncancer effects and slope factors for cancer risk) developed by most government agencies are based on dose-response relationships from animal data, with the human data used to support the hazard identification component of toxicity factor development. A major factor that has precluded the use of human data in the dose-response component of toxicity factor development is the concurrent exposure to multiple PFAAs in most or all study populations. Because serum levels of co-occurring PFAAs tend to correlate with each other, it is difficult to determine the dose-response relationship for individual PFAAs. Notwithstanding, German Human Biomonitoring Commission (2018) the German Environment Agency (2016) developed Human Biomonitoring Values (serum levels below which adverse effects are not expected) and the European Food Safety Authority (EFSA 2018) developed Tolerable Weekly Intakes for PFOA and PFOS based on human data from the general population. These values are lower than many of the values that are based on toxicity data from animals. It is noted that the approaches and policies used to develop these European human-based values may differ from those used by U.S. agencies in toxicity factor development.

See Section 17.2.4 for additional discussion of epidemiologic studies that have been conducted on PFAS.

7.1.4 Animal Toxicology Studies

This section focuses on the most notable toxicological effects in mammalian studies of certain PFCAs, PFSAs, and FECAs. All PFAS covered in this section for which data are available cause increased liver weight; additional effects common to some of these PFAS include immune system, hematological (blood cell), and developmental toxicity, as well as more severe types of liver toxicity. Of the four PFAS that have been tested for carcinogenicity in rodents, PFOA, PFOS, and the GenX chemical HFPO-DA caused tumors while PFHxA did not.

In general, toxicity is dependent on both intrinsic potency of the compound (Gomis et al. 2018) and its toxicokinetics. Longer chain PFAAs are generally toxic at lower administered doses than shorter chain compounds because their slower excretion results in a higher internal dose from the same administered dose. Similarly, for those PFAS that are excreted much more rapidly in female rats than in males (Section 7.1.2 and Table 17-7), higher doses in females than in males are needed to achieve the same internal dose.

Toxicological data from animal studies are used as the basis for almost all human health toxicity factors (for example, Reference Doses, cancer slope factors) for PFAS, with the few exceptions from Europe that are based on human data (Section 7.1.3); all current PFAS standards and guidance values for environmental media are based on animal toxicology data (also see Sections 8.3 and 9.1). As is the case for toxicology studies in general, the doses used in most of these studies are higher than the doses to which humans are generally exposed from environmental contamination. Conversely, unlike most other environmental contaminants, PFAS have been associated with health effects in humans at much lower exposure levels than the doses used in animal toxicology studies.

Table 17-8 (provided as a separate Excel file) provides information on toxicological effects in mammalian species (hazard identification information) for the following PFAS:

- PFCAs including PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, and PFDoA
- PFSAs including PFBS, PFPeS, PFHxS, PFHpS, and PFOS
- FECAs including ADONA and the GenX chemical HFPO-DA.

Section 17.2.5 also summarizes information on systemic effects; reproductive and developmental effects, and chronic toxicity and tumorigenicity of these PFAS.

- Largest publicly available toxicological data sets for: PFOA and PFOS
- Considerable data for: PFBA, PFHxA, PFNA, PFDA, PFBS, and the GenX chemicals HFPO-DA and its ammonium salt
- One or a few studies for: PFHpA, PFUnA, PFDoA, PFHxS, and ADONA
- No toxicological data were located for PFPeA, PFTTrDA, PFTTeDA, PFPeS, PFHpS, PFNS, or PFDS.

Most studies were conducted in rats and mice, with a few studies in nonhuman primates (monkeys) and other species such as rabbits. The National Toxicology Program (NTP 2019b, c) has conducted 28-day studies of seven PFAS (PFHxA, PFOA,

PFNA, PFDA, PFBS, PFHxS, PFOS) in male and female rats that evaluated numerous toxicological endpoints and provided serum PFAA data for each dosed group; results of these studies are included in Table 17-8 (provided as a separate Excel file). Although the doses at which effects occurred are not provided in this section or in the supporting appendix material, it is emphasized that No Observed Adverse Effect Level (NOAELs) and Lowest Observed Adverse Effect Level (LOAELs) vary widely between compounds for a given endpoint, between different endpoints for the same compound, and between species (and sexes in some cases) for the same compound and endpoint. Furthermore, the effects noted may not have been observed in all studies in which they were evaluated.

NTP (2020) has also conducted a chronic carcinogenicity study of PFOA administered in feed to rats that assessed the contribution of combined gestational and lactational (perinatal) exposure as compared to exposure beginning after weaning. It was concluded that there was clear evidence of carcinogenic activity in male rats based on the increased incidence of liver tumors and pancreatic acinar cell tumors, and some evidence of carcinogenic activity in female rats based on increased incidence of pancreatic acinar cell tumors. Non-neoplastic lesions were increased in the liver and pancreas in males and in the liver, kidney, forestomach and thyroid in females. There were very few significant differences in effects when exposure began in the perinatal period compared to when it began after weaning.

See Section 17.2.5 for additional discussion of studies in animals that have evaluated the effects of PFAS on noncancer and cancer endpoints.

7.1.5 Data Gaps and Research Needs

Although many studies relevant to health effects of PFAAs have become available in the last few years, important data gaps remain for most of the PFAAs and FECAs discussed here and in Section 17.2, as well as for many additional PFAS used in commerce or found in AFFF. The data gaps (discussed in more detail in Section 17.2.6) include:

- Human half-lives and other toxicokinetic data are not available for some PFAS found in drinking water and other environmental media.
- Currently available data indicate that reactive intermediates may form in the body from the metabolism of PFAA precursors to PFAAs. More studies are needed to understand the toxicologic significance of these intermediates.
- With the exception of PFOA, there is a lack of epidemiologic data from communities exposed to AFFF, PFOS, and/or other PFAS in drinking water.
- Additional toxicology data are needed for some PFAAs found in environmental media, including drinking water. In particular, very little toxicologic data are available for PFHpA, and no information was located for PFPeA. There is also a need for toxicologic studies on the effects of PFAS mixtures.
- Multigeneration studies of the reproductive and developmental effects of additional PFAS are needed.
- Chronic toxicity and carcinogenicity studies are currently available for only four PFAS (PFHxA, PFOA, PFOS, GenX), and are needed for PFHxS, PFNA, ADONA, and other PFAS to which humans may be exposed.
- The majority of the many thousands of PFAS, including those in commercial use, have very limited or no toxicity data. This is a critical data gap in health effects information for PFAS.
- Similarly, current NHANES biomonitoring includes only 11 PFAS, primarily PFAAs. There is limited or no biomonitoring data for many other PFAS produced or used in the United States, some of which are known to be bioaccumulative in humans.

7.2 Ecological Toxicology

This section is organized around currently available toxicity information for invertebrates (aquatic/benthic/terrestrial), vertebrates (fish, birds, reptiles/amphibians, mammals), and plants. Toxicological data were obtained from a general literature review as well as querying of the USEPA Ecotox Database (USEPA 2019c). However, as discussed below, this is an active area of research, and interested readers are encouraged to query the literature for updated research and reviews. PFAS ecotoxicology data summary tables have been developed as a separate Excel spreadsheet. The Excel file includes ecotoxicology data for aquatic species (Table 7-1), non-mammalian terrestrial species (Table 7-2) and mammalian wildlife species (Table 7-3).

7.2.1 Introduction

Biomonitoring studies across a variety of organisms, habitats, and geographies show that certain PFAS compounds can accumulate in wildlife and that exposures are occurring on a global scale (Reiner and Place 2015; Giesy and Kannan 2001). Therefore, it is important to understand how such exposure and bioaccumulation may manifest in adverse effects,

particularly as they relate to ecological communities. Information on bioaccumulation of PFAS is addressed in Section 6.5. Section 7.1 focuses on the toxicological effects of PFAS on humans and summarized toxicity data from experimental exposures of laboratory animals. This section provides an overview of available, published toxicological data relating exposure of PFAS to toxic effects on aquatic, benthic, and terrestrial organisms, with the goal of broadening the reader's understanding of known or potential effects in ecological systems, as well as highlighting areas where more data are needed. This information can also be applied for use in ecological risk assessments (ERAs), particularly in light of the fact that ecological risk of PFAS is currently neither well understood nor uniformly assessed or regulated. However, the reader is encouraged to review the primary source literature from which cited ecotoxicity values have been derived to confirm and understand the basis and assumptions of the cited literature before using this information in an ERA.

This review shows that ecotoxicity data are available for aquatic invertebrates, particularly for PFOA and PFOS, with most studies focused on aquatic invertebrates. Although there are numerous studies on PFAS exposure in terrestrial vertebrates (for example, mammals, reptiles, birds), and ample toxicological studies in laboratory animals, there is, overall, relatively little to no ecologically relevant toxicity data for terrestrial vertebrates in the wild. Although some mechanistic studies have been conducted with aquatic organisms, little has been done with other organisms and even less has been done with different classes of PFAS in aquatic and terrestrial wildlife.

The focus of most ecotoxicity studies to date has been primarily on PFOS and PFOA. Therefore, most of the data discussed and summarized in this section are for those compounds. However, data for other PFAS compounds, including short-chain PFAS and precursors (Section 2.2), are also presented where available. Given the historical differences among older analytical methods and more recent advances in analyzing PFAS, the focus of the ecotoxicity studies covered in this review is generally on those published from approximately the year 2000 and later.

PFAS ecotoxicology data summary tables have been developed as a separate Excel spreadsheet containing toxicity information for PFAS compounds:

- Table 7-1: aquatic and benthic invertebrates, aquatic plants, and fish
- Table 7-2: terrestrial invertebrates, microorganisms and plants
- Table 7-3: mammalian wildlife

It is important to note that neither this spreadsheet nor this section is intended to represent an exhaustive review of PFAS ecotoxicity studies. Ecotoxicity of PFAS is an area of active research, with new information emerging regularly. Toxicological effects presented and discussed herein are generally those considered most relevant to ecological communities—mainly survival, growth, and reproduction. Both acute and chronic exposure studies are included. Although data have been generated for other toxicological endpoints, these studies are not the focus of this section, but may occasionally be referenced.

In general, studies indicate that PFAS toxicity in invertebrates is chemical-specific and varies with the type of organism and environmental factors. There is a paucity of field studies for avian and mammalian wildlife species, and confounding factors such as the co-occurrence of other stressors (other pollutants, physical stressors, etc.) make it difficult to definitively associate PFAS exposure with adverse outcomes. Only one recent avian study on tree swallow egg hatching outcomes is known to date (Custer et al. 2014), and field-based effects studies on mammals are difficult to find (ECCC 2018). However, laboratory animal studies suggest potential relationships between PFAS tissue concentrations and immunological, hematological, liver, kidney, and reproductive effects (DeWitt 2015; ECCC 2018).

The abundance of biomonitoring data suggests that PFAS exposure is occurring in wildlife; however, the lack of toxicity data for this group of organisms represents a significant data gap. This highlights the need for additional study of this class of compounds in general, as well as the need for expansion of toxicity studies to a larger group of PFAS and to a greater variety of taxa, and for field studies that may assess population-level effects.

Relative aquatic toxicity for PFAS is discussed in the following sections using descriptive criteria developed by the USEPA within their Design for the Environment Program for the Alternatives Assessments and the Safer Choice Program. These criteria are expressed as relative toxicity based on effects concentrations ranging from less than 0.1 mg/L (very high toxicity) to greater than 100 mg/L (low toxicity); criteria are provided in Table 7-4.

Table 7-4. Hazard criteria for aquatic toxicity studies from USEPA (in mg constituent/L water)

Toxicity	Very High	High	Moderate	Low	Very Low
USEPA: Aquatic Toxicity (Acute)	<1.0	1-10	>10-100	>100	NA
USEPA: Aquatic Toxicity (Chronic)	<0.1	0.1-1	>1-10	>10	NA

Note: Refer to the PFAS ecotoxicology data summary Table 7-1 in the separate Excel spreadsheet for toxicological endpoints and values.

7.2.2 Invertebrates

7.2.2.1 Aquatic

There are more toxicity data available for PFOS than for other PFAS compounds. A summary of the range of acute toxicity to aquatic organisms can be found in Table 7-5. PFAS have a very wide range of toxicities to aquatic organisms under acute exposure scenarios following the USEPA Hazard Criteria (Table 7-4), but overall, they would be classified as having moderate to low toxicity. One exception with this generalization is that of mussel exposures to PFOS and PFOA in the marine environment, where no effect was seen at 0.0001 mg/L but was measured at 0.1 mg/L (Fabbri et al. 2014); this would result in high hazard using the USEPA Hazard Criteria.

Compared to acute studies, there are relatively few chronic studies in aquatic invertebrates. PFAS for which we have chronic effects data include PFOS, PFOA, and PFNA. Life cycle tests with multiple taxa have been conducted to evaluate the chronic toxicity of PFOS to freshwater aquatic invertebrates. The chironomid (*Chironomus tentans*) is currently reported as having the greatest sensitivity to chronic exposure, where effects are seen at concentrations less than 0.0023 mg PFOS/L. Studies by Bots et al. (2010) and Van Gossum et al. (2009) indicated that damselflies (*Enallagma cyathigerum*) may also be similarly sensitive to PFOS, with NOEC values less than 0.01 mg/L. In the marine environment, a life cycle toxicity test with the saltwater mysid, yielded a NOEC of 0.24 mg PFOS/L based on growth and number of young produced (Drottar and Krueger 2000b). Finally, there is one chronic study available for PFNA in which a 21-day exposure of *Daphnia magna* resulted in significant decrease in growth at 0.04 mg/L (Lu et al. 2015).

Some PFAS may potentially cause adverse effects in aquatic invertebrates to span across multiple generations following the initial exposure. Marziali et al. (2019) evaluated effects over 10 generations of *C. riparius* initially exposed at 0.01 ug/L of PFOA, PFOS and PFBS; all treatments showed reduced growth in at least several generations, with no observed induced tolerance to the studied PFAS.

Table 7-5. Summary of aquatic invertebrate ecotoxicity data for PFAS

PFAS	Carbon Chain Length	Range of Toxicity Values-EC or LC50 (mg/L)*	References
Acute Studies			
PFBA	4	182-521	(Ding et al. 2012) (Barmantlo et al. 2015)
PFBS	4	2,183	(Ding et al. 2012)
PFHxA	6	1,048	(Barmantlo et al. 2015)
PFOS	8	59-169	(3M Company 2003) (Boudreau et al. 2003)
PFOS-Marine	8	0.0001-9.4	(Fabbri et al. 2014); (Robertson 1986)
PFOA	8	131-477	(Ji et al. 2008; Ding et al. 2012)
PFOA-Marine	8	0.0001-0.1	(Fabbri et al. 2014)
PFNA	9	31-151	(Zheng et al. 2011)
PFDA	10	26-163	(Ding et al. 2012)
PFUnA	11	19-133	(Ding et al. 2012)
PFDoDA	12	28-66.3	(Ding et al. 2012)

PFAS	Carbon Chain Length	Range of Toxicity Values-EC or LC50 (mg/L)*	References
Chronic Studies			
PFBS	4	LOEC 4.8	(Sant et al. 2018)
PFOS	8	NOEC <0.0023-94.9	(MacDonald et al. 2004) (Boudreau et al. 2003)
		LOEC 0.0023-42.9	
PFOA	8	NOEC 3.125- >100	(Li 2010; Ji et al. 2008)
		LOEC 6.25-12.5	
PFNA	9	LOEC 0.04	(Lu et al. 2015)
<p>Note: Refer to the PFAS ecotoxicology data summary Table 7-1 in the separate Excel spreadsheet for toxicological endpoints and values.</p> <p>EC50 = median effective concentration. The concentration of test substance which results in a 50 percent reduction in growth or growth rate</p> <p>LC50 = Concentration that is lethal to 50% of test population</p> <p>LOEC = lowest observed effect concentration</p> <p>NOEC = no observed effect concentration</p>			

Benthic Organisms and Sediment Toxicity

Toxicity to benthic organisms is generally the result of exposure to the chemical in overlying water and/or sediment porewater. Effects levels (for example, LC50, EC50, NOEC) based on sediment concentrations (for example, mg of chemical/kg of sediment) of PFAS were not identified in publicly available studies. Bakke et al. (2010) provided PFOS concentration ranges for sediment quality classified as background, good, moderate, bad, and very bad. The PFOS threshold for “good” sediment, for which no toxic effects are expected, is 0.22 mg/kg; however, no toxicity data are provided to justify this value. A few aquatic toxicity studies have been conducted on benthic organisms for PFAS, with most focusing on PFOS. With so few studies available and with variability in test organisms and testing methods, it is difficult to define PFAS toxicity thresholds for benthic organisms or to determine if benthic organisms are similarly sensitive to PFAS compared to other aquatic invertebrates. Table 7-6 summarizes toxicity ranges for PFOS, PFOA, and PFBS in benthic invertebrates from the limited available information.

Table 7-6. Summary of benthic invertebrate ecotoxicity data for PFAS

PFAS	# of Effects Conc.*	Range of Toxicity Values (mg/L)	References
Acute (freshwater and saltwater)			
PFOS (acid)	n=5	0.00001 (NOEC) - 59 (LC50)	(Drottar and Krueger 2000b; Fabbri et al. 2014; OECD 2002; MPCA 2007)
PFOA (acid)	n=2	0.00001 (NOEC) - 0.0001 (LOEC)	(Fabbri et al. 2014)
Chronic (freshwater and saltwater)			
PFOS (salt)	n=22	<0.0023 (NOEC) - >0.150 (EC50)	(MacDonald et al. 2004)
PFOA (acid)	n=2	0.0089, 100 (NOEC, chronic)	(MacDonald et al. 2004; Stefani et al. 2014)
PFBS (acid)	n=2	0.0077 (NOEC, chronic)	(Stefani et al. 2014)
<p>Note: Refer to Table 7-1 in the separate Excel spreadsheet for the total number of reported effect and no-effect concentrations (from one or more studies, as well as for toxicological endpoints and values.</p>			

7.2.2.2 Terrestrial Invertebrates

Compared to aquatic invertebrates, there are relatively fewer studies on the effects of PFAS on terrestrial invertebrates.

Overall, these few studies indicate a moderate to high toxicity. See Table 7-2 in the separate Excel spreadsheet for available toxicity information for PFOA and PFOS in terrestrial invertebrates. Brignole et al. (2003), as summarized in Beach et al. (2006), summarized results of acute oral and dermal studies of PFOS conducted on the honeybee (*Apis mellifera*), although the dose was reported in terms of mass of PFOS per bee, which may not be relevant for evaluating ecological risks. However, these studies, when converted to a dose per kilogram of food (2 mg PFOS per kg sugar solution), suggested that PFOS was highly toxic to honeybees. Mommaerts et al. (2011) identified in a chronic oral dosing study on the bumblebee (*Bombus terrestris*) an LC50 of 1.01 mg PFOS/L sugar water and noted that PFOS exposure caused detrimental reproductive effects (decreased ovarian size).

Effects on fecundity from exposure to various PFAS compounds have been shown to carry down through multiple generations in the roundworm *Caenorhabditis elegans*. Tominaga Tominaga et al. (2004) conducted a multigenerational study in *C. elegans* exposed to PFOA, PFOS, and PFNA, finding that concentrations orders of magnitude lower than those causing lethality decreased worm abundance, and that effects were observed even in the fourth generation. Other studies have evaluated the mechanisms of PFAS toxicity. Xu et al. (2013) indicated that exposure to PFOS induced oxidative stress and DNA damage in the earthworm, *Eisenia fetida*. Stylianou et al. (2019) evaluated food chain transfer of PFOS-treated *E. coli* to *C. elegans* and noted distinct gene expression profiles associated with development, innate immunity, and stress response.

With regard to soil invertebrate toxicity testing, studies (while few in number) suggest a low to moderate toxicity of PFOS and PFOA, with toxicity generally occurring on a parts per million scale. Table 7-7 summarizes the range of acute and chronic toxicity values identified for various terrestrial invertebrates. These studies have mainly focused on the earthworm *Eisenia fetida*.

Sindermann et al. (2002) conducted a 14-day chronic soil study on *E. fetida* with PFOS and identified a NOEC of 77 mg PFOS/kg soil, a LOEC of 141 mg/kg, and an LD50 of 373 mg/kg. Other chronic earthworm studies indicated toxic concentrations of a similar magnitude, with LC50s ranging from 84 mg/kg–447 mg/kg (Mayilswami 2014) (Zareitalabad, Siemens, Wichern, et al. 2013). The Norwegian Pollution Control Authority NPCA (2006), as reported in Danish Ministry of the Environment (2015), conducted acute soil toxicity tests in *E. fetida*, looking at reproductive endpoints for PFOA, PFOS, and the short-chain 6:2 fluorotelomer sulfonate (6:2 FTS). Results of this study indicated that overall the evaluated PFAS exhibited a moderate-high toxicity. Reproductive effects (decreased number of cocoons, decreased hatchability, and decreased number and weight of juveniles) for PFOS and PFOA were noted. 6:2 FTS toxicity was found to be less than that for either PFOS or PFOA in the same study. Karnjanapiboonwong et al. (2018) conducted a 21-day soil study with *E. fetida* on bioaccumulation, mortality, and weight loss with PFBS, PFHxS, PFNA, and PFHpA and generally observed no effects at soil concentrations below 100 mg/kg, with the exception of PFBS, which resulted in a modest (although statistically significant) decrease in survival at 1 mg/kg.

The limited amount of terrestrial invertebrate data presents a data gap; additional toxicity studies are needed to better characterize ecotoxicological effects in this group of organisms. Additionally, it will be important to understand how field/soil conditions (for example, organic carbon content, pH, etc.) may influence toxicity. For example, Princz et al. (2018) found that PFOS toxicity for two different species of soil invertebrates was approximately two to four times greater when organisms were tested on sandy loam versus clay loam soils.

Table 7-7. Summary of terrestrial invertebrate ecotoxicity data for PFAS

PFAS	Range of Toxicity Values: NOEC, LOEC (mg/kg)	References
Acute Studies		
PFOS	77, 141 (survival)	(Sindermann et al. 2002)
PFBS, PFHxS, PFNA, PFHpA	1, 100 (survival)	(Karnjanapiboonwong et al. 2018)
Chronic Studies		
PFOS	1, 447 (survival) 1 (growth), 233 (reproduction)	(Mayilswami 2014) (Xu et al. 2013; Sindermann et al. 2002) (Princz et al. 2018) (Zhao et al. 2014) (Zareitalabad, Siemens, Wichern, et al. 2013)

PFAS	Range of Toxicity Values: NOEC, LOEC (mg/kg)	References
PFOA	1 (growth), 84 (survival)	(He, Megharaj, and Naidu 2016) (Zareitalabad, Siemens, Wichern, et al. 2013)
6:2 FTS	30 (reproduction), 566 (growth)	(NPCA 2006)
PFBS, PFHxS, PFNA, PFHpA	100 (weight loss, mortality)	(Karnjanapiboonwong et al. 2018)

Note: Refer to Table 7-2 in the separate Excel spreadsheet for toxicological endpoints and values.

7.2.3 Vertebrates

The following sections describe available toxicity data for vertebrate species, including fish, amphibians/reptiles, birds, and mammalian wildlife.

7.2.3.1 Fish

Table 7-8 summarizes the range of toxicity values observed for fish following PFAS exposures. Acute freshwater LC50 values based on survival for PFOS range from 7.8 to 22 mg/L for Rainbow trout (*Oncorhynchus mykiss*), to 9.1 mg/L for Fathead minnow (*Pimephales promelas*) (Robertson 1986; Palmer, Van Hoven and Krueger 2002).

There are relatively few chronic PFOS studies using PFOS, but (Drottar and Krueger 2000b) calculated a chronic NOAEL based on early life stage mortality to be 0.29 mg/L. Palmer et al. (2002) also calculated an acute NOAEL of 6.3 mg/L for *Oncorhynchus mykiss*. Saltwater acute values based on survival for *Oncorhynchus mykiss* were calculated to be 13.7 mg/L.

Other than PFOS, there are limited aquatic ecotoxicity data for 'other' PFASs. Within the summary data presented here, acute exposure durations were 6-days. One study was noted that investigated the chronic toxicity of PFNA following a 180-day exposure; the LOEC ranged from 0.01-1 mg/L depending on the endpoint (Zheng et al. 2011).

Table 7-8. Summary of fish ecotoxicity data for PFAS

PFAS	Carbon Chain Length	Range of Toxicity Values: EC or LC50 (mg/L)	References
PFBA	4	2,200 (developmental); >3,000 (survival)	(Ulhaq et al. 2013)
PFBS	4	450 (developmental); 1,500 (survival)	(Ulhaq et al. 2013)
PFOS	8	7.8-22 (survival)	(Robertson 1986; Palmer 2002)
PFOA	8	430 (survival)	(Ulhaq et al. 2013)
PFNA	9	84	(Zhang et al. 2012)
PFDA	10	5 (developmental); 8.4 (survival)	(Ulhaq et al. 2013)
Chronic Studies			
PFOS	8	NOEC 0.29; EC50 7.2	(Drottar and Krueger 2000b; Oakes et al. 2005)
PFNA	9	LOEC 0.01 (growth)	(Zhang et al. 2012)

Note: Refer to Table 7-1 in the separate Excel spreadsheet for toxicological endpoints and values.

7.2.3.2 Amphibians/Reptiles

There are relatively limited toxicity data available for PFAS effects on amphibians, including several studies on various species of frogs; no studies on reptiles were found in the literature search. The data available for PFOS and PFOA show a wide range of effects-based concentrations. Table 7-9 summarizes the range of acute and chronic toxicity data for amphibians.

More amphibian data are available for PFOS, and indicate mortality generally tends to occur at levels of 10 parts per million

or higher, whereas nonlethal effects may occur at approximately 1–2 ppm (that is, moderate to high toxicity) or lower (Ankley et al. 2004; Yang et al. 2014; Fort et al. 2019).

(Ankley et al. 2004) conducted a 5-week study on PFOS toxicity in the northern leopard frog (*Rana pipiens*) and observed that LC50s decreased with increasing test duration time; LC50s ranged from 12.5 mg/L at 1 week to 6.2 mg/L at 5 weeks. This study also anecdotally noted the presence of kinked tails, as well as a delayed time to initial metamorphosis and differences in limb bud and foot paddle emergence observed in the 1, 3, and 10 mg/L groups. A PFOS study (based on a 3M study reported in OECD, 2002) on another frog species, African clawed frog (*Xenopus laevis*), suggested toxicity at concentrations of similar magnitude to those observed in the Ankley study, and identified inhibition of growth and malformation during development (based on a 3M study reported in OECD, 2002).

Only one amphibian study was identified for PFOA, which suggested moderate aquatic toxicity (Yang et al. 2014).

Table 7-9. Summary of amphibian ecotoxicity data for PFAS

PFAS	Range of Toxicity Values-NOEC/LOEC (mg/L)	References
Acute Studies		
PFOS	3.6–81	(Yang et al. 2014; Stevens and Coryell 2007b) (Ankley et al. 2004; OECD 2002)
PFOA	115 (mortality)	(Yang et al. 2014)
Chronic Studies (EC10)		
PFOS	2 (longevity)	(Yang et al. 2014)
PFOA	5.89 (longevity)	(Yang et al. 2014)
Note: Refer to Table 7-1 in the separate Excel spreadsheet for toxicological endpoints and values.		

7.2.3.3 Birds

There are currently only several published studies available that address PFAS toxicity in avian wildlife species (Newsted et al. 2005; Newsted et al. 2007; Newsted et al. 2008); these studies indicate a low to moderate toxicity in birds. The northern bobwhite quail (*Colinus virginianus*) and the mallard duck (*Anas platyrhynchos*) were exposed to PFOS (Newsted et al. 2005; Newsted et al. 2007) or PFBS (Newsted et al. 2008) via the diet. The LC50s reported following exposure to PFOS are 212 mg/kg-feed and 603 mg/kg-feed for the northern bobwhite quail and the mallard duck, respectively, indicating a moderate toxicity (Newsted et al. 2005); generally, no effects were observed at feed concentrations of 70 mg PFOS/kg-feed or less. In a separate chronic diet study, Newsted et al. (2007) found that while a feed dose of 10 mg PFOS/kg-feed did not result in mortality, clinical signs of toxicity in quail were observed at 5 weeks of exposure. Mortality in both quail and mallard was observed at feed concentrations of 50–150 mg/kg. The chronic NOAEL and LOAEL for PFOS reported for both species were 10 and 50 mg/kg-feed, respectively (Newsted et al. 2007); the quail appeared to be more sensitive to PFOS than the mallard.

Some egg injection studies suggest exposure to PFOS may adversely affect chick development during incubation. For example, Molina et al. (2006) found that exposure to PFOS lowered the rate of hatching success and caused changes in the liver in the leghorn chicken. However, there is some concern regarding the use of these data in risk assessments due to issues related to the method of exposure and other methodological issues that can influence the outcomes of the studies. Although these studies are useful for evaluating mechanisms and creating structure-activity relationships, they may not be appropriate for direct application in risk assessments.

Quail and mallard appear less sensitive to PFBS. Acute dietary exposure to PFBS resulted in NOAELs of 3,160 and 5,620 mg PFBS/kg-feed for the bobwhite quail and mallard duck, respectively, for the lethal endpoint (Newsted et al. 2008). A NOAEL for bobwhite quail reproduction following dietary exposure to PFBS was reported at 900 mg/kg-feed.

Although there are few PFAS laboratory toxicity studies for birds, there are even fewer field studies. Custer et al. (2012) evaluated PFOS exposure in tree swallows, identifying a negative association between PFOS concentration in eggs and hatching success. One issue with the findings from this field study is that the greatest observed effects on hatching were typically found in areas that also had other significant contamination issues (PCBs, PAHs, mercury); however, the influence of these other contaminants was not addressed in the study. Co-exposure of common environmental contaminants should be taken into consideration when reviewing these types of field studies.

7.2.3.4 Mammalian Wildlife

PFAS exposure to wildlife is occurring on a global scale and across a variety of habitats (Reiner and Place 2015). Sections 5.5.2 and 5.5.3 discussed studies that evaluated bioaccumulation of PFAS. Wildlife may accumulate PFAS from direct exposure to air, dust, water, soil, and sediments, as well as through diet. Maternal transfer of PFAS is also a relevant exposure route, as these compounds have been shown to cross the placenta (Gronnestad et al. 2017; Houde et al. 2006). PFAS have also been shown to biomagnify, so higher trophic level predators have higher PFAS levels in tissues compared with prey items (Reiner and Place 2015). Of the PFAS compounds analyzed in wildlife exposure studies, PFOS is the one most frequently detected, and at the highest concentrations, in tissue samples (Reiner and Place 2015). Concentrations in biotic media have also been observed to vary with age, sex, and species.

Given the widespread occurrence of PFAS in wildlife, it is important to understand if such exposure manifests in adverse effects and ultimately how exposure may impact wildlife populations. Laboratory animal models show that, in general, PFAS compounds are readily absorbed and distributed among protein-rich tissues (liver, serum, kidney) in mammals, and that certain PFAS (particularly long-chain compounds) have a relatively long half-life in the body. Toxicity tests on laboratory mammals (mice, etc.) have shown that exposure to PFAS may result in adverse effects on the hepatic, endocrine, and immune systems; development; and certain types of cancers, as discussed in Section 7.1.4.

Based on the findings from mammalian toxicity studies in laboratory animals, one might expect to find similar effects in mammalian wildlife (at similar exposure levels). Laboratory studies focusing on growth, reproduction, and survival effects on laboratory mammals provide data to support the development of toxicity reference values for use in ERA of wildlife species. Examples of these data are provided Table 7-3 in the separate Excel spreadsheet, but this table is not intended to be exhaustive. NOAELs and LOAELs can be derived from these studies for use in ERA as shown (as further discussed in Section 9.2, Ecological Risk Assessment), but these values should be used with caution and understanding of their associated uncertainty. Many of these studies may have also included other endpoints, such as systemic or metabolic endpoints, that are not typically used for ERA and may demonstrate effects at lower doses than the growth, reproduction, and survival effects.

Although there are numerous studies evaluating toxicity of PFAS in laboratory animals (as discussed in Section 7.1.4), and there are numerous exposure studies in mammalian wildlife, very few studies have evaluated PFAS toxicity with respect to wildlife exposures. The studies that have been conducted typically evaluated relationships between the concentrations of a small number of PFAS compounds in various protein-rich biological media (for example, blood serum, liver) and expression of select biomarkers. One study on sea otters related concentrations of PFOA and PFOS in liver tissue to health condition and to possible immune effects (Kannan, Perotta and Thomas 2006).

Table 7-10 summarizes these studies.

Table 7-10. Summary of PFAS toxicity studies in mammalian wildlife

Species	Summary of Findings	Reference
Sea otter <i>Enhydra lutris</i>	Higher PFOS/PFOA concentrations in liver samples found in diseased otters versus nondiseased group	(Kannan, Perotta and Thomas 2006)
Bottlenose dolphin <i>Tursiops truncatus</i>	Significant positive associations between serum total PFAS concentrations and multiple immunological, hematopoietic, renal, and hepatic function endpoints	(Fair et al. 2013)
Wood mouse <i>Apodemus sylvaticus</i>	Significant positive relationship between liver PFOS concentration and hepatic endpoints (relative liver weight, microsomal lipid peroxidation level); significant negative association with serum alanine aminotransferase (ALT) activity	(Hoff 2004)
Wild pig <i>Sus scrofa</i>	No significant correlation between PFAS liver concentrations and multiple blood, hepatic, and immunological endpoints, whereas significant correlations were observed for other pollutants (for example, dioxin-like compounds, PCBs, organohaline pesticides)	(Watanabe et al. 2010)
Note: Refer to Table 7-3 in the separate Excel spreadsheet for toxicological endpoints and values.		

It is important to note that while certain associations have been observed between PFAS concentrations and various immunological, hematopoietic, renal, and hepatic function biomarkers, these associations are not necessarily indicative of actual impairment to an individual organism or within a larger population.

Perhaps one of the biggest challenges with wildlife toxicity studies is that wildlife are exposed to multiple chemical, biological, and physical stressors, making it difficult to determine whether noted effects are directly related to PFAS, to other stressors, or to a combination of stressors. The accumulation of other types of POPs, such as PCBs, dioxins, and pesticides, and metals such as mercury, in wildlife has been well established and, in some studies, related to effects. Arctic mammal studies have reported relationships between organohalogen exposure and endocrine disruption, reduced immune function, and adverse effects on the liver and other organs (Letcher et al., 2010). Numerous nonchemical environmental factors such as climate change, habitat loss, and seasonal availability of food may also confound toxicity studies, making it difficult for field studies to discriminate those effects related solely to PFAS. As an example, Watanabe et al. (2010) found no association between PFAS levels and a variety of biomarkers in wild pigs, whereas the study found significant positive associations between these parameters and other types of contaminants (for example, PCBs) that were also detected in liver tissue samples.

Currently, there are few data points available for mammalian wildlife, and the current literature focuses on bioaccumulation and specific endpoints that may not be ecologically relevant, as discussed above. Additionally, studies have traditionally focused on protein-rich tissues such as liver or blood serum, because PFAS preferentially bind to proteins, which can potentially underestimate the total body burden of PFAS. Thus, exposure cannot be fully characterized from these studies, and pinpointing correlations between target organ or whole-body effects and PFAS exposure is not possible at this point in time. A better understanding of mammalian exposures to the broad spectrum of PFAS compounds, precursor compounds, and mixtures of PFAS, as well as other environmental contaminants, is critical in advancing this field of study. Given the challenges with conducting field studies, this information could be obtained in part through more robust dosing studies in mammals that are representative of various wildlife taxa, and on toxicological endpoints that are directly relevant to population-based effects; however, more field studies are also needed to confirm laboratory models. Groups such as the U.S. Department of Defense's Strategic Environmental Research and Development Program (SERDP) and the Environmental Security Technology Certification Program (ESTCP) have recently identified such critical data needs (SERDP-ESTCP 2017).

7.2.4 Plants

The following sections describe available toxicity data for aquatic and terrestrial plants.

7.2.4.1 Aquatic Plants

Data on the toxic effects of PFAS on aquatic plants are limited, with available studies focusing on PFOS included in Table 7-1 in the separate Excel spreadsheet. The acute toxicity (EC50s) of PFOS to aquatic plants generally ranges from roughly 31 to 108 parts per million (mg/L), with NOEC values from the same studies being approximately 7–30 mg/L; (Boudreau et al. 2003; Sutherland and Krueger 2001; Drottar and Krueger 2000a). Chronic effects (EC50s) were found to be similar to acute values, but varied over a wide range, depending on species and endpoint (2–305 mg/L), with NOECs from the same studies ranging from 0.3 to 11.4 mg/L (Hanson et al. 2005; Boudreau et al. 2003; Desjardins et al. 2001a, b, c).

7.2.4.2 Terrestrial Plants

There are limited PFAS toxicity data for terrestrial plants; a review of the literature yielded only a few soil phytotoxicity studies, summarized in the See Table 7-2 in the separate Excel spreadsheet and in Table 7-11 below. Brignole et al. (2003) evaluated PFOS exposure (21 days) on a variety of crop plants (alfalfa, onion, ryegrass, soybean, tomato, flax, and lettuce) using emergence, survival, and shoot height and weight as endpoints, and demonstrated effects occurring at concentrations ranging from 57 mg/kg to over 1,000 mg/kg. Other studies (Li 2009; Zhao et al. 2011) conducted on both PFOS and PFOA on multiple crop plants found a wide range of toxicity among species and also within species for *Brassica rapa chinensis*. The most sensitive species may be *Triticum aestivum* where the 30-day NOEC reported was 1 mg/kg (Zhao et al. 2014). Toxicity may also be moderated by soil characteristics; for example, Zhao et al. (2011) showed that the amount of organic matter in soil significantly influenced toxicity, where higher organic carbon content decreased both accumulation of PFOA and PFOS and phytotoxicity. See the Table 7-2 in the separate Excel spreadsheet for a summary of phytotoxicity information for PFOA and PFOS.

Table 7-11. Summary of terrestrial plant ecotoxicity data for PFAS

PFAS	Range of Toxicity Values-NOEC/LOEC (mg/kg)	References
Acute Studies		
PFOS	<3.9 (growth)- >1,000 (survival)	Qu et al. 2010 ; (Zhao et al. 2014) (Li 2009); (Brignole et al. 2003)
PFOA	103 (growth)-812 (growth)	(Li 2009; Zhao et al. 2011)
Chronic Studies		
PFOS	1 (growth)	(Zhao et al. 2014)
PFOA	30 (growth)	(Zhao et al. 2014)
Note: Refer to Table 7-2 in the separate Excel spreadsheet for toxicological endpoints and values.		

7.2.5 Uncertainties and Conclusions

This section presented ecotoxicological information from an array of studies with the intent of providing the reader with an overview of the types of organisms and ecotoxicity studies available for PFAS compounds in the current literature. This section also presented available information about the ranges of concentrations of PFAS (notably, PFOS) in soil, sediment, and water that have been associated with adverse effects. In summary, ecotoxicity studies demonstrate a wide range of effects concentrations across the various terrestrial and aquatic biota. In general, aquatic invertebrates appear to be more sensitive to PFOS and other PFAS compounds than their terrestrial counterparts. Differences in species sensitivities, analytical methods, environmental substrate, test conditions, and reproducibility of results make it difficult to generalize overall effects, and some species may be more or less sensitive than others.

Although there are numerous studies on the toxicity of select PFAS to aquatic invertebrates, these studies are generally limited to a very small number of PFAS compounds (typically PFOS, and to a lesser extent, PFOA). Because PFAS represent a broad spectrum of compounds, it is important to expand ecotoxicity studies in this field to evaluate additional PFAS, including short-chain and precursor compounds, as well as “next generation” replacement compounds. Furthermore, the available studies indicate a wide range of effects levels for PFAS compounds in aquatic invertebrates, suggesting a level of complexity that has not yet been adequately assessed.

Significantly fewer toxicity studies are available for other groups of aquatic or benthic organisms, and few to no studies are available for avian or mammalian wildlife or plants, presenting a significant gap in our understanding of how the widespread presence of PFAS in the environment may be affecting ecological communities. Additional (or any) data on toxicological endpoints most relevant to community-level effects, such as survival, growth, and reproduction, will be extremely beneficial in understanding potential ecological impacts.

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8 Basis of Regulations

The PFAS Team developed a training module video with content related to this section, it is the Risk Assessment and Regulations video.

This section describes various federal and state regulatory programs that apply to PFAS. Because state regulations for PFAS in environmental media are changing rapidly, only a few state regulations are summarized in this section, as examples. ITRC also maintains updated tables of PFAS water values, and PFAS soil values from state, federal, and some international countries posted as an Excel file). This section also includes a brief explanation of examples of various health-based criteria. ITRC also has tables posted as an Excel file of the basis for PFOA and PFOS values in the United States that is updated periodically.

Section Number	Topic
8.1	Introduction
8.2	Regulatory Programs
8.3	Differences in the Available Regulations, Advisories, and Guidance

8.1 Introduction

PFAS became contaminants of emerging concern in the early 2000s. In recent years federal, state, and international authorities have established a number of health-based regulatory values and evaluation criteria. As with the case for most emerging contaminants, the regulatory process dealing with PFAS is in various stages of development, and the values and criteria being established vary between individual states, the U.S. government, and international agencies. This section describes examples of various federal and state regulatory programs and includes links to tables that provide established PFAS health-based criteria.

The terms “regulatory” or “regulation” are used in this document to refer to requirements that have gone through a formal process to be promulgated and legally enforceable as identified under local, state, federal, or international programs. The terms “guidance” and “advisory” apply to all other policies and numerical values.

8.2 Regulatory Programs

8.2.1 Background to Regulation of PFAS

The scientific community is rapidly recognizing and evolving its understanding of PFAS in the environment, causing an increased pace of development of guidance values and regulations. Human health protection is the primary focus of the PFAS regulations, guidance, and advisories developed to date. Regulations and guidance have focused on the PFAAs, precursor compounds, and FECAs. Like many other emerging contaminants, the regulatory and guidance values for PFOS and PFOA can vary across programs, with differences due to the selection and interpretation of different key toxicity studies, choice of uncertainty factors, and approaches used for animal-to-human extrapolation. The choice of exposure assumptions, including the life stage and the percentage of exposure assumed to come from non-drinking water sources, may also differ. Thus, both differences in scientific conclusions and public health policy choices affect the myriad of regulatory and guidance initiatives for PFAS. See the tables of the basis for PFOA and PFOS values in the United States for the specific differences underlying drinking water or groundwater regulations and advisories for PFOA and PFOS.

In addition to values that specify health-based concentration limits, agencies have used various strategies to limit the use and release of PFAS. For example, the USEPA worked with the eight primary U.S. PFAS manufacturers and processors to eliminate PFOA and many PFOA precursors and higher homologues by 2015 (USEPA 2017a). Additionally, the Organisation for Economic Co-operation and Development OECD (2015a) has described various international policies, voluntary initiatives,

biomonitoring, and environmental monitoring programs to control PFAS. More information regarding the history of these developments is in Section 2.4.

Authority for regulating PFAS in the United States is derived from a number of federal and state statutes, regulations, and policy initiatives. This section provides a brief overview of the major federal statutes and regulatory programs that govern PFAS.

8.2.2 Federal PFAS Regulations

Within the United States, currently both the USEPA and the FDA have regulatory or guidance initiatives for PFAS. The USEPA has the authority to regulate PFAS under several different acts and programs, as provided below; however, USEPA has not yet listed PFAS as hazardous wastes or substances under its available statutory authorities, including the Resource Conservation and Recovery Act (RCRA), Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), Emergency Planning and Community Right-to-Know Act, or the Clean Air Act. To date, USEPA has also not established regulations for any PFAS under the Safe Drinking Water Act.

Through the Office of Regulatory Affairs, the Office of Management and Budget maintains a list of regulatory actions which have been initiated by the USEPA and certain other federal agencies. That list is updated periodically to give the status of the regulations, and is available at <https://www.reginfo.gov/public/Forward?SearchTarget=RegReview&textfield=PFAS>.

Through the National Defense Authorization Act for Fiscal Year 2020 (the NDAA), Congress mandated a number of actions that the Department of Defense (DOD) must comply with on PFAS, while also adding in a number of separate requirements for the USEPA (<https://www.congress.gov/bill/116th-congress/senate-bill/1790/text>).

Some of the requirements of the NDAA for the DOD include:

- Sharing PFAS monitoring and detection data with municipalities and drinking water utilities that are adjacent to installations
- Providing “a clearinghouse for information” about exposure of DOD personnel and their families or communities to PFAS through drinking water
- Entering into cooperative agreements with States to address testing, monitoring, removal and remediation of any PFAS contaminated media originating from DOD activities
- Providing blood testing for PFAS for all DOD firefighters during their annual physical exam
- Ensuring that no water contaminated with PFOA or PFOS above USEPA’s health advisories from DOD activities is used for agricultural purposes

For the USEPA, some of the requirements of the NDAA include finalizing the 2015 proposed significant new use rule (SNUR) under the Toxic Substances Control Act (TSCA), and adding reporting requirements for certain PFAS under the Toxics Release Inventory (TRI) program. Both of these are discussed below.

8.2.2.1 Toxic Substances Control Act (TSCA)

TSCA authorizes the USEPA to require reporting, record keeping, testing, and restrictions of chemicals and chemical mixtures that may pose a risk to human health or the environment. Section 5 of TSCA authorizes the USEPA to issue Significant New Use Rules (SNURs) to limit the use of a chemical when it is newly identified, or when a significant new use of an existing chemical is identified, before it is allowed into the marketplace (USEPA 2017a). From 2002 to 2013, USEPA issued four final SNURs covering 271 PFAS, including PFOS and PFOA. The first three SNURs covered PFAS included in the 3M Corporation’s voluntary phaseout of PFOS. The 2013 SNUR required notification to USEPA prior to manufacture or import of seven PFAS that had been reviewed by USEPA under the TSCA New Chemicals Program, but had yet to be commercially manufactured or imported into the United States. This SNUR also included long-chain PFCAs and their salts and precursors that were used in carpets or to treat carpets (USEPA 2015e). Collectively, these SNURs placed notification requirements on the manufacture (including import) of specific PFAS for new use. The SNURs allowed for continued, low-volume use of some PFAS in photographic/imaging, semiconductor, etching, metal plating, and aviation industries (USEPA 2017a). In January 2015, USEPA proposed another SNUR to require notification to USEPA before any future manufacture (including import) of PFOA and PFOA-related chemicals, including as part of articles, and processing of these chemicals.

The proposed SNUR did not place a regulatory restriction on the imports of fluoropolymers dispersions and emulsions containing PFOA or its salts (FluoroCouncil 2018). As a result of changes made to section 5(a) of TSCA when TSCA was amended in June 2016, USEPA undertook developing a supplemental SNUR for the import of certain long-chain PFCA and

PFSAs as part of categories of certain articles (USEPA 2018i).

As required by the NDAA, the USEPA finalized the supplemental SNUR in June 2020 and published the final notice in the Federal Register in July 2020 (<https://www.govinfo.gov/content/pkg/FR-2020-07-27/pdf/2020-13738.pdf>). The 2020 SNUR designates as a significant new use the manufacture, import, or processing of a specific subset of long chain perfluorocarboxylates (LCPFAC) for any use that was not ongoing as of December 15, 2015 and for all other LCPFAC chemical substances for which there were no ongoing uses as of January 21, 2015. The SNUR also prohibits the import of certain LCPFAC as part of a surface coating on articles, and the import of carpet containing perfluoroalkyl sulfonate chemical substances, without USEPA review.

The USEPA continues to review new PFAS through USEPA's New Chemicals Program before approving commercialization.

8.2.2.2 Safe Drinking Water Act (SDWA)

The SDWA is the federal law that protects public drinking water supplies throughout the nation (USEPA 1974). Under the SDWA, the USEPA has authority to set enforceable Maximum Contaminant Levels (MCLs) for specific chemicals and require testing of public water supplies. The SDWA applies to all public water systems (PWSs) in the United States but does not apply to private domestic drinking water wells nor to water not being used for drinking.

The USEPA has not established regulations for any PFAS under the SDWA; however, in its 2019 PFAS Action Plan (USEPA 2019h), the agency indicated that it would take steps to evaluate the need for MCLs for PFOA and PFOS. In February 2020, the agency proposed a preliminary Regulatory Determination to develop drinking water standards for PFOA and PFOS, and initiated a 60-day public comment period. If the Regulatory Determination is finalized subsequent to the USEPA's review of comments, the agency will initiate the process to establish a national primary drinking water regulation (an MCL) for these two PFAS. The SDWA specifies the following three requirements for making a Regulatory Determination regarding MCL development:

- The chemical may have an adverse effect on the health of persons.
- The chemical is known to occur or there is a substantial likelihood that it will occur in PWSs with a frequency and at levels of public health concern.
- In the sole judgment of the EPA administrator, regulating the contaminant presents a meaningful opportunity for health risk reductions for persons served by PWSs.

More information regarding USEPA's PFAS Action Plan is found below in this section.

In May 2016, USEPA established a lifetime health advisory (LHA) of 70 ng/L for PFOA and PFOS in drinking water. This LHA is applicable to PFOA and PFOS individually or in combination if both chemicals are present at concentrations above the reporting limit (USEPA 2016c, d). The LHA supersedes USEPA's 2009 short-term (week to months) provisional health advisories of 200 ng/L for PFOS and 400 ng/L for PFOA (USEPA 2009c). The LHA for PFOA and PFOS is advisory in nature; it is not a legally enforceable federal standard and is subject to change as new information becomes available (USEPA 2016c, d). USEPA states that the LHAs "provide Americans, including the most sensitive populations, with a margin of protection from a lifetime of exposure to PFOA and PFOS from drinking water" (USEPA 2016e pg.2).

Much of the current occurrence data available regarding PFAS in public drinking water was generated by USEPA under the SDWA Unregulated Contaminant Monitoring Rule (UCMR) program (USEPA 2017g). USEPA uses the UCMR to collect data for chemicals that are suspected to be present in drinking water but that do not have health-based standards set under the SDWA. The third round of this monitoring effort, or UCMR3, included six PFAAs:

- perfluorooctanesulfonic acid (PFOS)
- perfluorooctanoic acid (PFOA)
- perfluorononanoic acid (PFNA)
- perfluorohexanesulfonic acid (PFHxS)
- perfluoroheptanoic acid (PFHpA)
- perfluorobutanesulfonic acid (PFBS).

Samples were collected during a consecutive 12-month monitoring period between 2013 and 2015 from large PWSs serving more than 10,000 people, and a limited number of smaller systems determined by USEPA to be nationally representative. Based on USEPA's UCMR3 reported limits of between 10 and 90 ng/L depending on the specific PFAAs, at least one of the six PFAAs listed above were detected in 194 out of 4,920 PWSs tested (~4%), which serve about 16.5 million people in 36 states

and territories (Hu et al. 2016).

Occurrence data produced by the UCMR program, not only for PFOA and PFOS, but also for other PFAS as well (Table 8-1 and Table 17-3) are used by the USEPA and some states to help determine which substances to consider for future regulatory action. All of the data from the UCMR program are published in the National Contaminant Occurrence Database (NCOD) and available for download from USEPA’s website (USEPA 2017g).

Table 8-1. UCMR3 occurrence data for PFOA and PFOS

Exceed LHA (70 ppt)	Reporting Limit (ppt)	Number of PWSs	PWS (%)
PFOS	40	46	0.9
PFOA	20	13	0.3
Σ PFOA + PFOS ¹		63	1.3

¹PWSs that exceeded the combined PFOA and PFOS health advisory (USEPA 2016d; 2017o)

PFOA and PFOS were listed on Contaminant Candidate List 3 (CCL 3) in 2009 and are currently listed on CCL 4 published in late 2016. Inclusion on the CCL 4 indicates that the USEPA Office of Water was considering deriving MCLs for these specific PFAS. As noted above, if the USEPA finalizes the preliminary Regulatory Determination for PFOA and PFOS, it will move the process of MCL derivation to the next step in the regulatory process.

In addition, when the USEPA determines there may be an “imminent and substantial endangerment” from a contaminant that is present in or likely to enter a PWS, under Section 1431 of the SDWA it may issue emergency administrative orders (EAOs) to take any action necessary to protect human health if state and local authorities have not acted (42 U.S.C. §300i). USEPA has issued several such EAOs to protect public and private water supply wells contaminated with PFOA or PFOS (USEPA 2009e, 2014b, 2015a).

USEPA issued a PFAS Action Plan (USEPA 2019h) in February 2019 and an update a year later (USEPA 2020b). In addition to the evaluation of the need for an MCL for PFOA and PFOS, that Action Plan included the following main actions that encompass more than just safe drinking water issues:

- Develop interim groundwater cleanup recommendations to address groundwater contaminated with PFOA and PFOS
- Finalize draft toxicity assessments for Gen X chemicals and PFBS
- Develop additional toxicity values for PFBS, PFHxA, PFHxS, PFNA, and PFDA
- Conduct chemical safety reviews as new PFAS are developed and enter the market and issue proposed supplemental SNURs
- Incorporate the latest research results for additional PFAS into USEPA’s online drinking water treatment database
- Evaluate listing of PFOA and PFOS as hazardous substances
- Evaluate performance and identify costs associated with treatment and remediation approaches to address PFAS in the environment
- Support communities that have PFAS releases by using federal enforcement authorities where relevant and appropriate
- Develop an interactive map providing the public with available information on sources and occurrence of PFAS
- Develop coordinated messaging on PFAS across the federal government
- Develop a risk communications toolbox for PFAS to be used for the public
- Evaluate the listing of PFAS chemicals to the Toxics Release Inventory
- Determine if available data for PFAS are sufficient to establish ambient water quality criteria for human health
- Explore identifying industrial sources that may warrant regulation through national Effluent Limitation Guidelines and Standards (ELGs) and the setting of minimum levels of control needed for National Pollutant Discharge Elimination System (NPDES) permits
- Develop toxicity information for a larger group of PFAS and potentially address groups of PFAS
- Add PFAS monitoring to UCMR5, using newer analytical methods for a wider suite of PFAS, while achieving lower minimum reporting levels than earlier UCMRs
- Develop an inventory of PFAS data for media other than drinking water

- Assess ecological risk from PFAS exposure
- Evaluate air transport of PFAS.

8.2.2.3 Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)—“Superfund”

PFAS, including PFOA and PFOS, are not listed as CERCLA hazardous substances but may be addressed as CERCLA pollutants or contaminants, for example, as defined by section 101 (33) of CERCLA (40 CFR 300.5). As listed above in Section 8.2.2.2, under its PFAS Action Plan (USEPA 2019h), USEPA is evaluating listing PFOA and PFOS as hazardous substances. The action plan also includes a priority action to develop interim cleanup recommendations for groundwater contaminated with PFOA and PFOS. The USEPA released a draft recommendation for public comment in spring 2019, which includes using a screening level of 40 ppt for each (individually) of PFOA and PFOS (hazard index of 0.1), and using 70 ppt combined as a preliminary remediation goal. CERCLA investigations are beginning to include PFAS when supported by the CSMs (for example, (USEPA 2017d). PFAS are often included in a remediation site’s 5-year review, when supported by site-specific information. According to USEPA, as of April 2018, there were active PFAS investigations occurring at 32 federal facility National Priorities List (NPL) sites and 17 non-federal sites, and these numbers are expected to continue to increase as PFAS are included in more remediation programs (Peter Gravatt, Director of USEPA’s Office of Ground Water and Drinking Water, ITRC PFAS team presentation April 24, 2018). Section 9 provides a discussion and recommendations for how to consider PFAS during a site-specific risk assessment.

CERCLA Protection of Human Health. CERCLA requires, among other things, that Superfund response actions ensure protectiveness of human health and the environment, and compliance with laws and regulations that constitute “applicable or relevant and appropriate requirements” (ARARs); the statute also provides possible ARAR waivers in limited circumstances. The lead agency (as defined in 40 CFR 300.5) identifies potential ARARs and to-be-considered values (TBCs), based in part on the timely identification of potential ARARs by states. Risk-based goals may be calculated and used to determine cleanup levels when chemical-specific ARARs are not available or are determined not to be sufficiently protective (USEPA 1997a). The ARAR process can be complex and can result in impacts on scope, budget, and public acceptance components of a project (USEPA 2019k).

The tables of PFAS water values, and PFAS soil values from state, federal, and some international countries posted as an Excel file include current state regulatory and guidance values for PFAS. These values are not necessarily automatically recognized as ARARs and must be evaluated by the lead agency to determine their ARAR status. In the Superfund program, USEPA regions evaluate potential ARARs, including state standards, on a site-specific basis to determine whether a specific standard or requirement is an ARAR for response decision and implementation purposes. Determining if a state requirement is promulgated, substantive, and enforceable are some of the factors in evaluating whether a specific standard may constitute an ARAR or TBC (40 CFR 300.5 2001; 40 CFR 300.400 2019, (g); USEPA 1988, 1991).

As mentioned above, risk-based cleanup goals may be calculated when chemical-specific ARARs are not available or are determined not to be protective (USEPA 1997). The USEPA’s Regional Screening Levels (RSLs) Generic Tables (USEPA 2017l) and the RSL online calculator(USEPA 2017k) are used by risk assessors to identify screening levels and preliminary remedial goals for contaminants of potential concern at a site. These goals are typically based on toxicity values that have been selected in accordance with the USEPA’s published hierarchy (USEPA 2003a). Currently, PFBS and the potassium salt of PFBS are the only PFAS listed in the RSL generic tables. For PFBS and its salt, the generic tables provide a noncancer reference dose (RfD), screening levels for soil and tap water, and soil screening levels for the protection of groundwater. As stated in its PFAS Action Plan, USEPA is in the process of developing toxicity values for PFBS and GenX chemicals. Draft toxicity assessments were posted on November 14, 2018, for public review(USEPA 2018d, e). When finalized, these toxicity values may be incorporated into the RSL table for these PFAS, as well. The online RSL calculator currently supports site-specific calculations for PFBS, PFOA, and PFOS in tap water and soil. The noncancer RfDs derived by the USEPA Office of Water are provided as Tier 3 toxicity values for PFOA and PFOS. The USEPA 2016 cancer ingestion slope factor is also provided for PFOA, but screening levels are based on the noncancer endpoint. The USEPA also provides tables and a calculator for removal management levels (RMLs). In general, RMLs are not final cleanup levels, but can provide a reference when considering the need for a removal action (for example, drinking water treatment or replacement) (USEPA 2016b).

Because RSLs and RMLs are periodically updated, they should be reviewed for revisions and additions before using them. RSLs and RMLs are not ARARs, but they may be evaluated as TBCs. The USEPA has emphasized that RSLs and RMLs are not cleanup standards (USEPA 2016g) and suggests that final remedial goals be informed by a baseline risk assessment so that site-specific information can be incorporated. Section 9 provides more information on site-specific risk assessment for PFAS.

CERCLA Protection of the Environment. CERCLA requires that remedies also be protective of the environment. Risk-based cleanup goals that are protective of the environment are site-specific and depend in part on the identification of the ecological receptors to be protected. To date no U.S. regulatory agency has established ecological criteria for PFAS. Another example of a risk-based goal is a cleanup standard for a chemical in soil that is protective of groundwater quality and is developed on a site-specific basis. Given the challenge associated with deriving accurate physical and chemical properties for PFAS (Sections 4.1 and 5.1), site-specific values will need to be derived.

8.2.2.4 Resource Conservation and Recovery Act (RCRA)

RCRA provides USEPA with the authority to regulate hazardous waste management, nonhazardous solid waste facilities and practices, and underground storage tanks holding petroleum or certain hazardous substances. No PFAS have been formally listed as RCRA hazardous waste for regulation under this program. However, there are at least a couple of examples where action on PFAS was taken under the auspices of RCRA. For example, in 2004 USEPA pursued violations of RCRA and TSCA at an E.I. DuPont de Nemours and Company (DuPont) facility in West Virginia due to environmental release of the hazardous constituent PFOA (USEPA 2015c). In the case of DuPont, the facility already had a RCRA permit for hazardous waste disposal and was under a Corrective Action Permit. Some states, Texas, for example, are regulating certain PFAS under their RCRA permits and requiring investigation and cleanup.

In February 2017, a U.S. District Court denied motions to dismiss RCRA “imminent and substantial endangerment” claims relating to PFAS (*Tennessee Riverkeeper, Inc. v. 3M Co.*, No. 5:16-cv-01029-AKK, 2017 WL 784991 (N.D. Ala. Feb. 10, 2017)). This case involved the alleged continuing contamination of the Tennessee River and associated public drinking water supplies with PFAS that the plaintiff claims originated from a local manufacturing facility and two local landfills. There were several arguments that the claims should be dismissed. One argument by the landfill owners was that the claims were an attack on existing, valid permits that included a solid waste permit authorizing disposal in the landfill of PFAS-bearing materials. The court denied the motion to dismiss, stating that the permits only authorize disposal of nonhazardous waste, and there is a dispute over whether the PFAS-containing material is a hazardous waste. Additionally, there are a continually growing number of citizen lawsuits filed under RCRA in state courts throughout the United States. Thus, the applicability of RCRA regulations and statutes to PFAS does not appear to be settled and can be complicated.

8.2.2.5 Clean Air Act (CAA)

Under the CAA, USEPA is required to regulate toxic air pollutants from large industrial facilities. USEPA may develop standards for controlling certain air toxic emissions from sources in a specific industry group. Within 8 years of establishing emission standards, USEPA must determine whether the standards are sufficiently protective of human health and protect against adverse environmental effects. This determination also considers improvements in air pollution controls and evaluates effective and feasible alternatives.

According to the USEPA (2018j) website on PFAS Laws and Regulations, the CAA applies to discharges of PFAS to air under National Emission Standards for Hazardous Air Pollutants; however, there are no air emission standards for PFAS at this time. There is no indication how far along USEPA is in this process for regulating PFAS under the CAA.

8.2.2.6 Clean Water Act (CWA)

Since 1972, the CWA has given the USEPA authority to control water pollution by regulating discharges into the nation’s surface water by setting wastewater standards for industry. There are no federal water quality standards for any PFAS at this time. However, USEPA released the Final 2016 Effluent Guidelines Program Plan in May 2018, which listed PFAS as a topic for future investigation (USEPA 2018f). The USEPA plans to review PFAS surface water discharges from industrial categories for both long-chain and short-chain PFAS. The regulation of PFAS in discharge effluents is discussed below in Section 8.2.3.

8.2.2.7 Toxics Release Inventory (TRI) Program

The Toxics Release Inventory (TRI) program requires the annual reporting of environmental releases of approximately 800 chemicals which the USEPA has concluded cause:

- Cancer or other chronic human health effects
- Significant adverse acute human health effects
- Significant adverse environmental effects

For chemicals regulated under the TRI, facilities that manufacture, process or use these chemicals in amounts above established levels must submit annual reporting forms for each chemical.

As stipulated by the NDAA, the USEPA finalized a rule requiring 172 PFAS be added to the list of chemicals that must be reported under the TRI program (USEPA 2020c). The PFAS that are subject to TRI reporting requirements include all PFAS listed as an active chemical substance under TSCA's Section 8(b)(1) inventory. Each of the PFAS has a 100-pound reporting threshold. Reporting for the 2020 calendar year is due in July 2021; these data – as with all TRI data – will be publicly-available approximately one year after they were reported (USEPA 2020d).

8.2.2.8 U.S. Food and Drug Administration (FDA)

One of the responsibilities of the FDA is regulation of “food contact substances” (FCSs), chemicals added to or components of “food contact materials” (FCMs), such as food wrappers and packaging. The FDA currently regulates certain PFAS used as grease-proofing agents for food packaging via a Food Contact Notification Program within the Center for Food Safety and Applied Nutrition's Office of Food Additive Safety. The PFAS used in FCMs and their known degradants and impurities have all undergone review for human health and environmental safety concerns through the food contact notification process, which required submission of chemical, toxicological, and environmental information on the FCS itself and on any potential impurities.

Currently, the FDA has banned three perfluoroalkyl ethyl compounds from use in food packaging material (81 FRN 5, Jan. 4, 2016, Indirect Food Additives: Paper and Paperboard Components): diethanolamine salts of mono- and bis (1 H, 1H, 2H, 2H perfluoroalkyl) phosphates with even-numbered alkyl groups in the range of C8-C18; pentanoic acid, 4,4-bis [(*gamma-omega*-perfluoro-C8-20-alkyl)thio]; and perfluoroalkyl substituted phosphate ester acids, ammonium salts formed by the reaction of 2,2-bis[([*gamma*],[*omega*]-perfluoro C4-C20 alkylthio) methyl]-1,3-propanediol, polyphosphoric acid, and ammonium hydroxide. Side-chain acrylate and methacrylate fluoropolymers are currently approved and used within the United States for FCS.

In July 2020, the FDA announced that three manufacturers had agreed to a voluntary phase out of FCS that contain 6:2 fluorotelomer alcohol (6:2 FTOH). A fourth manufacturer had previously stopped sales of 6:2-FTOH-containing products in the US. The phase-out will begin in January 2021; the FDA predicted that it may take up to 18 months after that time to exhaust existing supplies of food contact papers that contain 6:2 FTOH (USFDA 2020).

As of August 2020, there were approximately 60 specific FCS with PFAS that are listed on FDA's inventory of effective FCS notifications (recognizing its approval for specific uses, designated in the application).

8.2.2.9 Other Federal Agency Actions

Other U.S. federal agencies and programs are actively involved in PFAS-related matters; however, their work largely focuses on data generation and analysis to help inform regulations/restrictions/regulatory action. These federal programs often provide valuable information, guidance, and resources for state regulatory and public health agencies. For example, the U.S. Centers for Disease Control and Prevention (CDC) National Health and Nutrition Examination Survey (NHANES) program provides valuable information about human exposure to chemicals. Since 1999, the NHANES program has been providing an assessment of the exposure of the U.S. population to a small subgroup of PFAAs. This information is useful to scientists and regulatory agencies to understand “background” (that is, likely nonsite-related) human exposure levels and trends over time. CDC has recently expanded their NHANES analysis to include evaluation of PFAAs in serum and urine (Kato et al. 2018).

Under the Superfund Amendments and Reauthorization Act of 1986 (SARA) [42 U.S.C. 9601 *et seq.*] amendment to CERCLA (or Superfund) [42 U.S.C. 9601 *et seq.*], the U.S. Department of Health and Human Services, Agency for Toxic Substances and Disease Registry (ATSDR) was established to assess the potential public health risk from exposure to hazardous substances commonly found at National Priorities List facilities. CERCLA provides ATSDR with the authority to develop toxicological profiles that describe the health effects of these hazardous substances and to support site-specific response actions with health consultations and/or exposure investigations. A full description of ATSDR's actions regarding PFAS is on their web page (ATSDR, 2018a). On June 20, 2018, ATSDR issued a revised draft *Toxicological Profile for Perfluoroalkyls* for public comment (ATSDR 2018e). In this revision, the agency discussed potential human health risks related to 14 specific PFAS and derived “provisional intermediate Minimal Risk Levels” (MRLs) for PFOA, PFNA, PFOS, and PFHxS. ATSDR stated that these provisional MRLs are intended to serve as “screening levels” for identifying contaminants and potential health effects that may be of concern at hazardous waste sites and are not intended to be used for regulatory action, including to define cleanup or action levels.

The U.S. Geological Survey (USGS) has had an emerging contaminants program for over a decade within which they measure emerging contaminants, including PFAAs, in various environmental media and ecological receptors. The objective

of their work is to characterize environmental occurrence, sources, and source pathways that may contribute to environmental exposure. This has been a useful source of information for scientists and regulatory agencies on occurrence, fate, and transport of PFAS. Information on the USGS program can be found on their web page (USGS 2017).

The U.S. Department of Defense SERDP and ESTCP are jointly managed with USEPA and the U.S. Department of Energy to develop the latest science and technology to improve DOD's environmental footprint and mission capabilities. Beginning in fiscal year 2011, SERDP and ESTCP have funded a significant number of projects related to developing a better understanding of PFAS occurrence, fate and transport, ecotoxicity, and remediation treatments, as well as investigating the next generation of fluorine-free firefighting foams. More information on SERDP and ESTCP funding projects and statements of need can be found on their website (SERDP-ESTCP 2019).

8.2.3 State PFAS Regulations and Guidance

State regulatory agencies often have the delegated authority to regulate and enforce environmental and public health requirements, although the 50 states have different priorities, resources, and processes. Several states have been actively involved with addressing PFAS contamination across multiple regulatory programs. Examples of key state programs for water, soil, remediation, hazardous substances, and consumer products are described below, and information about regulatory, advisory, and guidance values is discussed in Section 8.2.3.4. The information below is meant to provide examples only; the ITRC tables of PFAS water values, and PFAS soil values from state, federal, and some international countries posted as an Excel file should be consulted for more current and detailed information.

The ITRC PFAS team and the Environmental Council of States (ECOS) jointly issued a survey to state agencies to identify the various ways in which each state may be addressing PFAS, as discussed in Section 8.2.3.6.

The following subsections provide several different categories of state-adopted laws and regulations along with examples of each.

8.2.3.1 Product Labeling and Consumer Protection Laws

Several states have programs regulating PFAS in consumer products, including product labeling. Note that due to the state legislative review and finalization process, only bills that have been finalized into law are discussed below.

In November 2017, PFOS and PFOA were listed as potential developmental toxicants under California's Proposition 65 (California Office of Environmental Health Hazard Assessment [CA OEHHA] (2018)). The listing includes labeling requirements for manufacturers, distributors, and retailers, and will prohibit companies from discharging PFOA or PFOS (or their related salts) to sources of drinking water if the discharges would result in exposures that exceed a health-based "safe harbor" level, which has not yet been defined as of September 2019 by the state. The California Department of Toxic Substances Control Safer Consumer Products program is also addressing PFAS. This program has labeled the entire family of PFAS as "Candidate Chemicals" and is drafting "Priority Product" work plans to evaluate the use of these chemicals on "converted textiles or leathers such as carpet, upholstery, clothing, and shoes" (CA DTSC 2019a) and food packaging (CA DTSC 2019b).

Washington State has required the reporting of PFOS in children's products since 2012 (Washington State Legislature 2008). The 2017 Children's Safe Products Act update added reporting of PFOA in children's products starting in January 2019. Washington also tests products for chemicals to ensure manufacturers are reporting accurate information. In 2018, Washington enacted two laws addressing PFAS in specific products: AFFF (Washington State Legislature 2018a) and food contact materials (Washington State Legislature 2018b). After July 2018, PFAS-containing AFFF is not allowed to be used for training. After July 2020, PFAS-containing AFFF will not be allowed for sale or distribution. The AFFF sale ban does not apply to the U.S. Department of Defense, FAA, oil and gas terminals, or chemical plants. The AFFF restrictions do not apply to the use of AFFF in response to fire emergencies. After 2022, PFAS will be banned in food packaging materials if results of the Department of Ecology's alternatives assessment identify safer alternatives.

8.2.3.2 State of Washington Chemical Action Plans

Chemical action plans (CAPs) identify, characterize, and evaluate uses and releases of specific persistent, bioaccumulative, and toxic (PBT) chemicals or metals. Washington State prepares CAPs under an administrative rule (Washington State Legislature 2006). Washington has prepared an interim PFAS CAP and is planning to release recommendations to address PFAS contamination in 2019. The CAP, as developed so far, recommends setting state drinking water levels or advisory levels for PFAS, expanding water testing near potential sources of contamination, developing cleanup levels for PFAS, and evaluating and producing best practices for cleaning up soils, surface water, and groundwater. The CAP also recommends

investigating other sources of PFAS by requiring manufacturers of products containing PFAS to provide information regarding safety of their products and performing assessment of alternatives to PFAS in AFFF, food contact paper, and textiles. More information on the Washington CAP process for PFAS is available from their web page (Washington State Department of Ecology 2018).

8.2.3.3 Designation of Hazardous Waste or Hazardous Substance

Regulations that target select PFAAs as hazardous wastes or hazardous substances have not been promulgated in most states. Formal PFAA regulations as hazardous substances have been promulgated in Vermont, New York, New Jersey, Colorado, and Alaska (ITRC State Survey 2018, unpublished), and are under development in several other states. Vermont regulates PFOA and PFOS as hazardous wastes when present in a liquid at a concentration ≥ 20 ppt, but allows exemptions for 1) consumer products that were treated with PFOA and are not specialty products; 2) remediation wastes managed under an approved CAP or disposal plan; and 3) sludge from wastewater treatment facilities, residuals from drinking water supplies, or leachate from landfills when managed under an approved plan (VT DEC 2016b, a).

In 2017, the New York State Department of Environmental Conservation (NYDEC) finalized regulations that identify PFOA (the acid) and its salt, ammonium perfluorooctanoate and PFOS (the acid) and its salt, perfluorooctane sulfonate, as hazardous substances that may be found in Class B firefighting foams (NY DEC 2017a). The regulations specify storage and registration requirements for Class B foams that contain at least 1% by volume of one or more of these four PFAS, and prohibit the release of 1 pound or more of each into the environment during use. If a release exceeds the 1-pound threshold, it is considered a hazardous waste spill and must be reported; cleanup may be required under the state's Superfund or brownfields programs (NY DEC 2017a).

8.2.3.4 Drinking Water, Groundwater, Soil, and Remediation Programs

Several states have developed standards and guidance values for PFAS in drinking water, groundwater, and soil (see the ITRC tables of PFAS water values, and PFAS soil values from state, federal, and some international countries posted as an Excel file). Many states have either adopted the USEPA LHAs for PFOA and PFOS or selected the same health-based values, choosing to use the concentrations as advisory, nonregulated levels to guide the interpretation of PFOA and PFOS detections. As with any contaminant of potential concern at a remediation site, available toxicity values that meet USEPA policy requirements (USEPA 1993, 2003a, 2013e) can be used to derive screening levels for groundwater and soil. As of May 2018, the USEPA has not adopted the PFOA and PFOS toxicity values as "Tier 3" to officially derive an RSL; however, the necessary information is available within the online USEPA RSL calculator and screening levels for PFOA, PFOS, and PFBS are readily available (USEPA 2017k). Section 9 provides more information on site-specific risk assessment for PFAS.

In addition to the process using the USEPA RSL calculator discussed above, some states have developed screening levels for PFOA and PFOS in soils assuming direct contact and/or ingestion. See ITRC tables of PFAS water and soil values and USEPA (2017l) At least a couple of states (for example, Alaska, Connecticut) have developed values for protection of groundwater (ITRC State Survey 2018, unpublished).

Some states, such as California and Minnesota, have "antidegradation" policies aimed at protecting the quality of groundwater and (in California) high quality (or Tier 2) surface waters. Those policies can be used in decisions on cleanup and discharge under permits. As an example, in California, the State Water Resources Control Board adopted Resolution 68-16 as its antidegradation policy. When evaluating the discharge or cleanup of chemicals, the Regional Water Quality Control Boards are required to initially set the effluent limitation or cleanup standard at the background concentration of each chemical. This is done regardless of whether there is a drinking water standard or other health-based value available. Final discharge or cleanup values consider potential health impacts, designated beneficial uses of the water body, and technical and economic feasibility in their development.

8.2.3.5 Surface Water Discharge and Permitting

National Pollutant Discharge Elimination System (NPDES) permits use a standard process for developing effluent limits for pollutants. Effluent and receiving water limitations would be established in the same manner as other pollutants. Michigan is currently the only state with a PFAS discharge standard. The Michigan Department of Environmental Quality Rule 57 Water Quality Values can be found on their web page (MI EGLE 2019).

8.2.3.6 Other State Regulations or Programs

Another concern for PFAS is in the application of biosolids from municipal wastewater treatment plants to land for disposal or reuse. In the ITRC 2018 State Survey on PFAS, no state indicated that they had regulations on PFAS in biosolids application

to land. However, Alaska, Delaware, Illinois, Michigan, Montana, New York, Vermont, and Wisconsin were in the process of considering and/or developing such regulations. In March 2019, Maine began requiring land applicators of biosolids to test for PFOA, PFOS, and PFBS before application, and prohibited application of biosolids if those PFAAs exceed specific levels (2.5 ppb for PFOA, 5.2 ppb for PFOS, and 1900 ppb for PFBS) (ME DEP 2019).

New Hampshire has an ambient air limit for ammonium perfluorooctanoate of 0.05 ug/m³ (24-hour) (NH DES 2016).

On March 6, 2019 California's Water Resources Control Board held a public meeting where it unveiled its PFAS Investigation Plan (CA Water Boards 2019). That plan has been reassessed and there is now only a second phase with no timeline. One part of the reassessed plan has been completed which was issuing informational orders to plating shops. The next set of orders will be issued to wastewater treatment plants (to be completed spring 2020). After those orders are completed, informational orders will be issued for biosolids application areas and potentially bulk fuel/chemical facilities with AFFF capabilities. Sampling of domestic water supply wells in the vicinity of these sites is also planned. Results will be available on the CA Water Boards (2020) web page.

Finally, some states have issued state regulations or programs related to AFFF. For example, New York, Vermont, and Massachusetts have established AFFF take-back programs in an attempt to reduce the potential discharge of PFAS associated with AFFF into the environment. Other states (for example, New Hampshire) are in the process of developing an AFFF take-back programs. See Section 3 for a more detailed discussion on AFFF and related regulations and guidance.

8.3 Differences in the Available Regulations, Advisories, and Guidance Regulatory

Human health protection is the primary focus of the PFAS regulations, guidance, and advisories developed to date. Internationally, including in the United States, the nonpolymer PFAS have been the regulatory focus, primarily nonpolymer long-chain PFAAs. There are a number of draft toxicity evaluations available for different PFAS. This is an area of active research. Additional information is presented in Section 7.1 and 17.2.

As of September 2019, regulatory human health-based guidance values and/or standards have been derived for 16 PFAAs, two polyfluoroalkyl precursors, and one fluorinated ether carboxylate (FECA) by state and/or federal agencies in the United States. The values for these nonpolymeric PFAS vary across programs, with differences due to the selection and interpretation of different key toxicity studies, choice of uncertainty factors, and approaches used for animal-to-human extrapolation. The choice of exposure assumptions, including the life stage and the percentage of exposure assumed to come from non-drinking water sources, also differs. PFOA and PFOS have the vast majority of regulatory guidance and/or standards available, and the key differences in regulatory decisions within the United States for those chemicals can be seen in the ITRC tables posted as an Excel file of the basis for PFOA and PFOS values. These same key decision points also underlie the differences that exist in the other perfluoroalkyl substance regulatory values, but are not documented in the tables. Some examples that describe differences in these toxicity values for PFAAs, including some of the bases of these values, their commonalities are the focus of the remainder of this section.

Table 8-2 provides the underlying definition and context for the various federal regulations, standards, and guidance values that may apply to PFAS in the United States.

Table 8-2. Definition of terms associated with drinking water and/or groundwater standards or guidance

Term	Acronym	Agency	Definition	Link
Minimum Risk Level	MRL	CDC ATSDR	<p>An MRL is an estimate of the daily human exposure to a hazardous substance that is likely to be without appreciable risk of adverse noncancer health effects over a specified duration of exposure. MRLs are intended to serve as screening levels to identify contaminants and potential health effects that may be of concern. MRLs are not intended to define cleanup or action levels for ATSDR or other agencies. (ATSDR 2018d) Importantly, the MRL is a daily dose, applicable for any oral exposure; it is not a threshold concentration in water or other environmental media.</p>	<p>https://www.atsdr.cdc.gov/mrls/index.asp</p>

Term	Acronym	Agency	Definition	Link
Regional Screening Level	RSL	USEPA Regions	<p>Default screening level tables including chemical-specific concentrations for individual contaminants in air, drinking water, and soil that may warrant further investigation or site cleanup. Generic screening levels (SLs) are based on default exposure parameters and factors that represent reasonable maximum exposure conditions for long-term/chronic exposures and are based on the methods outlined in EPA's Risk Assessment Guidance for Superfund, Part B Manual (1991) and Soil Screening Guidance documents (1996 and 2002). It should be emphasized that SLs are not cleanup standards. (USEPA 2019i)</p>	<p>https://www.epa.gov/risk/regional-screening-levels-rsls-users-guide#intro</p>

Term	Acronym	Agency	Definition	Link
Health Advisory	HA	USEPA Office of Water	Health advisories provide information on contaminants that can cause human health effects and are known or anticipated to occur in drinking water. EPA's HAs are nonenforceable and provide technical guidance to state agencies and other public health officials on health effects, analytical methodologies, and treatment technologies associated with drinking water contamination. (USEPA 2019b)	https://www.epa.gov/dwstandardsregulations/drinking-water-contaminant-human-health-effects-information
Maximum Contaminant Level	MCL	USEPA Office of Water	The highest level of a contaminant that is allowed in drinking water. MCLs are set as close to MCL goals as feasible using the best available treatment technology and taking cost into consideration. MCLs are enforceable standards. (USEPA 2018h)	https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations

As stated above, available PFAS regulations, guidance, and advisories are generally based on human health protection. However, the available values that are deemed protective of human health vary across international and U.S. jurisdictions. In general, there are similarities and differences in the understood toxicological effects, potencies, and modes of action for various PFAAs, and there are differences in the interpretation of relevant toxicological data for individual PFAAs.

Toxicological data from animal species are used as the basis for all of the U.S. PFAS human health toxicity factors and related standards or guidance. However, the European Food Safety Authority's PFOA and PFOS tolerable weekly inputs are based on human data. See Section 7 for a review of the toxicology data for PFAS. Many scientific considerations and decision points are involved in developing human health toxicity factors (such as RfDs) from animal toxicology data. For PFOA and PFOS, different scientific and regulatory policy conclusions have been made for nearly each decision point by different agencies. Examples of some of the key differences will be discussed below. Agency support documents should always be consulted for more specific details. The ITRC tables of PFAS water values, and PFAS soil values from state, federal, and some international countries posted as an Excel file). and ITRC tables posted as an Excel file of the basis for PFOA and PFOS values in the United States should be reviewed for more current and detailed information.

8.3.1 Determination of Key Study and Critical Effect

To date, PFAAs and FECA regulations, standards, and guidance have largely been based on potential noncancer effects. RfDs are used by most U.S. agencies to describe the estimate of a daily oral exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime (USEPA 2019d).

However, the USEPA, New Jersey Drinking Water Quality Institute (NJDWQI), and California OEHHA also considered potential cancer endpoints for PFOA and PFOS, and concluded that PFOA and PFOS are “suggestive” carcinogens and developed cancer toxicity values (cancer slope factor, CSF) for PFOA, while only OEHHA developed a CSF for PFOS. The threshold levels derived from RfDs by USEPA and NJDWQI are lower, that is, more protective, than those based on CSFs; thus, regulating or screening based on chronic noncancer risks was deemed to be protective of potential cancer risk by those entities. The methodology for deriving a chemical-specific toxicity values is generally applicable to both cancer and noncancer endpoints where dose-response relationships and weight-of-evidence analyses of available data sets are evaluated, and is described in detail, specific to PFOA and PFOS, below.

The first step in deriving a human health-based toxicity value (that is, RfD) is the review of applicable data to identify potential human health hazards (toxicity endpoints) based on sensitive effects that are consistently seen across several studies, are deemed related to an adverse health outcome or its known precursor, and are relevant to humans based on mode of action considerations. Not all agencies have utilized the same candidate studies and health endpoints for PFOA and PFOS due to differences in selection criteria and differences in opinion on the relevancy to human health and on adversity of effects seen in rodent bioassays. Older assessments relied upon primate studies due to concerns that rodent studies were not relevant to human health because of rodent-specific modes of action and toxicokinetics (USEPA 2009c), (NCDENR 2012) (MDH 2008)). The more recent derivations of PFOA and PFOS toxicity values are based on rodent studies with lower effect levels (compared to primate studies), citing potential modes of action that are relevant to humans and improved toxicokinetic models to extrapolate between species. Some agencies, such as the USEPA and NJDWQI, selected only key studies with serum measurements of PFOA or PFOS, which enable the use of the more advanced toxicokinetic modeling in serum levels; rodent bioassays without serum measurements were used as supporting studies in weight-of-evidence evaluation and decision-making. In general, all U.S. agencies with RfDs for PFOA and PFOS agree that liver effects, developmental effects, and/or immune effects are the most sensitive and relevant endpoints. However, methodologies for selection of the key studies and critical effects, and quantification of the RfD itself, vary widely. Some examples are discussed below; however, the ITRC tables posted as an Excel file of the basis for PFOA and PFOS values in the United States should be consulted for more current and detailed information.

8.3.1.1 PFOA

USEPA identified a subset of animal studies for their PFOA toxicity value derivation based on sensitivity and human relevancy of the endpoint, exposure durations of greater than 7 weeks, multiple dose groups, use of a concurrent control, and studies that provided serum data amenable for modeling. Although this last requirement, studies with measured serum levels, excluded some studies, USEPA noted that the remaining studies encompassed the range of doses evaluated and the LOAELs observed in studies that lacked serum data. The resulting candidate studies included endpoints such as immune effects (Dewitt et al. 2008), developmental effects (Lau et al. 2006), increased liver weight and necrosis (Perkins et al. 2004), reduced pup weight (Wolf et al. 2007), reduced relative body weight (BW), and increased relative kidney weight (Butenhoff et al. 2004). The Lau et al. (2006) developmental study (LOAEL for reduced ossification in proximal phalanges and accelerated puberty in male mice) ultimately yielded the lowest RfD based on USEPA’s kinetic extrapolation, and was deemed to be protective of the other endpoints (USEPA 2016h). USEPA (2016h) reviewed the studies of mammary gland development in mice, but chose not to consider this endpoint as a potential critical effect due to unknown mode of action and unclear functional significance. Minnesota Department of Health MDH (2018b) selected Lau et al. (2006) for their key study and critical effect, but also identified other health effects (liver effects, immune system effects, kidney weight changes, and other development effects) as effects of concern.

Conversely, NJDWQI (2018a) determined that the developmental effects noted in Lau et al. (2006) were not permanent structural changes and had unknown long-term consequences and unclear functional significance. Additionally, they noted that there was not a typical dose-response relationship in these effects with increasing dose (the greatest effects for delayed ossification and accelerated puberty occurred at the lowest dose, with less of an effect at higher doses) (NJDWQI 2017a). NJDWQI selected increased liver weight in mice (Loveless et al. 2006) as their critical effect for PFOA’s RfD. Additionally, they applied an uncertainty factor to account for delayed mammary gland development, persistent liver toxicity, and other potential developmental effects that they concluded could occur at lower exposure levels (NJDWQI 2017a). NJDWQI determined that the delayed mammary gland developmental effect (Macon et al. 2011) was a more sensitive critical effect that was scientifically valid; however, its use as the basis for chemical risk assessment was unprecedented and therefore, ultimately not chosen. Texas Commission for Environmental Quality (TCEQ) selected the mammary gland developmental effects in mice (Macon et al. 2011) as their critical effect, stating that it was the most health protective (TCEQ 2016). TCEQ did not have a requirement that serum PFOA levels be measured in the key study and used administered dose as the dose metric.

Rather than selecting just one key study, Maine's CDC selected six PFOA animal bioassays across multiple species (rats and mice) with increased liver weight and hepatocyte enlargement (Lau et al. 2006; Perkins et al. 2004 (three studies with varying conditions; Sibinski 1987; Butenhoff, Kennedy, Frame, et al. 2004). MDEP used the geometric mean of the benchmark dose limits from these six studies as their final point of departure (Maine CDC 2014).

8.3.1.2 PFOS

Similarly as for PFOA, USEPA identified a subset of animal studies for their PFOS toxicity value derivation based on sensitivity and human relevancy of the endpoint, exposure duration considerations, multiple dose groups, use of a concurrent control, and studies that provided serum data amenable for modeling. Using toxicokinetic models and dose-response modeling (both described below) of the selected studies and endpoints, USEPA concluded that the internal dose levels associated with developmental and liver endpoints were similar; endpoints considered as critical effects included offspring growth and survival, liver weight changes, liver histopathology, and changes in serum biochemistry indicative of systemic effects.

USEPA did not consider the monkey study from Seacat et al. (2002) appropriate because of the premature deaths of two of the six male monkeys at the LOAEL. However, this was the key study and critical effect from USEPA's provisional health advisory derived in (USEPA 2009c) and is the key study (critical effect of increased thyroid-stimulating hormone, reduced total T3, and reduced high-density lipoproteins) utilized by Maine Department of Environmental Protection (ME DEP) for their PFOS RfD and development of their Remedial Action Guideline (ME DEP 2016). In 2017, MDH selected the same key study and critical effect for PFOS as the USEPA but added a database uncertainty factor to the USEPA RfD for potentially more sensitive immune effects (MDH 2017a). In 2019, MDH selected a different key study in mice with immunotoxicity as the critical effect (MDH 2019a).

Regarding immune effects, USEPA concluded that there is a concern for PFOS-mediated immune effects, but determined that the available studies (including Dong et al. (2009)) were not amenable to use in RfD derivation. They state that both human dosing information and low-dose confirmation of immune effects in animals is lacking (USEPA 2016g). The USEPA derived an RfD for PFOS based on decreased neonatal rat BW from the two-generation study by Luebker, York, et al. (2005) because this key study and critical effect combination yielded the lowest RfD of the remaining studies (USEPA 2016g).

New Jersey derived their PFOS RfD based on the NOAEL for plaque-forming cell response in mice, an indication of immunosuppression (Dong et al. 2009), as the critical effect to determine their RfD. NJDWQI stated that this endpoint is more sensitive than the decreased neonatal BW from Luebker, Case, et al. (2005); Luebker, York, et al. (2005) and this immune effect is supported by other studies in mice and humans (NJDWQI 2018b). NJDWQI (2018a) discussed some concerns and issues related to USEPA's rationale and selection of the to Luebker, York, et al. (2005) endpoint.

Texas selected a study with hippocampus synapse structure effects (Zeng et al. 2011) as the critical effect to determine their RfD for PFOS. TCEQ (2016) stated that based on their calculations and examination of potential RfDs, use of Seacat et al. (2002) and protection against thyroid effects may not adequately protect against potential neurological developmental effects. Thus, TCEQ (2016) used Zeng et al. (2011), based on their toxicokinetic extrapolation methods (discussed below), for a lower and more health-protective RfD. NJDWQI (2018a) concluded that Zeng et al. (2011) provided only "mechanistic information" and did not include this study in their evaluation. USEPA discussed the results from Zeng et al. (2011) in their PFOS Health Effects Support Document; however, it is not clear why this study was not moved forward as a potential candidate for the PFOS RfD (USEPA 2016g).

8.3.2 Approaches Used for Animal-to-Human Extrapolation

Given that animal laboratory studies serve as the basis for human health risk assessments (HHRAs), derivation of human health toxicity values requires conversion of the dose administered to the test species to an appropriate human equivalent dose. In lieu of robust chemical-specific toxicokinetic and toxicodynamic information, the accepted default method to derive the human equivalent dose is by body-weight scaling to the 3/4 power (that is, $BW^{3/4}$), which relies upon the known relationship between BW and the various metabolic and physiological functions of humans compared to rodents (USEPA 2011b). The use of $BW^{3/4}$ scaling for deriving an RfD is recommended when the observed effects are associated with the parent compound or a stable metabolite in the absence of available chemical-specific toxicokinetic models (USEPA 2011b). When the necessary information is available, the preferred approach is to use chemical-specific physiologically based toxicokinetic modeling to convert toxicologically equivalent doses of orally administered agents from laboratory animals to humans. Another approach may include using chemical-specific toxicokinetic and toxicodynamic information to derive chemical-specific adjustments. For chemicals such as long-chain PFAAs that exhibit species-specific pharmacokinetic properties, chemical-specific adjustment using specific information about the species differences is most appropriate. The

type of chemical-specific pharmacokinetic information that is available dictates the complexity of the human equivalent dose extrapolation method, which may range from (1) using ratios of rodent to human clearance factors, to (2) using complex physiologically based pharmacokinetic models to extrapolate from administered (oral) dose to internal dose in the rodent, to internal dose in the human, and then to administered (oral) dose in the human.

Nonpolymeric long-chain perfluoroalkyl substances such as PFOA and PFOS exhibit marked differences in species-specific pharmacokinetics, mainly due to differences in elimination rates (because of higher renal reabsorption and serum protein binding in humans relative to rodents). To date, a wide range of technical approaches are employed to address these species-specific differences for PFOA and PFOS. Examples of some approaches are described here; however, the ITRC tables posted as an Excel file of the basis for PFOA and PFOS values in the United States should be consulted more current and detailed description of agency approaches.

The USEPA chose to rely on animal bioassays that collected internal serum measurements for PFOA and PFOS, then employ a pharmacokinetic model to estimate the animal's average serum concentrations for each study-specific exposure duration (USEPA 2016c, d). USEPA used the serum concentration at the NOAEL or LOAEL in the animal studies, rather than administered dose, for animal-to-human dose comparison. USEPA then used a first-order kinetic model for chemical clearance, using previously published single point estimates for elimination half-lives and volumes of distribution, to convert the serum concentration at the PFOA or PFOS NOAEL or LOAEL in the animal study to an external administered human (oral) dose that would result in the same serum concentration in humans.

NJDWQI's recommended MCL for PFOA and PFOS also relied upon studies that included serum measurements taken close to the end of the dosing period; NJDWQI conducted dose-response modeling and applied uncertainty factors to the internal serum levels measured at the end of the dosing period from the animal bioassays to derive a target human serum level. NJDWQI then calculated the RfD by applying the same PFOA clearance factors used by USEPA to convert the target human serum level to an administered dose in ug/kg-day.

Other agencies within the United States used different approaches for PFOA and/or PFOS. For example, Maine Department of Environmental Protection used all available animal studies (they did not limit their pool to only those studies with internal serum measurements) and used the ratio of clearance for the animal species over human clearance to convert the animal administered dose to a human equivalent dose. Agencies such as TCEQ used the ratio of elimination half-lives to convert the rodent administered dose directly to the human equivalent administered dose.

There are only a few toxicity values derived for short-chain PFAAs, and the methods to extrapolate from animal to human dose also vary and include either the use of BW scaling (allometric scaling of $BW_{\text{animal}}^{1/4}$ divided by $BW_{\text{human}}^{1/4}$) or the ratios of elimination half-lives. The USEPA (2014c) derived a subchronic and chronic toxicity value for PFBS, based on a subchronic rat study, and used body-weight scaling to derive the human equivalent dose. They stated that based on information available at the time of their derivation, including a lack of definitive information regarding pharmacokinetic differences between species, the use of BW scaling was most appropriate. USEPA (2018e) has a draft human health toxicity values report for PFBS.

More recently, the French National Agency for Food Safety, Environment, and Labor (ANSES) also used this same BW scaling approach when deriving their toxicity values for short-chain PFAAs such as PFBS, PFBA, and PFHxA (ANSES 2017). Use of the allometric BW scaling approach to calculate a human equivalent dose is the default approach for chemicals that do not exhibit species-specific adsorption, distribution, metabolism, or elimination processes, and absent chemical-specific information.

Chemical-specific support for the use of BW scaling to derive the human equivalent dose for some short-chain PFAAs has been demonstrated in recent studies. For example, Russell, Nilsson, and Buck (2013) and (Luz et al. 2019) found that elimination rates of PFHxA scale by BW, given that there are no known species-specific elimination mechanisms that dramatically alter elimination kinetics between species. Citing these reasons, the PFHxA toxicity value and related proposed drinking water standard derived by Michigan uses the allometric BW scaling due to this chemical-specific information. In contrast, the Minnesota Department of Health used the ratio of human to rodent half-lives to adjust the rodent-administered dose to a human equivalent dose for their derivation of PFBA and PFBS noncancer health risk limits (MDH 2018a, 2017c). MI also used the ratio of half-lives for PFBS to calculate the human equivalent dose for toxicity value derivation (MI SAW 2019; MI DHHS 2019).

The estimation of an RfD includes two additional components that are shown in the ITRC tables posted as an Excel file of the

basis for PFOA and PFOS values in the United States and includes the selection of the dose-response method and uncertainty factors. For dose-response evaluation, either the benchmark dose or the study NOAEL or LOAEL is utilized as the point of departure, as detailed in the tables. Uncertainty factors used include the standard risk assessment extrapolations as detailed in the tables, and also vary by agency.

8.3.3 Exposure Assumptions

For each of the exposure factors discussed in this section, See the ITRC tables posted as an Excel file of the basis for PFOA and PFOS values in the United States for the most current information and details.

8.3.3.1 Body Weights, Drinking Water Ingestion, and Exposure Durations

Once a human health toxicity value is derived in units of ug/kg-day (or ng/kg-day or mg/kg-day), the toxicity value is combined with exposure parameters to result in the ultimate threshold concentration in drinking water (guidance or standard). The choice of exposure parameters used can be a flexible science-based decision based on default assumptions or chemical-specific data, or may be set based on regulatory framework. The exposure parameters used under the U.S. CERCLA program (for example, USEPA regional screening levels) include default exposure parameters and factors that represent conditions for long-term/chronic exposures, including exposure frequency of 350 days per year, exposure duration of 6 years for a 15-kg child who drinks 0.78 L water per day, or 26 years for an 80-kg adult who drinks 2.5 L of water a day. In contrast to CERCLA, drinking water guidance values and standards (MCLs) developed by USEPA or states are generally based on lifetime exposure using default adult parameters, and they do not usually include a duration of exposure parameter. For PFOA and PFOS, USEPA and state agencies have not always relied upon these default exposure parameters. Some have decided to utilize exposure parameters that are specific for more sensitive subpopulations (infants, children, or lactating/pregnant women). For example, MDH developed a toxicokinetic model to estimate the total exposure to breast-fed and formula-fed infants (Goeden, Greene, and Jacobus 2019), and this model was used to derive standards in Minnesota, New Hampshire, and Michigan.

USEPA combined their toxicity values with exposure parameters specific for lactating women. According to USEPA, this addressed the potential increased susceptibility during pregnancy and lactation. USEPA used the rate of 54 mL/kg-day based on the “consumers only” estimate of combined direct and indirect water ingestion at the 90th percentile for lactating women from their Exposure Factors Handbook (see table 3-81 in USEPA (2011a).

Vermont used USEPA Office of Water toxicity values for PFOA and PFOS, but combined those toxicity values with exposure parameters specific for infants (0–1 year of age), assuming a drinking water intake rate of 0.175 L/kgBW-day (Vermont DOH 2016). Texas chose to combine their state-derived toxicity values with exposure parameters for children (ages 0–6 years); TCEQ (2016) used the default child BW of 15 kg and ingestion of 0.64 L-day, equivalent to 0.043 L/kg-day of water.

Minnesota is thus far unique in using specific exposure parameters based on exposure to breast-fed and formula-fed infants for the derivation of the PFOA and PFOS health-based guidance values. They selected the 95th percentile water intake rates or upper percentile breast milk intake rates (USEPA 2011a) and calculated breast milk concentrations by multiplying the maternal serum concentration by a calculated breast milk transfer factor of 5.2% for PFOA and 1.3% for PFOS (MDH 2018b, 2019a).

8.3.3.2 Relative Source Contribution

Humans can be exposed to nonpolymeric PFAS, including precursor chemicals, via multiple sources, including air, food, and consumer and industrial products. The most common route of exposure for the general public is via the diet, including water, and followed by indoor dust, especially for children. The relative source contribution (RSC) term is used in health-based guidance and standards developed by the USEPA under the federal SDWA and related state programs to account for potential non-drinking water exposures to chemicals. The concept ensures that when a criterion based on an RfD for noncancer effects is established for a single exposure pathway, such as drinking water, potential exposures that occur from other pathways are accounted for so that total exposure does not exceed the RfD. The default RSC of 20% means that the drinking water pathway is assumed to contribute only 20% of the RfD, and all other exposure pathways contribute the remaining 80%. In practice, therefore, the drinking water concentration based on RfD and drinking water consumption assumptions is multiplied by the RSC (for example, 20%) to account for the other pathways. Following USEPA’s exposure decision tree (USEPA 2000c), USEPA determined that significant potential sources other than drinking water ingestion exist; however, they concluded that information is not available to quantitatively characterize exposure from all of the different sources. Therefore, USEPA adopted a default RSC of 20% (0.20) for PFOA and PFOS drinking water health advisories.

The RSC term generally does *not* exist in CERCLA/RCRA-based remediation programs because baseline risk assessments specifically investigate and quantify risks associated with all potential site-specific exposure routes (not just drinking water), and then consider a receptor’s cumulative risk. Therefore, there is no downward adjustment to a residential groundwater (termed “tap water” by USEPA) drinking water screening level, for example, to account for potential other exposures—all site-specific exposures are quantified.

Some state agencies have incorporated RSC when deriving their state guidance/standards for long-chain PFAAs. For example, New Jersey Department of Environmental Protection adopted a 50% RSC for PFNA (NJDWQI 2015) and a 20% RSC for PFOA and PFOS (NJDWQI 2017a, 2018a), which they state also “implicitly accounts for greater exposures to breast-fed and formula-fed infants than older individuals.” Minnesota used an RSC of 50% based on their analysis of biomonitoring serum concentrations from local and national general populations (MDH 2017b, a).

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9 Site Risk Assessment

The PFAS Team developed a training module video with content related to this section, it is the Risk Assessment and Regulations video.

This section discusses the specific challenges associated with assessing and characterizing potential risks to human and ecological receptors exposed to PFAS in the environment. This includes challenges associated with quantifying the degree of exposure, assessing the hazard associated with PFAS, quantifying the dose-response relationship, and characterizing risks to support effective risk management decision-making. Generally, the challenges associated with performing a site risk assessment where the release of PFAS to the environment is suspected are not necessarily unique. Like any other chemical for which there is limited information, knowledge, or other technical complexity, working through the steps necessary to complete a risk assessment would be similar.

Section 15.3 provides a case study example illustrating how the New Jersey Department of Environmental Protection used risk assessment science to help support the development of fish consumption advisories for select water bodies in New Jersey. Section 17.3 provides additional information related to PFAS risk assessment, including (1) exposure pathways relevant for different exposure media, (2) considerations when calculating exposure point concentrations, and (3) selecting bioconcentration/bioaccumulation factors.

Section Number	Topic
9.1	Human Health
9.2	Ecological Risk Assessment
9.3	Uncertainty

9.1 Human Health

9.1.1 Toxicity Assessment

The toxicity assessment of a site risk assessment involves (1) hazard identification and (2) dose-response assessment. Hazard identification involves determining whether exposures to a chemical can cause an increased risk of an adverse human health effect; dose-response assessment involves quantifying the relationship between the degree of exposure to the chemical and the incidence or severity of the potential adverse effects. More background on each of these steps is detailed in other guidance (USEPA 1989; ITRC 2015a) and is not repeated here.

This section discusses specific complications that may be encountered in completing the toxicity assessment for a site risk assessment involving PFAS.

9.1.1.1 Availability of Toxicity Values from a Variety of Sources

A toxicity value (for example, oral CSF, systemic inhalation reference concentration) is a numerical expression of the dose-response relationship for a given substance. It is used in combination with estimates of chemical exposure to calculate quantitative estimates of cancer risk or noncancer hazard (USEPA 1989). Several state, national, and international regulatory and advisory agencies have developed human toxicity values for various PFAS that could be potentially used in conducting risk assessments or in support of establishing policies for PFAS risk management. Given this variety of sources, specific complications can be encountered in determining which toxicity values to use in conducting a risk assessment:

- Selection of toxicity values for PFAS is dependent on which PFAS are present at a given site. PFAS identification and quantification may vary based on analytical method.
- Differences among toxicity values for PFAS could arise because agencies may rely on different toxicity value derivation methods, may select critical studies by different criteria, may use different uncertainty factors, and may make different judgments about the prioritization of individual PFAS for toxicity value derivation (Table 9-1).

- Available toxicity values may change over time as the results of new studies become available. Newer toxicity values derived by regulatory agencies may be based on more recent and/or different information, methods, and studies than older values, as well as differences in scientific professional judgment and/or different statutory policy requirements. These differences are described in more detail in Section 8.3.
- All values may not be relevant to all jurisdictions. For example, toxicity values developed by the USEPA may not be accepted in some states or in other countries.

Table 9-1. Example of variability in derived noncancer RfDs for PFOA and PFOS

Noncancer Toxicity Values for Human Health Risk Assessment (ng/kg body weight*day)				
Source	PFOA	Basis	PFOS	Basis
USEPA (2016c) USEPA (2016d)	20	Delayed bone development and accelerated male puberty in mice (following developmental exposure)	20	Reduced growth rate of offspring (following developmental exposure)
ATSDR (2018e) DRAFT	3	Behavioral and skeletal effects in mice (following developmental exposure) Based on a study USEPA did not select for consideration, and a newer study from 2016	2	Used same study, but noted additional effect (delayed eye opening) Added a 10X uncertainty factor to protect for immunotoxicity

There are several options and procedures for selection of toxicity values, as has been described in ITRC guidance (ITRC 2015a). For site risk assessments performed in the United States, USEPA, DOD, and other agencies have recommended a tiered hierarchy (Tier 1-Tier 3) of toxicity value sources to guide selection and use (USEPA 2003a, 2013e); (ECOS-DOD 2007). This recommendation has since been implemented in numerous USEPA OSWER (Currently known as Office of Land and Emergency Management) directives (USEPA 1993, 2003a) that further establish a hierarchy and process for selecting toxicity criteria. For PFAS chemicals as of September 2019:

- Tier 1 values are peer-reviewed toxicity values published on the USEPA’s Integrated Risk Information System (IRIS).
 - There are no PFAS chemicals in IRIS with published values.
- Tier 2 toxicity values include Provisional Peer-Reviewed Toxicity Values (PPRTV).
 - Only for PFBS.
- Tier 3 toxicity values include those from additional USEPA and non-USEPA sources. They can include values that may or may not have been peer reviewed. As recommended by USEPA (2003a), in using values from Tier 3 sources, it may be appropriate to prioritize those that are the *most current*, have a *transparent* basis, are *publicly available*, have been *peer reviewed*, and are acceptable to local jurisdictions.
 - Available toxicity values for PFAS chemicals are Tier 3 values.
 - Additional definitions and discussion of PFAS toxicity values that are available for use are provided in Section 7 and Section 17.2.

9.1.1.2 Lack of Toxicological Values for Many PFAS

There are more than 4,700 PFAS that could have been, or may be, on the global market (OECD 2018), although the uses of each of these PFAS may not be known (KEMI 2015b). More information about PFAS in use is included in Section 2. A large number of PFAS are considered bioavailable. However, toxicity values have been developed for only a few PFAS compounds for which sufficient information is available. Because of the lack of hazard and dose-response information for other PFAS and the extensive level of effort needed to develop toxicity values, there are no readily available toxicity values for the majority of PFAS.

This lack of information prevents the establishment of compound-specific risk-based concentrations that can be helpful for a variety of applications, including data screening (used to help guide site investigation) and site-cleanup decision-making. In the absence of toxicity values, regulatory agencies and the regulated community are left with uncertainty regarding the potential risks associated with human exposure to impacted environmental media at sites, technically defensible risk management programs may be difficult to create, and the regulated community cannot be responsive to concerns about

environmental risk.

An approach often used in HHRA in the absence of compound-specific toxicity values is to use toxicity values developed for structurally or chemically similar surrogate compounds with similar biological activity. In the case of PFAS, this would be for PFAS from the same structural subgroup (for example, long-chain perfluorocarboxylic acids). The use of surrogates, however, introduces uncertainty, because surrogates may produce adverse health effects by mechanisms different from the compound of concern, the dose-response curve for a surrogate may be different, and the target organ or toxicity endpoint may be different from the compound of concern. In the absence of chemical-specific toxicity values, preparation of health risk assessments may be limited to qualitative methods and have a higher level of uncertainty as a result.

Further information and guidance are needed to identify appropriate surrogates for PFAS that do not currently have available toxicity values. As part of their PFAS Action Plan (USEPA 2019h), USEPA is working on developing an approach to PFAS toxicity testing that could lead to a methodology for inferring the toxicology of a given PFAS based on the toxicology of a PFAS subset. This involves applying computational and high throughput toxicology tools for PFAS toxicity testing on a larger scale to enable faster understanding of potential toxicity for the universe of thousands of PFAS, most of which have little or no published toxicity data.

9.1.2 Exposure Assessment

The exposure assessment of a site risk assessment involves characterizing the exposure setting, identifying relevant exposure pathways and scenarios, and quantifying the magnitude, frequency, and duration of potential human exposure to chemicals in environmental media. More background on the performance of exposure assessments is detailed in other guidance (USEPA 1989; ITRC 2015a) and is not repeated here.

This section discusses specific complications that may be encountered in completing the exposure assessment for a site risk assessment involving PFAS. It should be recognized that the exposure assessment does not generally account for the presence of all PFAS at a site due to limitations in analytical methods. Therefore, there are uncertainties in the characterization of exposures (and associated risks) at PFAS sites that should be acknowledged in the uncertainty analysis section of the risk assessment.

9.1.2.1 Determining Scenarios for Potential Human Exposure

A site-specific conceptual exposure model should be developed during the planning stage of the HHRA, confirmed by stakeholders, and updated as additional information and data are obtained (Section 3 of the RISK-3 guidance (ITRC 2015a)). The specific exposure scenarios that are applicable to an HHRA for PFAS include those that could occur in media at the release area (the site) and in media at distant locations (with the extent depending on PFAS properties and the site setting). In general, an HHRA for PFAS may be complex in comparison to HHRAs for other types of chemicals (for example, due to the persistence of PFAS, the complexities associated with PFAS toxicity, and complexities associated with estimating future concentrations or modeling their fate and transport, and the need to include more media than is typical. Figures 9-1, 9-2 and 9-3 are provided below to illustrate conceptual site models (CSMs) for four sources (two sources are illustrated in Figure 9-3) of PFAS. Section 2.6 discusses potential environmental releases of PFAS. A detailed discussion of fate and transport processes for PFAS and environmental media that may be affected is presented in Section 5.

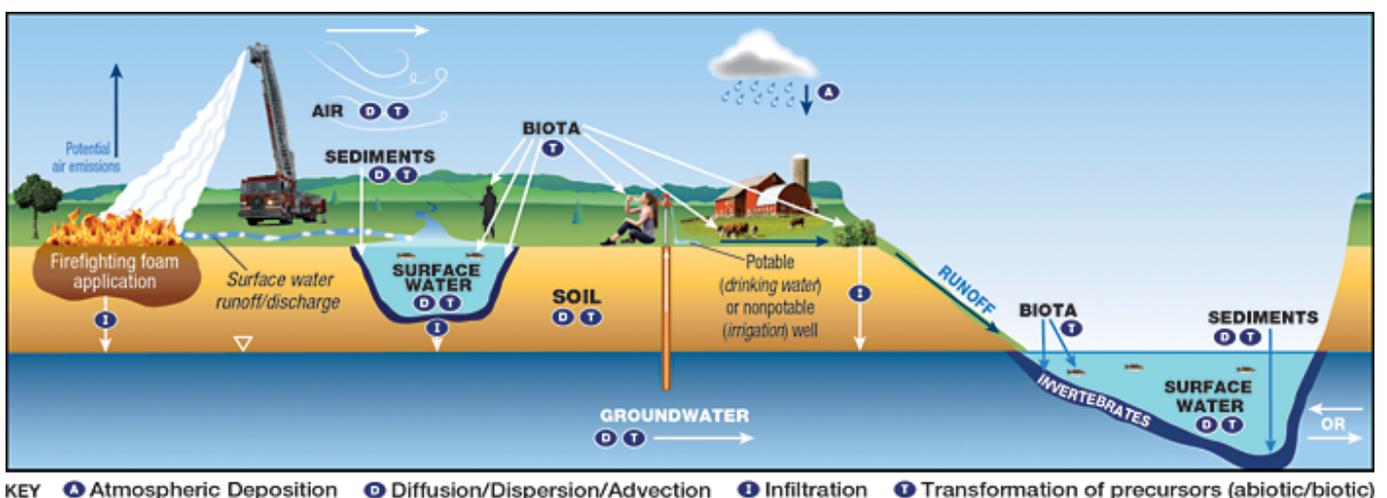


Figure 9-1. CSM for fire training area.

Source: Adapted from figure by L. Trozzolo, TRC. Used with permission.

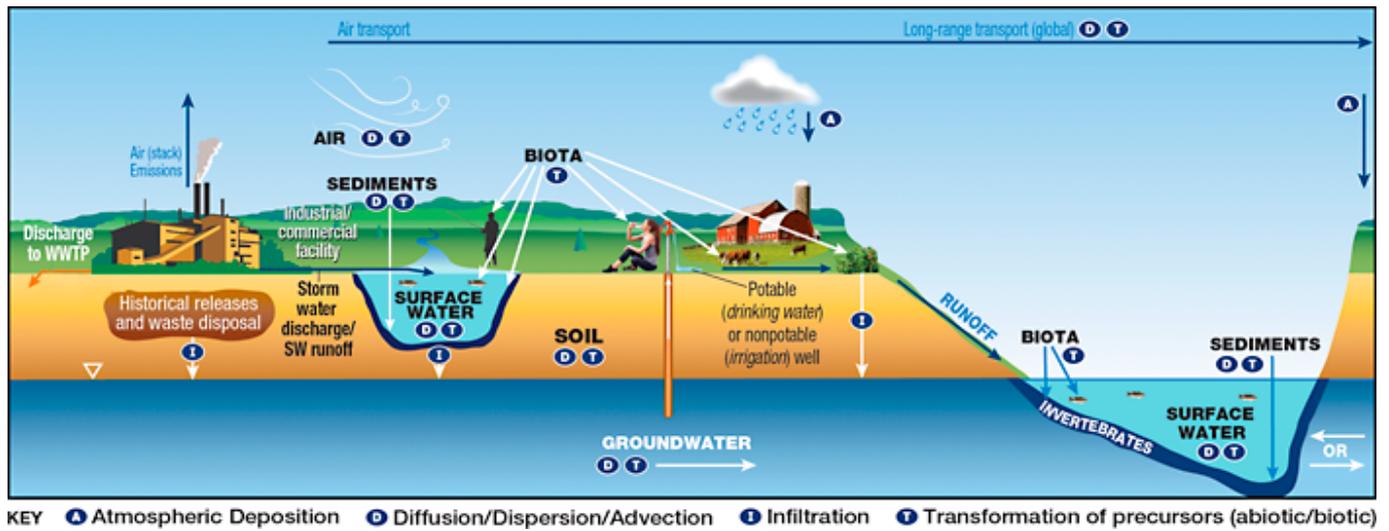


Figure 9-2. CSM for industrial sites.

Source: Adapted from figure by L. Trozzolo, TRC. Used with permission.

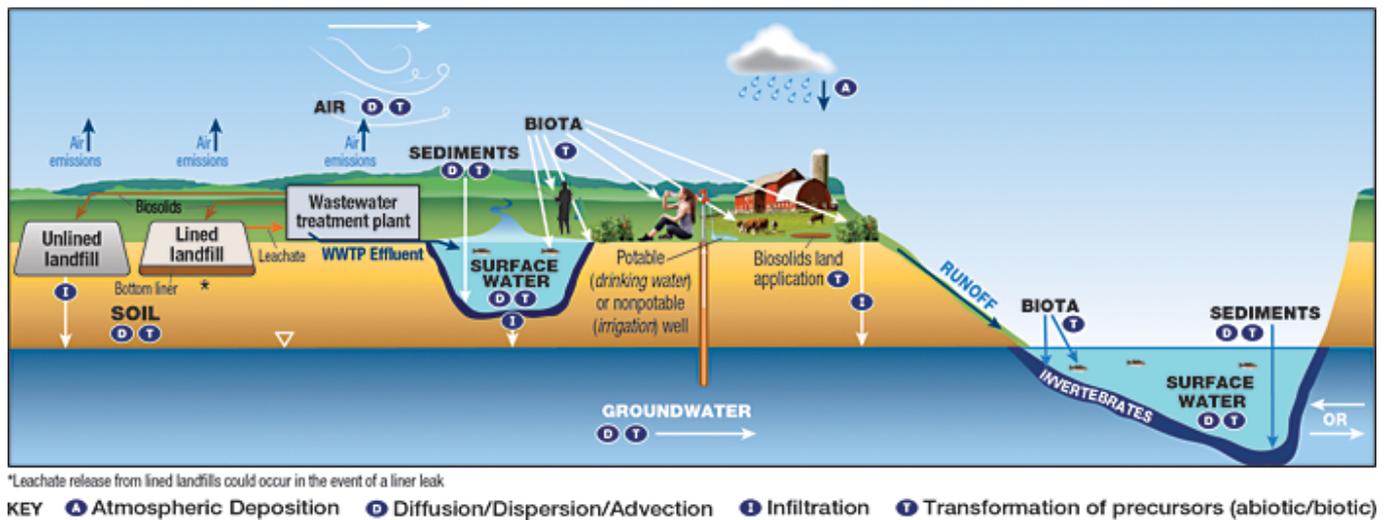


Figure 9-3. CSM for landfills and WWTPs.

Source: Adapted from figure by L. Trozzolo, TRC. Used with permission.

Various exposure scenarios may be possible for a given site, and which specific exposure scenarios should be included in a HHRA is a site-specific decision.

The highest exposures to PFAS can occur during early life stages (ages 0–18) (Winkens et al. 2017). Exposures to infants from breast milk of exposed mothers (Figure 9-4) or formula prepared with contaminated water are higher (on a BW basis) than in older age groups (Fromme et al. 2009; Mogensen et al. 2015; Verner et al. 2016b, a; Post, Cohn, and Cooper 2012). The higher exposures during pregnancy and to infants are of concern because fetuses and infants are sensitive subpopulations for developmental effects of some PFAS, including PFOA and PFOS (USEPA 2016h, g), as discussed in Section 7.1. Therefore, exposure scenarios that include fetuses, infants, children, adolescents, and women of childbearing years should be considered in HHRAs.

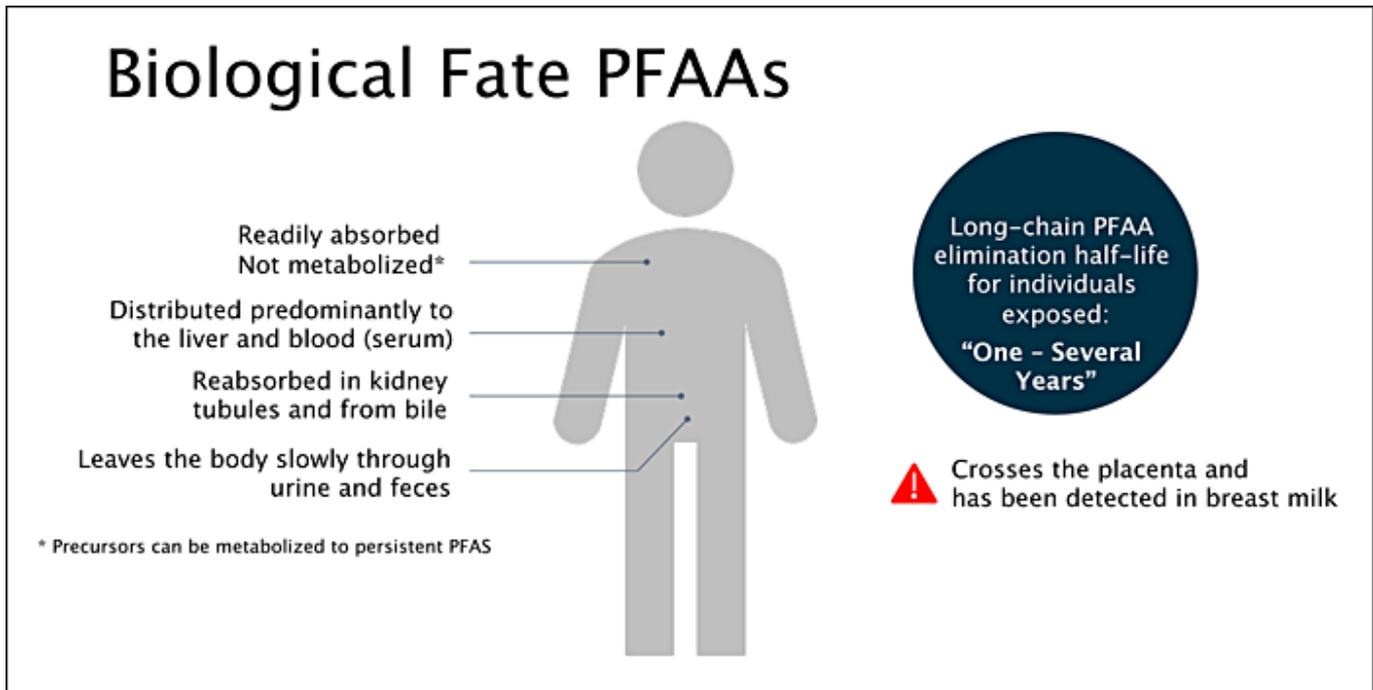


Figure 9-4. Biological fate of long-chain PFAAs.

Figure 9-5 illustrates the predominant exposure pathways. More detailed information about these exposure pathways, as well as other environmental medium-specific issues affecting potential human exposure scenarios, are provided in Section 17.3.1.

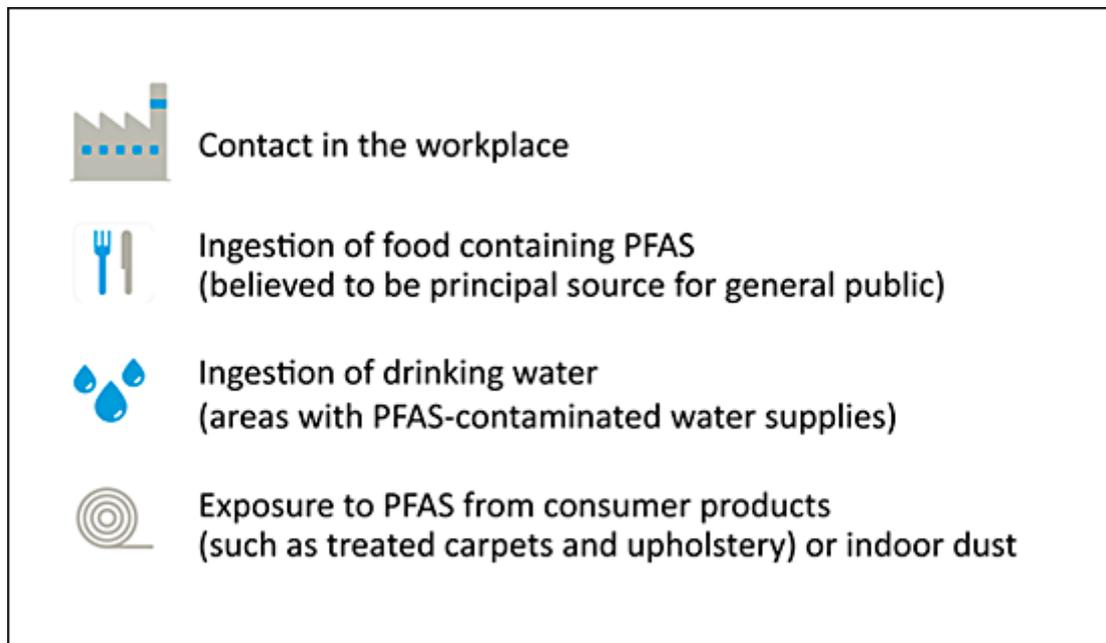


Figure 9-5. Predominant human exposure pathways.

9.1.2.2 Calculating Exposure Concentrations for PFAS via Fate and Transport Models

When using fate and transport models to calculate exposure point concentrations (EPCs) for PFAS, it is important to note that individual PFAS have different chemical properties that affect their fate in the environment (Section 5). Some PFAS are mobile, persistent, and bioaccumulative (in wildlife and humans), and others are not. Perfluoroalkyl acids (PFAAs) are persistent, and long-chain PFAAs bioaccumulate in humans (USEPA 2003b; ATSDR 2018c; NTP 2016; CONCAWE 2016). USEPA has compiled an online resource for PFAS information that includes guidance on environmental behavior and site characterization (USEPA 2017b). The National Groundwater Association (NGWA) has also published a resource on PFAS that includes information about fate and transport (NGWA 2017 (NGWA 2017)). Additional information is included in Section

17.3.2.

When using environmental fate and transport models for estimating EPCs in biota, modeling should be focused on the part of the organism that may be consumed either by humans or by ecological receptors. PFAS generally bind to proteins and accumulate in protein-rich tissues, including the blood, liver, and kidneys (ATSDR 2018c). Currently, models for plant uptake are limited, but several studies have documented uptake of PFAS from soil amended with PFAS-contaminated biosolids (Blaine et al. 2013; Blaine, Rich, Sedlacko, Hundal, et al. 2014; Wen et al. 2016). Section 17.3.3 includes information about selecting bioaccumulation and bioconcentration factor values.

Measured concentrations at exposure points may differ from modeled EPCs. This may be due to other sources of PFAS (for example, a nearby site that had a PFAS release to the ground and that subsequently leached to groundwater) also contributing to concentrations at the exposure point and the limitations of the models currently available.

9.1.3 Risk Characterization

The risk characterization of a site risk assessment combines the results of the exposure assessment and the toxicity assessment to provide a quantitative estimate of risk (ITRC 2015a). It also may include a qualitative narrative designed to provide decision makers with information regarding key assumptions, uncertainties, or other issues that would be important to understand when making risk management decisions. More background on the performance of risk characterizations is detailed in other guidance (USEPA 1989; ITRC 2015a) and is not repeated here.

Because risk characterization involves combining the toxicity assessment and exposure assessment, the complexities discussed in Sections 9.1.1 and 9.1.2 manifest themselves in the risk characterization. There are, however, additional specific complications that may be encountered in completing the risk characterization for a site risk assessment involving PFAS. This section discusses those specific complexities.

9.1.3.1 Assessing the Cumulative Effects of Exposure to PFAS

The overall potential for noncancer effects due to human exposure to more than one chemical is estimated using the hazard index (HI), which is computed as the sum of calculated chemical-specific hazard quotients (HQ). As explained by USEPA (1989), "This approach assumes that simultaneous subthreshold exposures to several chemicals could result in an adverse effect. It also assumes that the magnitude of the adverse effect will be proportional to the sum of the ratios of subthreshold exposures to acceptable exposures." Risk characterizations commonly produce initial estimates of HI by calculating the sum of all HQs. When the HI is estimated to be greater than 1, there may be potential concern for adverse health effects. However, when this initially estimated HI is greater than 1, refinement of the HI estimate by segregating HIs by effect and mechanism of action may be appropriate to support a risk management decision.

For PFAS, as discussed in Section 7.1, there are several possible adverse health effects associated with exposure. Table 9-2 provides a general summary of the possible noncancer adverse health effects associated with various PFAS. The information in this table can be used to segregate HIs by potential adverse effect in the risk characterization when risks associated with exposure to specific PFAS are being evaluated. Table 17-8 (provided as a separate Excel file) includes additional limitations and considerations regarding this information.

Table 9-2. Summary of potential noncancer health effects of various PFAS

Adapted from (ATSDR 2019a) Health Consultation PFAS HC-508.

	# of Carbons	Liver	Developmental	Reproductive	Immune	Hematologic	Thyroid	Neuro-behavioral	Tumors
Perfluoroalkyl Carboxylates									
PFBA	4	■	■	■	□	■	■	□	□
PFPeA	5	□	□	□	□	□	□	□	□
PFHxA	6	■	■	■	□	■	■	□	□ (Negative)
PFHpA	7	■	□	□	□	□	□	□	□
PFOA	8	■	■	■	■	■	■	■	■
PFNA	9	■	■	■	■	■	■	□	□
PFDA	10	■	■	■	■	■	■	■	□
PFUnA	11	■	■	□	■	□	□	□	□
PFDoA	12	■	■	■	■	■	□	■	□
Perfluoroalkyl Sulfonates									
PFBS	4	■	■	■	■	■	■	□	□
PFHxS	6	■	■	□	□	■	■	■	□
PFOS	8	■	■	■	■	■	■	■	■
Per- & Polyfluoroalkyl Ether Replacements									
ADONA	6	■	■	□	□	■	□	□	□
HFPO-DA GenX	6	■	■	■	■	■	■	□	■

Effect reported in one or more laboratory animal study
 Effect was evaluated but not found, or effect has not been evaluated

9.1.3.2 Characterizing Cancer Risk for Exposure to PFAS

As discussed in more detail in Section 7.1, (USEPA 2016h, g, 2018g) described PFOA, PFOS, and GenX as having suggestive evidence for human carcinogenicity. The International Agency for Research on Cancer (IARC) has also classified PFOA as *possibly carcinogenic to humans* (Class 2B). (USEPA 2005a) carcinogen risk assessment guidance provides for development of a slope factor for chemicals with “suggestive evidence” when supported by available data. USEPA (2016d) has developed a CSF for PFOA of 0.07 mg/kg-day based on testicular tumors. In the case of PFOS and GenX chemicals, although USEPA concluded that there is suggestive evidence of carcinogenic potential in humans based upon liver and thyroid impacts observed in chronic rat studies, the results lacked a dose-response relationship. Because of this limitation, USEPA judged the database too limited to support a quantitative assessment of carcinogenicity. Likewise, the NJDWQI (2018b) developed a slope factor for PFOS of 9×10^{-6} ng/kg-day for comparison purposes, but concluded that it is too uncertain to use as the basis for a drinking water value.

Although USEPA and some select states have derived oral CSFs for a select few PFAS, risks associated with PFAS (including derived risk-based values and screening levels) have been primarily based on noncancer effects. CalEPA’s OEHHA (2019), however, is unique in that they have issued notification levels for drinking water exposure that are driven by carcinogenicity. This is predominantly because OEHHA applies additional factors in their calculations to reflect what they consider an increased susceptibility of infants and children to carcinogens, and OEHHA derived a CSF for PFOS, which USEPA did not. For site risk assessments, the derived CSFs developed by these agencies could be used (for example, USEPA derived an oral CSF for PFOA of 0.07 mg/kg-day).

Further discussion of the carcinogenicity of PFAS is presented in Section 17.2.4.2 (Carcinogenicity), Section 17.2.5.3 (Chronic Toxicity and Tumorigenicity), and Section 8.2.2.3 (CERCLA).

9.2 Ecological Risk Assessment

9.2.1 Ecological Effects Assessment

Identification of ecological risk-based toxicity thresholds is a challenge for many PFAS. Toxicity data are available as discussed in Section 7.2. Some of these data have been used to establish thresholds as discussed below.

9.2.1.1 Ecological Screening Thresholds

Currently, there are no U.S. federal PFAS guidelines or media screening thresholds available that are ecological risk-based. However, several states have established some criteria that are intended to protect aquatic organisms in their respective surface waters. In Michigan, ambient water quality criteria have been established for PFOS and PFOA based on Rule 57 17 (MI EGLE 2019). This rule is based on the USEPA Great Lakes Initiative (USEPA 1995), which provides procedures and

methodologies to derive numerical criteria that are protective of aquatic ecosystems. Rule 57 presents a two-tiered methodology in which Tier I procedures are essentially the same as the methods used to derive federal national water quality criteria (NWQC) (USEPA 1985) and Tier II can be used to derive values where the full extent of the toxicity data requirements of NWQC are not fulfilled. Rule 57 presents procedures to develop three categories of numeric criteria—final chronic values (FCVs), aquatic maximum values (AMVs), and final acute values (FAVs)—which can be developed under either Tier I or Tier II. Due to the greater uncertainties associated with Tier II values, given the lesser data requirements, these values tend to be more conservative than those derived with Tier I methodologies. The PFOA and PFOS numeric criteria for Michigan are all Tier II values due to the limited amount of peer-reviewed aquatic toxicity data. The final chronic values for the protection of aquatic life (flora and fauna) for PFOA and PFOS were 880 and 140 µg/L, respectively, while aquatic maximum values were 7,700 and 780 µg/L, respectively. In addition, the Michigan Department of Community Health (MDCH 2015) derived provisional PFOS surface water values for mammalian and avian wildlife based on Rule 57 guidance. The surface water avian wildlife value, based on eagles, kingfishers, and herring gull characteristics, was 0.035 µg PFOS/L. The mammalian wildlife value, based on otter and mink characteristics, was 0.084 µg PFOS/L.

The State of Minnesota has also derived several PFAS-based surface water criteria for the protection of aquatic biota. These values were based on guidelines in Minnesota Rules chapter 7050 (MR7050). Continuous chronic criteria for the protection of aquatic biota in surface water are for PFOA (1,700 µg/L) and PFOS (19 µg/L) (Stevens and Coryell 2007b; Stevens and Coryell 2007a). No other surface water values have been derived for PFAS in either state (Michigan or Minnesota) and values for other states are unavailable.

Environment and Climate Change Canada (ECCC, previously known as Environment Canada) has proposed ecological Federal Environmental Quality Guidelines (FEQGs) for PFOS in surface waters, fish tissue, wildlife dietary values, and bird eggs (ECCC 2018). The PFOS threshold for surface waters was derived from a species sensitivity distribution (SSD) based on long-term toxicity data that included data for amphibians, fish, invertebrates, phytoplankton, and macrophytes. The guideline to protect all aquatic life forms for indefinite exposure periods to PFOS in surface waters is 6.8 µg/L, and a fish tissue guideline value of 9.4 mg/kg wet weight (ww) was based on these fish data and bioaccumulation factors for bluegill from Drottar, Van Hoven, and Kruger (2002). The tissue threshold is intended for both freshwater and marine environments. It was not calculated with both food and water (direct media) BAFs, and thus it could be underprotective. However, (Giesy et al. 2010) did use Drottar, Van Hoven, and Kruger (2002) data to calculate an acute no-effect threshold of 87 mg/kg ww. To protect mammalian and avian consumers of aquatic biota, ECCC derived wildlife dietary toxicity reference values (TRVs) using mammalian studies and avian chronic toxicity data. For mammals, the dietary value for PFOS was 4.6 µg/kg ww food while the avian dietary value was 8.2 µg/kg ww food. Based on the avian reproduction studies that were the basis for the dietary values, a guideline of 1.9 µg/g ww whole egg was also derived for PFOS.

Screening level assessment values have also been derived for PFOA (Environment Canada 2012). Environment Canada derived several predicted no-effect concentrations (PNECs) for PFOA for ecological species. PNECs are intentionally conservative concentrations of chemicals designed to represent a concentration at which no adverse effects are likely. These PNECs for PFOA were based on LOAEL values from a limited set of single organism toxicity studies adjusted with uncertainty factors. FEQG values are developed from a distribution of acute and chronic studies conducted on groups of organisms with an intent to be protective of a set percentage of organisms in that category (for example, a 95% protection threshold). Thus, these PFOA PNECs are not equivalent to FEQGs, though they still provide utility for screening level ERA. The PNEC for aquatic organisms, based on a study with the freshwater alga *Pseudokirchneriella subcapitata*, was 20 µg/L; a mammalian wildlife study based on cynomolgus monkey (*Macaca fascicularis*) derived a liver-based PNEC of 158 µg/kg ww. However, given the uncertainties associated with these values, care should be taken in their application to ERA. FEQGs for PFOA are currently under development by ECCC (ECCC 2018).

The Australian and the New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand (ANZECC/ARMCANZ) have established draft protective concentrations for freshwater organisms exposed to PFOS and PFOA. The values, as shown in Table 9-3, were developed by the Cooperative Research Centre for Contamination Assessment and Remediation of the Environment (CRC CARE) (2018). Only the freshwater values have been adopted in the PFAS National Environmental Management Plan (HEPA 2018) for Australia and New Zealand. Instead, the freshwater values have been identified as interim thresholds for marine waters. The values from CRC CARE incorporated multiple studies and were based on SSD for each compound. The 90 and 95% protective thresholds for PFOS are 2.0 and 0.13 µg/L, respectively. These values are within the range of other published values (Giesy et al. 2010; Qi et al. 2011). A 99% protection value for PFOS was also proposed as 0.00023 µg/L, though this may be below ambient concentrations. All three of the PFOS protection values are taken from an SSD that includes studies on the low end that are

well below the majority of other data points. Further, as indicated in table B3 of CRC CARE (2018), data used in the SSD include a mix of effect levels (EC10) and no-effect levels (NOECs). Thus, decisions based on these values should be made with careful consideration.

For PFOA, the 90 and 95% protective thresholds were 632 and 220 µg/L, respectively; these are similar to those derived in Minnesota and Michigan. Marine threshold values for PFOS were 32 and 7.8 µg/L for the 90 and 95% protective levels. For PFOA, the 90 and 95% protective thresholds were 8,500 and 14,000 µg/L, respectively. It is of note that the threshold values for marine species were at least 1-2 orders of magnitude greater than those from freshwater. Thus, one should take care in using freshwater toxicity data or threshold values when evaluating marine and brackish systems, given the apparent differences in species sensitivity between these two environments. Likewise, caution should be used if employing marine values to evaluate other PFAS for which there are no freshwater threshold values.

Table 9-3. Aquatic thresholds developed by CRC CARE (CRC CARE 2018)

Species Protection (%)	PFOS (µg/L)	PFOA (µg/L)
Freshwater		
80	31	1,824
90	2	632
95	0.13	220
99	0.00023	19
Marine		
80	130	22
90	32	14
95	7.8	8.5
99	0.29	3

A number of thresholds for PFOS are also available from the European Union (EU) as described in the Environmental Quality Standards Dossier (EQS) for PFOS (European Union 2011, 2013). These include maximum acceptable quality standards (MAC-EQS) for freshwater and marine ecosystems, and annual average quality standards (AA-EQS) for the same ecosystems. Standards are also available for secondary poisoning (that is, consideration of biomagnification through the consumption of contaminated prey). These values are shown in Table 9-4.

Table 9-4. Environmental quality standards (EQS) for PFOS

Category/Description	Units	Value
Proposed MAC-EQS (freshwater)	µg/L	36
Proposed MAC-EQS (marine)	µg/L	7.1
Pelagic Community AA-EQS (freshwater)	µg/L	0.23
Pelagic Community AA-EQS (marine)	µg/L	0.023
EQS_{biota, sec pois}	mg/kg (ww)	0.033
EQS_{biota, sec pois} (freshwater)	µg/L	0.002
EQS_{biota, sec pois} (freshwater)	µg/L	0.00047
MAC-EQS = maximum acceptable environmental quality standard AA-EQS = annual average environmental quality standard Biota, sec pois = secondary poison standard for concentration in fish tissue		

A survey of reports from various regulatory agencies demonstrates that although ecotoxicity data are available for various PFAS, including PFBA, PFBS, and fluorotelomers (including 8:2 FTCA, 8:2 FTUCA, and several FTOHs), to date these typically consider only a few aquatic species that include *D. magna*, a green alga, and perhaps a fish species. Regulations require a robust data set covering several classes of organisms, and due to limitations in the number of classes of organisms represented in the published peer reviewed data, it is difficult to derive ambient surface water quality criteria. Lack of relevant toxicity data is a greater issue for terrestrial wildlife given that the only chronic, reproductive studies that have been conducted to date are in two species, bobwhite quail and mallard duck, with PFOS and PFOA. No ecologically relevant studies have been conducted with mink or an adequate surrogate. As a result, the development of benchmark or threshold concentrations for wildlife and aquatic organisms has been slow and incorporates greater levels of uncertainty in their derivation.

Research on observed effects in benthic invertebrates for direct exposure to sediments contaminated with PFAS is limited. There are no published benchmarks and little published research. Research has focused more on aqueous exposure pathways. Observational data and monitoring have been used in some cases to develop an understanding of what exposure may be associated with effects. A sediment no-effect threshold of 220 µg/kg, a chronic toxicity range of 220–630 µg/kg, and an acute short-term effects range of 630–3,100 µg/kg were established (Bakke et al. 2010) Norwegian Pollution Control Agency NPCA . These sediment thresholds were reported for PFOS concentrations in marine sediments, though they provide some basis for screening level risk decisions for both marine and freshwater. Caution should be observed in using these values because associated effects, if any, are unclear, and the original work is not readily available. Caution should also be used in applying these NPCA sediment values from marine waters to freshwater because the freshwater organisms could be more exposed (as explained in Section 9.1.2) and either more or less sensitive than marine organisms. In its EQSD for PFOS, the European Union (2011) took the position that there is insufficient data available to confirm the need for a sediment quality standard and insufficient data to derive a threshold, thus electing not to develop a value. Similarly, a workgroup in northern Italy concluded that there was no need for a sediment environmental quality standard (EQS) for PFOA, PFBS, PFBA, and PFPeA and that data for a sediment EQS for PFHxA were insufficient (Valsecchi et al. 2017).

For soil, CRC CARE developed soil screening thresholds from SSDs for both PFOS and PFOA. The Canadian Council of Ministers of Environment (CCME 2018) have also developed several draft thresholds for PFOS in soil. A value protective of direct toxicity was developed from an SSD of plant and invertebrate IC25 values (the concentration at which a 25% reduction in a non-lethal biological measurement, such as growth or reproduction, occurs). Food chain models were used to develop values protective of soil and food ingestion by wildlife. CCME (2018) also developed a soil screening value protective of aquatic life for use at sites where off-site migration to nearby surface water bodies may be a concern. These values from CCME were issued draft for public comment, and final FEQGs have not yet been established. Soil threshold values for other PFAS, however, are limited.

9.2.1.2 Ecological Receptor Variability

A second major challenge with toxicity assessment for ERA is accounting for the large number of receptor types and the associated unknown variable sensitivity to PFAS. Although it is commonly understood that sensitivity to contaminants can vary widely across kingdoms or across classes of animals, the challenge for PFAS may be greater due to the lack of knowledge about this family of compounds. Studies have documented the presence of PFAS in various aquatic species since the 1950s (Danish EPA 2015; Giesy and Kannan 2001, 2002)), such as bottle-nosed dolphins (Houde et al. 2006), seals (Butt et al. 2008), squid (Yang et al. 2012), alligators (Bangma et al. 2017), and polar bears (Smithwick, Mabury, et al. 2005; Smithwick, Muir, et al. 2005; Greaves and Letcher 2013). The detection of PFAS within organisms is clear evidence of exposure. Unlike many other commonly detected contaminants, however, the availability of toxicological data for PFAS is limited relative to the broad range of organisms within which PFAS have been detected.

Standard ERA practice includes developing TRVs that consider measures of exposure and effects that could adversely impact populations of wildlife (for example, chronic studies on reproduction, growth, and survival). Mammalian studies on numerous sublethal endpoints (for example, systemic, immunological, developmental, respiratory, cardiovascular, gastrointestinal, ocular, hepatic) have been conducted for PFOS, PFOA, and other PFAS and are well described in the *Draft Toxicological Profile for Perfluoroalkyls* (ATSDR 2018e), but these are less commonly used for TRV development for ERAs. These sublethal, mostly systemic or organ function-based TRVs are really only used for ERAs in the absence of reproduction, survival, or growth data. Mammalian TRVs for the purposes of ERA can be developed for the majority of the Third Unregulated Contaminant Monitoring Rule (UCMR3) PFAS compounds listed in Section 8.2.2.2. Avian oral dosing studies useful for ERA are less available. The dietary acute and chronic studies by Newsted et al. (2005); Newsted et al. (2007) examining PFOS exposure in mallard (*A. platyrhynchos*) and bobwhite quail (*C. virginianus*) may be the only currently published work relevant

to ERA. Newsted et al. (2005) and Molina et al. (2006) have also reported the results of bird egg injection studies using PFOS, while Cassone et al. (2012) and Norden, Berger, and Engwall (2016) have published *in ovo* studies with other PFAS. A caution with interpreting these egg studies is the uncertainty as to whether naturally accumulated concentrations have the same adverse effect as concentrations administered via injection *in ovo*. There also can be differences when measuring whole egg, yolk, or albumin (Custer, Gray, and Custer 2010). Finally, there is currently not enough data for modeling egg tissue concentration for these chemicals.

Reptiles are among the least studied vertebrate taxa in ecotoxicology (Hopkins 2000; Weir, Suski and Salice 2010) despite contamination threatening reptile populations worldwide (Gibbons et al. 2000). To date, there are no published reptile toxicity data available for any PFAS, although studies have shown PFAS tissue concentrations from some reptile species (Wang, Zhang, et al. 2013; Bangma et al. 2017). Amphibian toxicity data are also lacking, with just one study on northern leopard frogs (*Rana pipiens*) (Ankley et al. 2004) and one on African clawed frogs (*Xenopus laevis*) (Palmer and Krueger 2001).

For lower trophic-level organisms such as plants and invertebrates, toxicological data are typically generated through studies with direct exposure to spiked media. Studies are available to develop thresholds for use in ERAs, as has been done by both ECCC (2018) and CRC CARE (2017a). Giesy et al. (2010) and ECCC (2018) generated PFOS SSDs for freshwater aquatic organisms, from which thresholds were derived. CRC CARE presented SSDs for PFOS and PFOA for marine waters and for soil to establish their thresholds. Giesy et al. (2010) noted that some guidelines for developing criteria from SSDs rely heavily on the four lowest effect concentrations; thus, results can be skewed if one genus or species is significantly more sensitive than others. In the freshwater SSD for PFOS generated by Giesy et al. (2010), *Chironomus tentans* (a species of midge) were 40 times more sensitive than the next most sensitive species, the fathead minnow (*Pimephales promelas*). However, the ECCC (2018) SSD does not show the same difference in sensitivity with a reported fish 14-day growth LOEC for Japanese rice fish (*Oryzias latipes*) below the *C. tentans* 10-day NOEC. For marine waters, fish are among the most sensitive organisms for both PFOS and PFOA as shown in SSDs (CRC CARE 2017a), but by just an order of magnitude or less. SSDs produced by CRC CARE (2017a) did not use any of the same data and showed lettuce to be more sensitive to PFOS than earthworms, but found the opposite occurred for PFOA.

SSDs have not been published for avian, mammalian, reptilian, or amphibian species. Although SSDs could possibly be generated for laboratory mammalian species, perhaps the most studied organisms for PFAS, there would not be a significant breadth of applicability to wildlife species. Mammalian SSDs would include mostly rat and mouse studies with a few monkey and rabbit studies. Extrapolation to other orders would be required, leaving an uncertainty. Existing data would be more conducive to an effects distribution because the number of species within the class of organisms would be so limited. Insufficient published data are available for a robust SSD or even an effects distribution for avian, reptilian, or amphibian animals.

Available toxicological data clearly do not adequately cover the range of organisms that are exposed to PFAS or within which PFAS have been detected. Nor does the data have much breadth for chemicals beyond PFOS and PFOA. Sensitivity variation for aquatic organisms is evident from the SSDs, and likely sensitivity ranges for untested wildlife leave a clear knowledge gap for some or even most ERAs. However, this problem is not unique to PFAS. As with many other bioaccumulative and biomagnifying compounds, this knowledge gap can be addressed by using available data from surrogate organisms (for example, the closest taxonomic laboratory test species) and making some assumptions. The uncertainty in the potential difference in sensitivity needs to be acknowledged and discussed within ERAs. However, pending the outcome of quantitative analysis, risk conclusions and even risk management decisions are possible on a site-specific basis. Although extrapolations with surrogates is a common practice in ERA, caution should be used and decisions should be made in concurrence with regulatory agencies or other applicable stakeholders.

9.2.1.3 Ecological Toxicity of Mixtures

A third major challenge in effects assessment for PFAS is considering the toxicity of mixtures. At this time there are only limited data available to sufficiently understand the toxicity of more than just a few chemicals with respect to direct toxicity to lower trophic level organisms or exposure to upper trophic level wildlife. Structural and physical properties could be used to relate the toxicity of unknown PFAS to those with known toxicity. Giesy et al. (2010) explored quantitative structure-activity relationships (QSARs) for PFAS with the following conclusions, "Although the analysis given above indicates that structure-activity relationships can be derived from existing data, there are still numerous data gaps that need to be addressed to quantify the toxicity of different classes of perfluorinated compounds and the relative susceptibility of aquatic organisms and plants. When such data are available it will be feasible to develop more sophisticated models to predict the

toxicity of fluorinated compounds to aquatic organisms.” There are a number of ongoing research projects investigating multiple PFAS (primarily the UCMR3 chemicals) and their precursors. However, the relative toxicity, additivity, or synergistic effects of PFAS are not fully understood and still uncertain.

9.2.2 Ecological Exposure Assessment

Detections of PFAS in tissues of top predators within both aquatic and terrestrial ecosystems (Section 6.5) points to ongoing exposure from bioaccumulative and possibly biomagnifying PFAS (Section 5.5.3). Thus, accuracy and realism within exposure and risk estimates for PFAS are important to making informed risk management decisions. With the challenges of accounting for multiple exposure pathways, building strong food web and ecological exposure pathway models is an important foundation of PFAS ERAs. Once completed, these models can be used to identify the key receptors and measures of exposure to complete the assessments.

For aquatic ecosystems, published data from laboratory studies and specific field sites are available that include both BCFs, BAFs, and biota-sediment accumulation factors (BSAFs). These values, some of which are discussed and presented in Section 5 and Table 5-1 (provided as a separate Excel file), can be used to model the measures of exposure for aquatic ecosystems. (Larson, Conder, and Arblaster 2018) used such data to conduct food chain modeling in four different avian receptors. Published values for fish are common; however, to date these values are not standardized in how they are reported (for example, wet versus dry weight; organic carbon or lipid normalization). Most importantly, these data are highly variant (Table 5-1); Environment Canada (2006) reported that field BAFs for PFOS in Canadian biota range from 6,300 to 125,000. Burkhard et al. (2012) reported that within published data sources (Giesy et al. 2010; Houde et al. 2006), laboratory and field bioaccumulation metrics usually do not agree. According to Burkhard et al. (2012), field-generated BAFs (wet weight tissue to field water plus some ingestion) for PFOS exceed BCFs (wet weight tissue to lab water) predicted in the laboratory. This is undoubtedly due to the inability or inaccuracy of laboratory models to account for both direct and food ingestion exposure pathways. LaRoe et al. (2017) pointed out that laboratory values include only accumulation across the gill membrane. Thus, ERAs are challenged with attempting to address both pathways. Larson, Conder, and Arblaster (2018) demonstrated that using environmentally relevant sediment concentrations with standard food chain models with both BSAFs and BAFs suggested sediment pathways may be underrepresented and studied. Although the combination of direct and ingestion pathways is primarily a challenge for aquatic systems, assessing risk to wildlife exposed to multiple media (for example, amphibians, semiaquatic wildlife) is also problematic.

In addition to fish, accumulation values for benthic organisms (California black worm, *Lumbriculus variegatus*, Higgins (Higgins et al. 2007) and (Lasier et al. 2011); oysters, *Ostrea edulis*, (Thompson et al. 2011) and pelagic invertebrates (*D. magna*, (Dai et al. 2013) have also been reported. Example BSAF values from Lasier et al. (2011) for PFOS, PFOA, PFNA, PFBS, and PFHpA are all fairly low, ranging from 7 to 49.

Data for terrestrial systems are limited to primarily plants (agricultural crops) and earthworms, with little available for vertebrate prey tissue. One exception is Müller et al. (2011), which published data for a soil-to-caribou-to-wolf BAF used by ECCC (2018) in establishing a soil threshold protective of terrestrial carnivores at 2.6 mg PFOS/kg soil. In nearly all cases, these BAFs and BSAFs are available only for PFOS, though the Lasier et al. (2011) study can be used to identify BSAFs for five of the six UCMR3 PFAS.

Caution should be used in applying any of the published bioaccumulation or biomagnification data for desktop exposure estimates that are in turn used to justify remedial action. Several factors and uncertainties are associated with performing desktop food chain modeling with the limited amount of published data. Some of these considerations include the following:

- differences in diets of receptors at investigation sites versus that of studies documented in the published literature: differences in the proportions of prey items; differences in the uptake and elimination rates of PFAS or overall bioaccumulation of PFAS by the prey
- differences in physiology between the site receptors and those in published literature: capacity and magnitude of transformation; metabolism and uptake and elimination rates of PFAS; the amount/composition of protein-containing tissues to which PFAS bind; species home range and migration
- differences in physiochemical properties of the abiotic media containing PFAS between investigation sites and published study sites: bioavailability and uptake of PFAS; environmental processes (photolysis, hydrolysis, microbial aerobic and anaerobic metabolism); the presence of precursors. There is not a sufficient set of bioaccumulation data to date to account for these variations. Such studies were part of the 2019 Statements of Need for Strategic Environmental Research and Development Program (SERDP) grant projects.

These uncertainties are not completely unique to PFAS, as there are many other contaminants for which risk assessments are performed. Though there is some uncertainty with desktop food chain models for PFAS based on abiotic media, quantitative modeling does not need to be avoided. Two conclusions should be reached through food chain modeling with abiotic media and literature based BAFs/BSAFs/BCFs: either concentrations at the site are sufficiently low such that it can be concluded that risk to the environment is negligible and acceptable or concentrations suggest further evaluation by either refined baseline problem formulation or a baseline ecological risk assessment (BERA). Conducting BERAs for sites with PFAS should not be substantially different from BERAs for sites with other chemicals. Either in situ or ex situ direct toxicity tests with representative organisms can and should be performed when exceeding the limited ecological risk thresholds that are available. Likewise, measured concentrations of PFAS in prey should be obtained if desktop food chain modeled exposure exceeds TRVs. But the biggest challenges for measuring PFAS in biota have to do with the unique analytical chemistry method issues (Section 11). Challenges such as selecting the correct biota to sample, matching the prey items to the diets of upper trophic level biota, or obtaining sufficient tissue volume for chemical analysis may exist, but these issues are not unique to PFAS investigations.

9.2.3 Risk Characterization

Some aquatic toxicity data (Table 7-1 provided as a separate Excel file) are available for environmental risk assessment for a few PFAS, but wildlife data are still incomplete. Adequate, though not abundant, data are available for completing wildlife risk assessment, primarily for PFOS. The ability to complete risk assessments for other PFAS regularly analyzed and detected in environmental investigations (Section 6) is limited. However, with the exposure data discussed in Section 5.5 and Section 6.5, and methods discussed in Section 9.2.2, the foundations of a quantitative risk characterization can be completed for PFOS and to an extent, PFOA. Risk assessment for other PFAS can be made with some conservative assumptions and use of PFOS data as a surrogate. Such risk characterizations using nonsite-specific abiotic media, surrogate information, and tools can form the basis of screening level assessments. These screening assessments can be used to make more informed decisions regarding the need for site-specific assessments, including the collection of site-specific tissue data. However, within these screening assessments, discussion of the uncertainties and data gaps and assumptions made should be included to inform the risk management decisions.

9.3 Uncertainty

In performing a site risk assessment, including information and a discussion regarding key factors of uncertainty in the risk characterization can be important. As noted by USEPA (1989), the source and degree of uncertainty associated with the risk characterization is needed to help decision makers (for example, risk managers, stakeholders), with sufficient level of detail to allow them to make informed risk management decisions (National Research Council 2009).

As noted throughout this guidance, while the science of characterizing and evaluating potential risks associated with PFAS exposure continues to develop, there are still uncertainties that arise in conducting site-specific risk assessments for sites with PFAS impacts. This section lists potentially critical uncertainties that, depending on the methodologies and assumptions used in a particular site-specific risk assessment, may warrant a discussion to help decision makers and stakeholders interpret and appropriately use the results of a risk assessment.

9.3.1 Fate and Transport

Site-specific risk assessments typically characterize risks associated with potential contaminant exposure that could occur currently or in the future. To characterize potential future exposures, conservative models are often used as tools to predict the fate and transport of chemicals in the environment. With regard to PFAS fate and transport, uncertainties can be introduced as follows:

- Estimating future environmental concentrations due to airborne wet and dry deposition (Section 5.3.2)
- Estimating the transformation of PFAA precursors to PFAA daughter end products (Section 5.4.2, Section 10.4.4) in the environment
- Modeling groundwater transport considering such factors as chemical-specific retardation (Section 10.4.1) and back-diffusion (Section 10.4.3.3)
- Estimating the bioaccumulation/bioconcentration of PFAS (Section 5.5.2, Section 9.2.1, Section 9.2.2) in a particular animal/plant or via food chain modeling

9.3.2 Human Toxicity

Human health risk assessments typically involve the use of toxicity values that are derived in a manner that is intended to represent a “reasonable conservative estimate” (USEPA 2012a) of the dose-response in humans. All of the toxicity values that have been derived by agencies for PFAS for use in site risk assessments are based upon animal studies with human studies used to support the hazard identification component of the risk assessment (Section 7.1.4). There is also a lack of toxicity values for many PFAS, which with their absence could result in an underestimate of the risks associated with PFAS exposure.

Overall, with regard to PFAS human toxicity, uncertainties in conducting a risk assessment can be introduced as follows:

- Missing dose-response information for site-related PFAS to which receptors could be exposed (Section 7.1, Section 9.1.1.2)
- Using toxicity values for a particular PFAS as a surrogate for another (Section 9.1.1.2)

9.3.3 Ecological Toxicity

As with human health risk assessments, ERAs often use TRVs that are generic and not site-specific. These generic TRVs are conservative by design because they are used for screening purposes (USEPA 2004). Likewise, there is a degree of conservatism incorporated into the derivation of generic criteria (for example, ambient water criteria) to account for uncertainty (Section 9.2.1).

Overall, with regard to PFAS ecological toxicity, uncertainties in conducting a risk assessment stem from using toxicological information from surrogate organism(s) to evaluate potential risks for organisms for which toxicity studies do not exist (Section 9.2.1)

9.3.4 Accounting for Nonsite-Related PFAS

Site-specific risk assessments rely on site characterization information (and as needed, modeling) to help estimate the amount of exposure receptors could be subject to currently or in the future. Given the widespread presence of PFAS in the environment (Section 6), including the potential of upgradient off-site PFAS impacts to migrate onto subject properties (Section 10.5), discerning “background” anthropogenic or off-site PFAS impacts at a site from site-related impacts can be challenging. To streamline risk assessments, it may be conservatively assumed initially that concentrations of PFAS are entirely site-related. Doing so, however, may overestimate the risks associated with site-related releases.

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10 Site Characterization

The PFAS Team developed a training module video with content related to this section, it is the Production, Uses, Sources, and Site Characterization video.

The intent of this section is not to present general site characterization principles, but to highlight unique considerations for this family of emerging contaminants. It is assumed that site characterization will follow all applicable state and federal (CERCLA or RCRA) guidelines. The general principles of site characterization are similar for PFAS as for any contaminant, in that the physical setting, release specifics, proximity to receptors, and fate and transport characteristics will determine the sampling locations and requirements. Because of the toxicity, persistence, mobility, ubiquity, the large number of compounds in this family of chemicals, the variability and uncertainty of specific compounds and their criteria being regulated, and the emerging nature of PFAS, it is necessary to consider specific concerns in PFAS site characterization efforts.

Section Number	Topic
10.1	Site Characterization Issues Relevant to PFAS
10.2	Initial Steps
10.3	Site Investigation
10.4	Data Analysis and Interpretation
10.5	Source Identification

Exposure to PFAS can occur through a variety of transport pathways involving all environmental media, as is described in Section 5. Because ingestion of water is deemed a major route of exposure in humans, and the emerging nature of PFAS as contaminants of concern, regulatory interest has in the past several years been centered on this pathway. In turn, this focus has led to an increased emphasis on investigation of the connection between drinking water sources and groundwater, including direct use of groundwater as drinking water and connections between surface water and groundwater. Because of this regulatory and investigatory focus, this section places more emphasis on characterization of groundwater plumes than characterization of other media. Although groundwater may have in the past been more commonly the initial regulatory and investigatory focus, regulatory focus is broadening to other media such as surface water and biota and as a site-specific characterization process advances data are generally required from one or more other media including soil, sediment, surface water, stormwater, air, biota, or other media depending upon the nature, duration, and time of the release.

The guidelines below include general considerations for the most common types of PFAS sites.

10.1 Site Characterization Issues Relevant to PFAS

Historical investigations may have missed the potential for PFAS contamination at a site because, until recently, these chemicals were not regulated, were not considered a health or environmental concern, or PFAS sampling and analytical procedures may not have been available. As a result, PFAS plumes had years to develop and migrate without detection or characterization. Comparing a site timeline (for example, processes, layout, chemical use, and release history, and fire training and/or firefighting events when AFFF was used) with the timeline of PFAS development and use, and existing drinking water data (for example, UCMR3) can be helpful in evaluating the types and potential occurrences of PFAS releases. Once a potential source has been identified, a site investigation would step out from the source to characterize the nature and distribution of the release. However, if a PFAS site is like one of the many without an identified source (ATSDR 2018e), an understanding of the site timeline or a general understanding of potential PFAS use may not be available. For sites without a known source release, the investigation approach starts with a review of available site information.

The following are some important considerations that are specific to PFAS sites.

10.1.1 Evolving Science and Regulations

State of the science: Understanding of many aspects of PFAS, such as toxicology and behavior in the environment, is changing rapidly. This may require reevaluation of earlier assumptions and conclusions throughout the site characterization process.

Analytical methodologies: Analytical methodologies continue to be developed and improved. Specific attention must be paid to a wide variety of factors, such as analytical methods, detection/reporting limits, and parameter lists that are continuing to expand. See Section 11.2, Analytical Methods/Techniques, for more details.

Sampling methodologies: Questions exist regarding cross-contamination potential due to the presence of PFAS in consumer products; many regulatory agencies require a precautionary approach to sampling prohibiting the use of materials that may be treated with PFAS. See Section 11.1, Sampling, for more details.

Regulatory environment: The regulatory environment remains in flux, with changing regulatory limits, sampling procedures, and compounds of interest. Investigators must remain vigilant to identify impacts to the site characterization. See Section 8, Basis of Regulations, for more details.

10.1.2 Source, Fate, and Transport Properties

Sources: PFAS sources are discussed in Section 2.6, PFAS Releases to the Environment and AFFF releases are discussed in more detail in Section 3.2 Mechanisms for Release to the Environment. There are also “secondary sources,” such as PFAS concentrating into one portion of a plume (for example, groundwater into surface water) that then acts as a source to further groundwater contamination.

Pathways: PFAS may be present or migrate via pathways that are not often encountered with other compounds. For example, PFAS may be present in groundwater at a site via air deposition and no direct on-site release.

Complex transitions between media: The behavior of PFAS in the environment may deviate greatly from typical contaminants. Transitions between media may be complex because of specific characteristics of these compounds. For example, PFAS may disperse more upon reaching the water table than is typical for most other compounds, or a groundwater plume discharging into a surface water body may infiltrate into groundwater elsewhere, with contamination in the surface water acting as a secondary source. See Sections 5 and 6 for additional detail.

Partitioning: Binding of PFAS to organic carbon is not as strong as traditional hydrophobic compounds (for example, PCBs, PAHs). So K_{oc} alone may be a poor predictor of binding of PFAS to organic carbon (Section 4.2.9). Because various factors can affect sorption of PFAS to organic carbon, published K_{oc} values for PFAS cover a very broad range. To properly understand the context of PFAS analytical results, it is often important to collect additional parameters, such as total organic carbon (TOC) and pH, and consider the partitioning behavior of specific compounds.

Secondary Sources

Sources created through movement of contaminated media into an area that was previously uncontaminated, (for example, contaminated water from irrigation wells or reuse and application of biosolids), or an area where physical or chemical processes have concentrated PFAS, resulting in an additional source (for example, multi-media interfaces; see Sections 5 and 6).

10.1.3 Other Considerations

Historical view: Historical investigations may not have assessed PFAS contamination because it was not regulated, not a potential contaminant of concern, or analytical methods were unavailable at the time. Plumes may be extensive, having years or decades to develop before being discovered or addressed.

Balancing priorities: Because drinking water is a major pathway of exposure for PFAS and established plumes may have spread to downgradient areas, priority might be given to managing drinking-water exposure pathways over site characterization.

Monitoring-point construction: Investigators must be mindful of ways that monitoring-point construction may influence sampling results. For example, historical wells might have employed fluoropolymer tape (Section 11.1.2), or have screened intervals that make data interpretation difficult (owing to the uneven distribution of PFAS throughout a water column).

Widespread use: Because use of PFAS-containing products is widespread, there may be multiple sources in a given area that may act as additional or alternative sources of PFAS at a site. In addition, PFAS is often detected in low levels in samples from locations without an obvious source; there may be a need to evaluate site-specific anthropogenic background to determine contributions in groundwater or soils that are not due to an on-site release. See, for example, Strynar et al. (2012).

Site-Specific Anthropogenic Background

Concentrations of PFAS present in environmental media at the site that are not the result of or influenced by site activities or releases.

PFAS suite: Selection of a broad suite of compounds may prove useful for applications such as fingerprinting (if multiple sources are suspected) or understanding potential effects of precursor degradation (Section 10.5). Note that with currently available analytical methods, even a broad compound suite will not detect all PFAS.

Geologic heterogeneity: Because of the low regulatory limits that are used for delineation of groundwater impacts and the mobile nature of certain PFAS, extra emphasis should be placed on understanding the effects of hydrogeologic heterogeneity on the groundwater plume.

10.2 Initial Steps

A comprehensive site preliminary assessment commonly starts with developing an understanding of potential PFAS uses in the area, history of the site operations that potentially used the chemicals, air deposition patterns where PFAS may have been produced or processed (for example, manufacturer with PFAS emissions), and the regional geologic and hydrologic framework as it relates to contaminant transport to surface waters or drinking water wells. Following the preliminary assessment, a series of site investigations may be required at a sufficient resolution to capture the effects of the heterogeneities that direct contaminant distribution, fate and transport, and remediation effectiveness. However, there may be a need to prioritize the evaluation of certain exposure pathways (for example, drinking water wells) during the beginning investigations to quickly assess potential human exposures and because of constraints on resources and schedule.

When historical PFAS releases occur upgradient of drinking water sources, drinking water sampling may be the first indication that there is a problem. In areas where there is a concern that a PFAS source may be present, it is common to identify and sample nearby drinking water sources (for example, groundwater and surface water) to determine if PFAS are present in potable water sources and evaluate the potential exposure to human receptors. This approach is a policy for the Department of Defense (USDOD 2014b). In cases where sources are not well defined, reconnaissance sampling may be useful to inform the development of the CSM and site investigation. In these instances, drinking water source sampling has preceded typical site investigation work. Prior to further site characterization, proper notification to consumers and evaluating options to reduce or eliminate PFAS exposures, including alternative drinking water sources, may be required.

10.2.1 Initial Conceptual Site Model

CSMs are useful tools for the presentation and evaluation of site characteristics, releases, contaminant fate and transport, and exposure pathways. Generalized CSMs are presented in Figures 9-1, 9-2, and 9-3. The CSMs present most known and potential PFAS source areas, transport mechanisms, and pathways on a simplified physical setting. The CSMs also illustrate exposure routes and receptors. CSM development is an iterative process over the project life cycle with information obtained during site investigation, remedy design, and remedy implementation and optimization. Similar to the USEPA's data quality objectives (DQOs), it relies on a systematic objectives-based site characterization process (ITRC 2015b). The CSM for a PFAS site is developed with information on PFAS sources and releases (whether occurring on site or off site from groundwater, surface water, sediment, or air), site characterization, pathways, and potential receptors.

Some specific challenges related to identifying the nature and extent of impacts for CSM development for PFAS sites are described in the following sections.

10.2.1.1 Surface Water Body Secondary Sources

Because certain PFAS are mobile and resistant to breakdown in the environment, there have been cases of surface water creating very large dilute groundwater plumes through recharge (ATSDR 2008). Infiltration of PFAS along the course of surface water systems, including tidal zones, may result in widespread secondary sources to groundwater, further enlarging

the contamination area. In situations where PFAS-contaminated surface water is recharging groundwater, investigation of the potentially impacted groundwater should be conducted to fully characterize site-related contamination. Complicating surface water being a secondary source is that PFAS have been shown to concentrate at the surface water-air interface (Ju et al. 2008). PFAS contamination may also concentrate in naturally occurring surface water foam (due to an affinity to organic material in the foam and the higher PFAS concentrations at the surface water-air interface where the foam is formed). Therefore, site characterization must consider whether or not surface water bodies are the most downgradient extent of contamination.

10.2.1.2 Receptor Identification

Identification of potential ecological and human receptors as part of development of the CSM first includes identification of potential exposure pathways (for example, PFAS migration in groundwater to downgradient drinking water wells, creating human exposure to PFAS; or water containing PFAS entering surface water bodies, creating aquatic life exposure to PFAS). See Section 9 for additional information on receptor identification in the context of risk-based evaluations for PFAS.

10.3 Site Investigation

10.3.1 Development of Site Investigation Work Plan

PFAS investigation work plans should take into consideration the information provided in this guidance document (for example, Sections 2, 4, 5, 6, 9, and 11), including items such as sampling procedures and equipment to prevent cross-contamination, analytical methods and compounds to be reported, geographically variable and changing regulatory requirements and criteria, and site-specific environmental setting. From a general perspective the work plan will depend on the type of PFAS source and subsequent transport via various media. Attention should be paid to potential upgradient or nearby sources and potential secondary sources from irrigation, sludge, or biosolid application, the use of soils not recognized to be contaminated, and other anthropogenic factors affecting fate and transport of PFAS-contaminated media, such as discharge from landfills or wastewater treatment plants (WWTPs).

10.3.1.1 Geologic and Hydrogeologic Investigation

Evaluation of the geologic and hydrogeologic framework associated with the site is critical, and sometimes that framework may need to be addressed on a regional basis, as the PFAS impacts may extend significant distances from the site.

In development of a work plan, consideration should be given to obtaining adequate information to allow for applying Environmental Sequence Stratigraphy (ESS) or a similar assessment. ESS is an emerging best practice for understanding the geologic framework and related subsurface contaminant transport pathways, both regionally and underlying a site. The ESS approach is presented in USEPA Groundwater Issue Paper “Best Practices for Environmental Site Management: A Practical Guide for Applying Environmental Sequence Stratigraphy to Improve Conceptual Site Models” (USEPA 2017c).

Geochemical parameters that may be pertinent to potential PFAS migration and possible remedies also require consideration during the investigation. The understanding of soil and groundwater chemistry at the site (parameters such as pH, TOC, redox) is needed to assess transformation and migration in groundwater or desorption from soil. These and other geochemical data can be used to assess the viability of PFAS remedy options should remediation be necessary. For example, the groundwater’s general chemistry, including cations, anions, total dissolved solids, and fouling parameters (for example, iron, manganese, hardness, biofoulants), as well as other organic compounds in groundwater, may have a significant impact on the selection, design, and implementation of potential groundwater remedies.

10.3.1.2 PFAS-Specific Tools for Site Screening or Characterization

Investigative techniques to characterize source soils and determine the three-dimensional extent of soil and groundwater contamination should be considered. High-resolution site characterization techniques beyond those that provide lithologic or hydrologic information and are *specific* to PFAS are currently limited because reliable analytical procedures that are cost-effective and can be used for field screening are not readily available. However, analytical procedures that can be used in a mobile laboratory and achieve ng/L detection limits are becoming available. Use of a mobile laboratory can be expensive and is cost-effective only in specific situations when a sufficient number of samples can be collected in a short time period to keep the mobile laboratory at or near its capacity. Use of a mobile laboratory and the quick turnaround of results they provide allow for adaptive selection of additional sampling locations for delineation or other objectives. One of the main drawbacks associated with current field-screening methods is the inconsistency of results related to varying soil types and compositions. Other field-screening methodologies have either been tried or are in the research and development phase,

including ion selective electrodes to quantify PFOS and a mobile field-screening unit for PFOS and PFAS, both of which are attempting quantification to ng/L levels (Deeb 2016). Another method in the development stage is a synergistic approach for the targeted affinity-based capture of PFOS using a porous sorbent probe that may be able to obtain a detection limit for PFOS in water at about 0.5 ng/L (Cheng et al. 2020).

10.3.2 Nature of PFAS Sources

The nature of primary and secondary PFAS sources at a site will largely determine the extent of PFAS contamination at the site. Multiple factors may contribute to the nature of PFAS sources at a site. Key factors related to secondary sources to consider in development of a work plan include:

- Leaching from the vadose zone to the saturated zone: PFAS present in unsaturated soils are subject to downward leaching during precipitation or irrigation events that promote desorption of soil-bound contaminant mass (Sepulvado et al. 2011; Ahrens and Bundshuh 2014; Milinovic et al. 2015).
- Back-diffusion: PFAS dissolved in groundwater that accumulated in lower permeability silt/clay layers below the water table may diffuse into the higher permeability zones due to changing relative concentrations (Section 5.3.1).
- Desorption: PFAS resulting from desorption from solids in the vadose or saturated zones and resolubilizing in porewater or groundwater could occur when adsorption (that is, partitioning) is reversible (Milinovic et al. 2015); such desorption would have the effect of sustaining PFAS concentrations in porewater or groundwater.
- Nonaqueous phase liquids (NAPL) dissolution: PFAS entrained in NAPL in the subsurface may be associated with releases of chlorinated solvents and/or petroleum hydrocarbons.
- Other sources: Given the widespread use of some PFAS, additional sources upgradient or within a plume may be contributing to PFAS concentrations at a site. Site-specific anthropogenic background may be a contributing factor.
- Atmospheric deposition: PFAS are sometimes associated with stack or other air-emission sources and may contribute to regional PFAS concentrations.
- Overland runoff: Runoff and stormwater conveyance systems can impact surface water locations downstream of the actual source or groundwater along the course of the conveyance system.
- Groundwater seepage into surface water or surface water seepage into groundwater: Groundwater elevations surrounding surface water bodies (that is, gaining or losing) may influence the extent of a plume. Seepage rates and directions may change seasonally, with extreme weather events, or during periods of drought or precipitation.
- Subsurface features, including utility lines: Preferential pathways may result from subsurface features. For example, flow may seep into or out of nonwatertight sewer lines based upon groundwater elevations relative to the utility. The bedding material of a subsurface line may also convey groundwater.
- Multicomponent mixtures: At some sites, numerous PFAS may be present in one or more source zones. Mixtures may be present for several reasons, including, but not limited to, the following: multiple sources, varying time frames, and a mixture of compounds introduced during production (Sections 5 and 10.5).
- Precursors: Delineating, as practicable, the extent of precursors that may degrade to PFASs and PFCAs will help the investigator understand sources and potential long-term concentrations.

10.3.3 Extent of PFAS

As with other constituents, a site investigation for PFAS relies upon understanding the extent of sources as well as the extent of contaminant transport. A PFAS release can be localized or highly extensive, both horizontally and vertically. PFAS may be highly mobile in groundwater. In addition, PFAS plumes may have had years to develop, as discussed above. Therefore, PFAS plumes may be larger than expected. At some sites, more mobile shorter chain PFAS have been observed to extend relatively farther in groundwater than longer chain PFAS due to less retardation in groundwater. The partitioning behavior of PFAS is discussed in Section 5.2.

Depending upon site-specific conditions, several pathways need to be considered to assess potential upgradient sources. PFAS migration in air from industrial or commercial sources can influence soil or groundwater a great distance from larger sources (Section 6.1) (for example, (Barton 2010) and (Shin et al. 2011)). Data from urban soils and groundwater indicate that for sites near metropolitan areas, there may be measurable contributions of PFAS from other sources, unrelated to site-specific sources, see the Site-specific anthropogenic background text box in Section 10.1.3 (Xiao et al. 2015).

Comingling of contaminants has a potential to impact PFAS extent. For example, for PFAS sites associated with industry, fire

training, or emergency response that have a chlorinated solvent or other NAPL source, investigators need to consider potential effects on PFAS in the subsurface and related data collection requirements. Laboratory studies have demonstrated that sorption or partitioning of perfluoroalkyl acids may increase in the presence of trichloroethene DNAPL in bench-scale tests (McKenzie et al. 2016). Conceptual modeling of published PFAS data suggests that NAPL-water partitioning and NAPL-water interface interactions may significantly increase retardation of some PFAS in source zones (Brusseau 2018). This research suggests that if PFAS and NAPL are present in media that make effective source treatment unlikely—for example, in low-permeability soils or fractured rock—that fraction will represent a long-term contributor to groundwater plume persistence. At older sites where in situ (for example, oxidation) or pump and treat methods have been employed to reduce NAPL source areas prior to awareness of PFAS, those remedies may complicate characterization and distribution of PFAS. Depending upon the method employed, mobilization of PFAS may have increased (oxidative) or decreased (reductive) following treatment, and remedial actions may affect distribution and relative concentrations of individual PFAS (McKenzie et al. 2016; McGuire et al. 2014).

10.4 Data Analysis and Interpretation

There are a number of approaches, methods, and tools available for analyzing and interpreting site characterization data from a wide range of contaminated sites. Examples of approaches, methods, and tools that may be relevant to PFAS sites are described below.

10.4.1 Retardation Coefficients and Travel Time

It may be helpful to estimate retardation coefficients for PFAS to evaluate contaminant-specific velocity and travel time in groundwater, particularly for longer PFAS plumes. As discussed in Section 5.2.3, a linear sorption isotherm is typically assumed for PFAS sorption to organic matter in soil, and sorption coefficients. The Physical and Chemical Properties Table (Table 4-1) provided as a separate Excel file presents a range of available organic carbon partitioning coefficients for environmentally relevant PFAS.

However, as noted in Section 5.2, while common PFAS appear to be appropriately defined by linear sorption relative to organic carbon concentration when sufficient organic carbon is present, the current state-of-science supports K_{oc} being reported in relatively broad ranges on a compound-specific basis. Section 4.2.9 presents a discussion of potential limitations in using K_{oc} values as a predictor of sorption and PFAS mobility. It is also important to note that other geochemical factors (for example, pH, presence of polyvalent cations, and electrostatic processes) may also impact PFAS sorption to solid phases (Section 5.2.3). Due to the uncertainty regarding K_{oc} , it may be appropriate to evaluate transport of an individual PFAS using a range of partitioning coefficients to account for uncertainties in this parameter. In addition, empirical estimation of site-specific K_{oc} values in different areas of a site (for example, source zone versus downgradient plume) may be necessary if quantification of the retardation coefficient is important to its characterization.

For example, McGuire et al. (2014) described the calculation of site-specific K_{oc} values for various PFCAs and PFSAs at an AFFF-impacted site. These site-specific K_{oc} values were calculated based on seven pairs of co-located groundwater and soil samples, and fraction of organic carbon (f_{oc}) measurements at each sampling location. The soil samples were collected near or at the water table, which was about 4.6–6.1 m below ground surface. McGuire et al. (2014) found that there was a range of between one and three orders of magnitude in site-specific K_{oc} values for the PFAAs analyzed. This may reflect the enhanced sorption of PFAS that occurs at the NAPL-water or air-water interface (Brusseau 2018). There may be smaller ranges in K_{oc} values for PFAAs at greater depths below the water table and downgradient of a source zone (where NAPL is not present). When using this type of site-specific K_{oc} analysis method, it is also important that the groundwater samples be representative of conditions where the point soil samples are collected.

As another alternative to the use of K_{oc} values and the assumption of a linear sorption isotherm, in situ or ex situ studies may be used to develop parameters for simulation of PFAS transport. Such studies could allow development of pseudo-constants to use in model simulations. For example, lysimeter studies were used to establish relative rates of transport of PFOA and shorter chained PFCAs, and PFSAs as compared with PFOS (Stahl et al. 2013).

Desorption of PFAS from solids in the vadose zone or below the water table could occur when partitioning is reversible; such desorption would have the effect of maintaining PFAS concentrations in porewater or groundwater. There is uncertainty regarding the extent to which sorption is irreversible and rate-limited versus an equilibrium process (Section 5.2.3). It may be important to characterize the extent and kinetics of desorption that may occur as a result of remedial activities at the

site.

10.4.2 Mass Flux/Mass Discharge

Note that it may be challenging to estimate the relative mass flux contribution of multiple sources at some sites due to the low PFAS concentrations present in groundwater. In addition, it is important to consider the potential for increases in dissolved mass flux of some PFAS due to biotransformation reactions or desorption between transects.

ITRC (2010) presented a variety of methods available for estimating mass flux and mass discharge, including the use of transects of temporary or permanent monitoring wells across the width of a plume. Even simple methods such as the use of chemical isoconcentration figures to estimate mass discharge may be applicable for an initial order of magnitude estimate. Calibration of solute transport models is another method that may be used to estimate the mass discharge of PFAS from a source zone or at a point in a plume.

10.4.3 Contributions from Different Sources

The potential impact to a site from multiple sources, particularly in proximity to urban or developed locations, needs to be accounted for when assessing site data or identifying data gaps. Each source then needs to be assessed in terms of its specific contributions, and their relative importance or magnitude. Although there are no naturally occurring background levels of PFAS, it may be important to gain an understanding of the Site-specific anthropogenic background (see the text box in Section 10.1.3) concentrations that may be present at a site, as these can have significant implications for site characterization, assessing exposures, evaluating ecological and human health risks, and establishing site action and cleanup levels. Most states have guidance on how to establish site-specific background concentrations for their regulated contaminants.

Tools available to quantify relevant contributions from different types of sources are discussed below.

10.4.3.1 Atmospheric Deposition

Certain PFAS may be present in ambient air and may be elevated near sources such as landfills, WWTPs, fire training facilities, and manufacturing plants (Section 2.6). Many PFAS exhibit relatively low volatility; however, airborne transport of some PFAS can be a relevant migration pathway for some industrial releases. Sections 5.3.2 and 6.1 provide an overview of transport of aerosols and particulates via air. To assess relative contributions from atmospheric sources, air sampling for PFAS can be conducted. Additionally, air dispersion models, such as AERMOD or Industrial Source Complex (ISC3) Model, can be employed to estimate airborne PFAS concentrations and total wet and dry deposition rates at designated receptor locations. Examples where AERMOD could be beneficial during site characterization activities include sites with no obvious source area and sites in industrial areas with multiple potential sources of airborne PFAS. See Section 2.6 for additional details on the most typical PFAS source scenarios.

10.4.3.2 Vadose Zone Percolation

Recent research has illuminated the complexities of PFAS fate and transport in the vadose zone. PFAS surfactant properties can enhance or reduce PFAS sorption, in particular at high concentrations such as those encountered at release locations (Sections 5.2.2.2 and 5.2.3). At lower concentrations the air-water interface may have important implications for vadose zone transport (Section 5.2.4). Therefore, model simulations of PFAS transport in the vadose zone should be performed with appropriate caveats.

Models such as USEPA's VLEACH and Seview's Seasonal Soil (SESOIL) compartment model can simulate one-dimensional vertical transport in the vadose zone via diffusion, adsorption, volatilization, biodegradation, cation exchange, and/or hydrolysis; however, these models do not include air-water interface interactions that may be important to the vadose zone migration of PFAS and these models have not been validated for use with PFAS. For these reasons, these models may not be appropriate for use with PFAS at this time. Most PFAS are resistant to biotic or abiotic degradation, and in general PFAS are far less volatile than many other contaminants. However, it is noted that certain PFAS are volatile, for example, the FTOHs (Section 4.2.3 and Table 4-1). With the exception of the few volatile PFAS, the most important vadose zone processes to model are the physical transport processes.

Analytical leaching methods such as Synthetic Precipitation Leaching Procedure (SPLP), USEPA Method 1312; Toxicity Characteristic Leaching Procedure (TCLP), USEPA Method 1311; Leaching Environmental Assessment Framework (LEAF); and others may provide insight into the leachability of PFAS from vadose zone materials. Care should be taken in selecting a method to assess PFAS leachability that is appropriate for the settings and parameters that are present and considers the

end use of the data.

Given the complexity of predicting the mass discharge from vadose soils to groundwater, along with modeling and leaching methods, direct measures of mass discharge, including the use of soil lysimeters, may be considered.

10.4.3.3 Back-Diffusion

When evaluating fate and transport of PFAS in a groundwater plume, including time frame for remediation of PFAS, matrix diffusion may be an important process to consider (Section 5.3.1). As such, the potential impacts of diffusion on PFAS persistence in natural soils are a topic of ongoing research. Diffusion coefficients for PFAS are generally uncertain but are in development using measurements and models (Pereira et al. 2014). During the characterization of PFAS plumes, it may be beneficial to collect PFAS soil samples from the transmissive zone directly above a silt/clay layer, and at different depths into the silt/clay layer, to evaluate the potential for back-diffusion to be occurring presently or in the future if there is a decline in PFAS concentrations in the transmissive zone (see Parker, Cherry, and Chapman (2004) and Chapman and Parker (2005) for an example of this sampling approach).

10.4.3.4 Upgradient Site Contributions

PFAS persistence in the environment and their use in a multitude of industrial processes and commercial products result in potential for nonsite-related inputs, similar to other mobile contaminants (Figures 9-1, 9-2 and 9-3). Assessment of potential upgradient site inputs is recommended. The very low health advisory criteria for groundwater only increase the potential importance of identifying what might otherwise be considered “minor” upgradient sources and may result in alternate source identification (Sections 10.3.2 and 10.5). As part of site investigation of an air deposition release, soil data can be statistically compared to background samples, evaluated for vertical stratification, and assessed for spatial distribution relative to the potential source. Groundwater data from the site may be compared to data from other locations using cluster analysis to assess whether there was evidence of other source terms, or if the site in question appeared to be the sole source.

Alternate Sources

Sources that may exist within, upgradient, or near a site under investigation, that are distinct from the PFAS source being investigated.

10.4.4 Transformation Pathways and Rates

As discussed in Section 5.4, the transformation of precursors may result in increasing concentrations of PFAAs such as PFOS and PFOA along the flow path of a dissolved plume. Transformation reactions may occur due to aerobic biological or chemical oxidation. For example, McGuire et al. (2014) concluded that infusion of dissolved oxygen to bioremediate hydrocarbons downgradient of a former burn pit also likely caused the transformation of precursor compounds to PFAAs such as PFHxS. Some methods that may be used to assess the degree to which transformation is affecting PFAS plume extent and stability include:

- plotting concentration isopleths for precursors and various PFAAs (for example, McGuire et al. (2014)
- use of the total oxidizable precursor (TOP) assay to identify whether precursors are present that may be available for transformation to PFAAs at a point in the plume (Section 11.2.2)
- assessment of ratios of precursor and daughter product species at monitoring wells situated along the centerline of a plume, or the ratio of various PFAAs in various portions of a plume. For example, McGuire et al. (2014) plotted an isopleth map for the ratio of PFHxS to PFOS to show that in areas where dissolved oxygen was injected this ratio was as high as 50, and in other areas where bioremediation was not conducted this ratio was less than 1.
- use of concentration trends along a plume centerline and quantitative methods described in USEPA (1998) to estimate precursor transformation rates
- groundwater modeling to demonstrate that the relative plume lengths of different PFAAs with different retardation coefficients can be explained only through the transformation of precursors (for example, McGuire et

al. (2014))

- a literature review to identify potential precursor transformation mechanisms and evaluate whether site geochemistry and redox conditions are favorable for the occurrence of these mechanisms.

Another method that may be used to illustrate the occurrence of these transformations is radial diagrams. See the case study in Section 15.1.1.

Figure 10-1 shows three radial diagrams based on data from an AFFF release site (McGuire et al. 2014). Each radial diagram compares groundwater concentrations at a monitoring well within the oxygen infusion zone to concentrations at a well approximately 76 m upgradient. The radial diagram shown at the left of Figure 10-1 compares concentrations for five PFCAs between these two wells; the middle diagram shows concentrations from the TOP assay conducted using samples from each well; and the radial diagram on the right compares concentrations for four PFSA's.

These radial diagrams illustrate that oxygen infusion into groundwater likely stimulated the production of mainly PFHxA, PFPeA, PFHxS, and PFBS. The middle radial diagram shows that the difference in TOP assay results between the upgradient well and the well in the oxygen infusion zone does not explain the large PFAAs concentration increases that were observed at the well in the oxygen infusion zone. The TOP assay results were low at both wells throughout the area. This suggests that desorption and subsequent transformation of precursors were occurring within the oxygen infusion zone. These radial diagrams are also useful for evaluating relative concentrations of various PFAAs at each monitoring well. The use of radial diagrams for additional types of trend analysis is discussed further in Section 10.4.7.

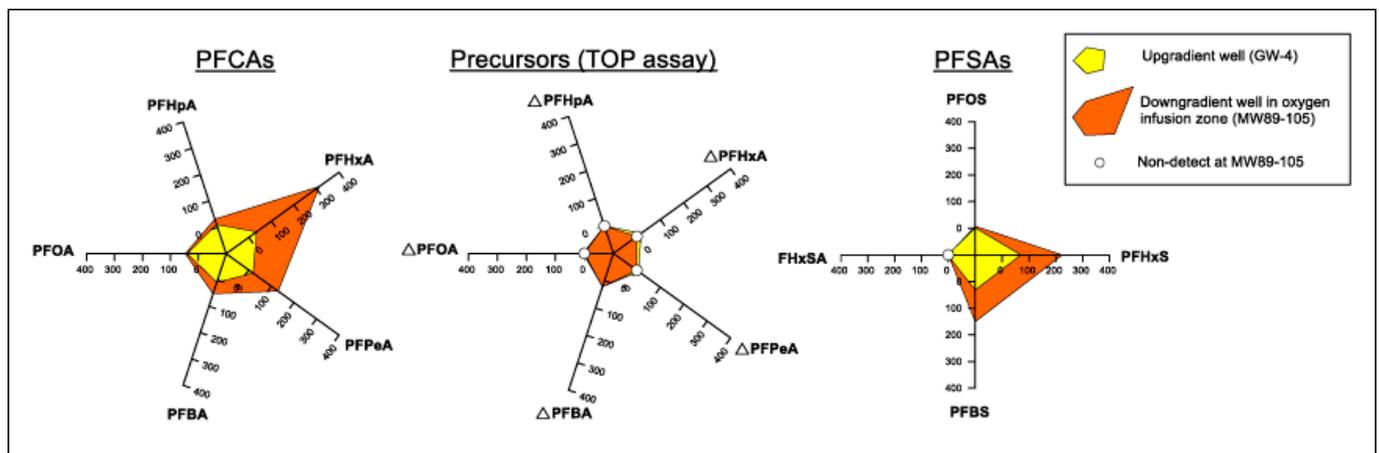


Figure 10-1. Radial diagrams showing the production of various PFAAs in the vicinity of an oxygen infusion zone at an AFFF release site remediated for hydrocarbons in groundwater.

Source: G. Carey, Porewater Solutions. Used with permission.

10.4.5 Assessing Plume Stability

In addition to evaluating potential transformations to PFAAs, it may be necessary to evaluate PFAS plume stability - whether the plume is stable, receding, or expanding. Many PFAS plumes are long-lived and mobile. Methods for evaluating plume stability include qualitative evaluations of temporal plume trends or statistical evaluations such as Mann-Kendall (ITRC 2013) (ITRC 2016; AFCEC 2012; USEPA 2009d).

Data uncertainties may have a greater than usual impact on plume stability evaluations because of the low concentrations assessed. Biotransformation of precursors may also have an impact on plume stability evaluations. As such, more frequent or longer duration monitoring may be required to confirm trends or plume stability.

10.4.6 Modeling PFAS Fate and Transport

Some modeling of PFAS fate and transport has been conducted recently (Barr 2017; Persson and Andersson 2016). Modeling the fate and transport of PFAS may have significant uncertainty contributed by precursor concentrations, transformation pathways, and biodegradation rates. In addition, desorption kinetics of PFAS are not currently well understood. Although modeling of PFAS transport may be appropriate under certain conditions, the uncertainty of PFAS transport simulations requires that the results be qualified. Site-specific data are important for evaluating some potential model input parameters such as K_{oc} , which can exhibit significant spatial variation. This is particularly true in source zones, the vadose zones, and at

or near the water table. There are situations where modeling of PFAS transport may not be appropriate due to a lack of site-specific input parameters.

10.4.7 Visualization Methods

One of the challenges associated with characterization of PFAS sites is the analysis of trends for a number of PFAS constituents that may be sampled in soil and groundwater, and then the communication of the results of these analyses to a less technical audience. Typical site characterization visualization methods such as plume maps, cross-sections, fence diagrams, 3D models may be used to depict the horizontal and vertical extent of PFAS plumes. Several other visualization methods may be helpful when analyzing PFAS data, including:

- bar charts that show the relative concentrations of individual PFAS constituents at each location to help evaluate PFAS composition trends in soil and groundwater (for example, figures 6 and 7 of 7 Field (2017), Figure 15-1)
- radial diagrams to illustrate:
 - transformations of precursors to PFCAs and/or PFSA's along a flow path (for example, see Section 15.1.1)
 - relative concentrations of constituents at each sample location to assist with source fingerprinting and to identify potential risk drivers in different parts of a plume
 - locations of potential hot spots
 - general extent of a PFAS plume.

Case study examples of these different methods are discussed in Section 15.1.

10.5 Source Identification

Source identification can be one of the challenges of PFAS investigations. Where records are available that document leaks, spills, and accidents, there may be a direct connection between sources and contaminant plumes. Where there are no documented releases, overlapping plumes, and/or known upgradient sources of PFAS contamination, multiple lines of evidence may be needed for source identification or distinguishing between two or more sources. As such, additional approaches for source identification or distinguishing between sources may be needed to connect releases to contaminated media. Source identification uses the evaluation of both typical and advanced chemical analyses to identify and differentiate among sources and age-date release events. Advanced techniques can include:

- chemical fingerprinting
- signature chemicals
- isotopic fingerprinting
- contaminant transport models
- molecular diagnostic ratios
- radionuclide dating
- microscopic analysis.

Although these techniques have limitations and are relatively new in application to PFAS, some of these tools have been used to identify regional and local PFAS sources. An overview of PFAS source identification analyses can be found in Dorrance, Kellogg, and Love (2017).

PFAS source identification should include all information regarding release mechanisms, as well as fate and transport mechanisms, as they are complementary and can cause environmental fractionation, which can influence chemical profiles. In addition, long-range wind-driven transport and deposition of some PFAS could be considered (Ahrens, Rakovic, et al. 2016; Davis et al. 2007).

Multiple lines of evidence are needed for reliable source identification because of the complexity of PFAS composition and source formulations, along with the potential for significant formation from precursors within a spill, which diminish the reliability of chemical fingerprinting. Additionally, information related to degradation expected based on case-specific conditions is needed for defensible chemical fingerprinting. With this being said, sources of PFAS could be deduced on a case-by-case basis, in particular when multiple independent lines of evidence are developed and as our knowledge related to fate and transport of different released commercial formulations improves. Library research, preliminary identification of potential PFAS sources, and information gathered from patents can assist in the identification of PFAS.

10.5.1 Source Identification Tools

Chemical fingerprinting involves the evaluation of the relative proportions of different substances in a mixture to link contaminants in the environment back to a specific on-site source or sources, an Alternate Source or Sources (see the text box in Section 10.4.3.4). The data from chemical analyses can be evaluated using various graphical, statistical, or geospatial techniques. These methods have been commonly used for petroleum and chlorinated compound source identification and can potentially be applied to PFAS, because the release of PFAS into the environment generally involves the release of a complex mixture of substances, including different subclasses of PFAS, as well as homologues and isomers of specific PFAS.

PFAAs are produced as a mixture of homologues of different chain lengths (Section 2.2). PFAAs produced by electrochemical fluorination contain both even and odd chain-length homologues. PFAAs produced by fluorotelomers contain mostly even chain-length homologues. Most commercial laboratories can report PFCA homologues ranging from C4 to C14 and select PFSA homologues between C4 and C12. USEPA (2009a) published PFCA profiles in various commercial products that showed different patterns of PFCA chain lengths. Chemical fingerprinting for source identification may be useful for PFAS sites; however, changes in raw materials and processes over time, as well as environmental fractionation, must be taken into account.

Examples of chemical fingerprinting for PFAS source identification can be found for wastewater treatment plants (Clara et al. 2008), differentiating AFFF sources (KEMI 2015a; Hatton, Holton, and DiGuseppi 2018) (Section 3), landfills (Lang et al. 2017; Xiao et al. 2012), surface water (Xie, Wang, et al. 2013), sediment (Qi et al. 2016), and groundwater (Yao et al. 2014). Multivariate statistical analyses (that is, principal components analysis (PCA), cluster analysis, unmixing models) and geospatial analysis have been used extensively to distinguish PFAS sources. Guelfo (2017) emphasized the importance of geospatial distribution of PFAS for source identification. Qi et al. (2016) used PCA–multiple linear regression, positive matrix factorization, and unmix models to identify four PFAS sources (textile treatment, fluoropolymer processing aid/fluororesin coating, textile treatment/metal plating, and precious metals). Zhang et al. (2016) used PCA, hierarchical clustering, and geospatial analysis to determine sources in the northeast United States, and Lu et al. (2017) used factor analysis to classify three categories of PFAS in impacted groundwater. Pan, Ying, Liu, et al. (2014) used PCA in water and sediment samples to distinguish between rural/agricultural and urban/industrial sources.

Evaluation of isomer profiles has been used to assess sources in multiple environments. PFAAs are generally identified as the straight-chain alkyl isomer. However, as discussed in Section 2.2, PFAA that are manufactured by electrochemical fluorination contain about 20–30% branched-chain isomers, while the fluorotelomerization process produces mainly straight-chain isomers (Prevedouros et al. 2006; Kissa 2001; Parsons et al. 2008). Laboratories generally report the concentration of a given PFAA as the total of the branched and linear forms; however, the concentration of the linear isomer and an estimated concentration for the branched isomers can be reported independently. The concentration of branched isomers must be estimated because standards do not yet exist for most branched-chain PFAA isomers (Section 11.2.1).

Benskin (2011) used the absence of branched PFCA isomers in dated sediment cores of two lakes to support the conclusion that oxidation of FTOH was the major atmospheric source of PFCAs in the lakes and not direct transport of PFOA. Fredriksson (2016) used isomer profiles along with homologue patterns to assess the sources of PFAS in avian eggs. The potential for environmental fractionation must be taken into account when evaluating isomer profiles because linear and branched-chain isomers have different physical and biological properties, adsorption, and bioaccumulation (Fredriksson 2016; Miralles-Marco and Harrad 2015). Other examples of isomer analysis for PFAS source identification include Shi et al. (2015), Benskin, DeSilva, and Martin (2010), and Karrman et al. (2011).

PFAS releases into the environment can include fluorinated substances that are not captured by current analytical methods and PFAS target analyte lists. Some of these substances are polyfluorinated and can be oxidized to form PFAAs that can be measured and reported. Such polyfluorinated substances are called “precursors.” The TOP assay, in which the samples are first oxidized and then analyzed for PFAAs, was developed to estimate the mass of these precursors. (See Section 11.2.2 for further information on the TOP assay). The results of PFAS analyses before and after oxidation can be used to generate a two-dimensional PFAS comparison and may be able to support source identification.

In practice, the TOP assay has a number of limitations, and the results are subject to interpretation. Although there is a published TOP procedure (Houtz and Sedlak 2012), each commercial laboratory has developed its own procedure and quality control steps, and these procedures have not been standardized, nor has interlaboratory validation been conducted. Comparability of TOP assay results between labs may not be possible and should proceed on a case-specific basis after careful review of the methods used and data validation. Another limitation is the potential for incomplete oxidation of precursors during the analysis in the presence of high levels of TOC or other compounds.

Quadrupole time-of-flight mass spectrometry (qTOF/MS) can be used to determine both the chemical formula and structure of unknown PFAS in a sample, but analytical standards are required for unequivocal structural identification (Newton et al. 2017; Moschet et al. 2017) (Barzen-Hanson et al. 2017). This method has the potential to greatly increase the number of identified PFAS and provide more accurate source identification.

Chiral fingerprinting through enantiospecific isomer differentiation is a potential method for source identification, although its use is still under development. Asher et al. (2012) applied this method to identify PFAS sources to an aquatic foodweb. However, they noted several limitations and assumptions when using this method for PFAS source identification.

10.5.2 Challenges and Reasonable Expectations

Factors of importance when considering the analysis of source identification of PFAS can include:

- *data quality*, where care must be taken to ensure that analytical results from different time periods, different methods, or different labs are comparable, as older data sets may provide incomplete information when compared to more recent data
- *target PFAS list*, where a reduced compound list may prevent full differentiation between sources. Linear versus branched (isomer) distinction may also be important.
- *temporal effect*, where an understanding of historical production, use, and release of PFAS becomes important, as is an understanding of differences between samples due to weathering processes that may be interpreted as different sources
- *spatial effect* of long-distance air deposition versus local sources
- *sample collection procedures* to ensure there is no cross-contamination from other sources during sampling
- *weight of evidence* based on multiple lines of inquiry.

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11 Sampling and Analytical Methods

The PFAS Team developed a training module video with content related to this section, it is the Sampling and Analysis video.

Due to the ubiquitous nature of the wide array of PFAS and the low parts per trillion screening levels, all aspects of a sampling and analysis protocol require a heightened level of rigor to avoid cross-contamination and achieve the level of accuracy and precision required to support defensible project decisions. This section focuses on providing the user with the appropriate tools and information to develop a site-specific sampling and analysis program to satisfy the project data quality objectives (DQOs). Accurate, representative data supports the development of a defensible CSM, and ultimately the final remedy.

Section Number	Topic
11.1	Sampling
11.2	Analytical Methods and Techniques
11.3	Data Evaluation

Information on sample collection for PFAS is sparse, with only a handful of guidance documents available for a practitioner to reference. Further, as there are limited peer-reviewed studies (Denly et al. 2019; Rodowa et al. 2020) on the potential for cross-contamination from commonly used sampling materials, most of these guidance documents default to a conservative approach in implementing measures and controls for prevention of cross-contamination (for example, washing cotton shirts with no fabric softener prior to use in the field). Although the actual methods of sample collection are similar to those used for other chemical compounds, there are several considerations for the practitioner when establishing a sampling program for PFAS. This includes selection of proper personal protective equipment (PPE), documentation of protocols for sample handling and decontamination procedures, use of nonbiasing material (for example, tubing, sample bottles, pumps) that could come into contact with the sample, and implementation of quality assurance/quality control (QA/QC) protocols to meet project DQOs, among other considerations. This section will give practitioners the tools needed to prepare a sampling program that adequately addresses project-specific DQOs and limits, to the extent practicable, potential cross-contamination and sources of potential bias.

Additionally, analytical methods are still evolving for PFAS analysis with several in development. Currently, only two USEPA methods are validated and published for the analysis of PFAS: USEPA Method 537.1, Version 2.0 (Shoemaker and Tettenhorst 2020) (which replaced USEPA Method 537.1, and USEPA Method 537 Version 1.1) and USEPA Method 533 (USEPA 2019f). These methods are applicable only to finished drinking waters. As a result, laboratories offering modified methods to analyze other media such as nonpotable water, groundwater, soil, sediment, air, and biota in the absence of published methods. These modifications are not specified in USEPA 537.1 or 533, resulting in variations from laboratory to laboratory and potentially inconsistent data. Because the quantification of PFAS within these media is key to completing a full site characterization, there is a demand for published methods that can accommodate the unique characteristics of each of these matrices and the changing complexity of the PFAS chemistry (our understanding of which continues to evolve). This section provides the essential PFAS-specific elements to understand and implement an analytical program using the USEPA 537.1 and 533 methodologies and touches on the various other qualitative techniques and procedures available to practitioners to meet DQOs and support the development of a defensible CSM.

This section will be updated as new information on sampling considerations and analytical methods/procedures becomes available.

11.1 Sampling

11.1.1 General

Sampling conducted to determine PFAS concentrations in water, soil, sediment, air, biota, and other media is similar to that

for other chemical compounds, but with several additional specific considerations and protocols. Typical guidance and procedures, such as ASTM International D 4823-95 and D 4448-01, USEPA compendium EPA 540/P-87/001a and OSWER 9355.0-14, USEPA SESDPROC-513-R2, and USEPA SESDPROC-305-R3, remain the basis for a PFAS sampling protocol. Examples of special considerations for PFAS sampling include the types of sampling equipment or materials used due to the widespread uses for and products containing PFAS; field and equipment blanks above and beyond what is normally required; the need for low laboratory quantitation limits; low state and federal screening levels, and in some cases, cleanup criteria; potential for background sources of PFAS in the environment; and the need for additional decontamination measures.

Examples of program-specific PFAS sampling protocols include:

- USEPA (2015b) Region 4, Science and Ecosystems Support Division, Athens, GA, *Field Equipment Cleaning and Decontamination at the FEC*, SESDPROC-206-R3, 2015
- Transport Canada (2017) *Per- and Polyfluoroalkyl Substances (PFAS) Field Sampling Guidance*
- Government of Western Australia (2016) *Interim Guideline on the Assessment and Management of Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS)*
- USDOD EDQW (2017) Environmental Data Quality Workgroup, *Bottle Selection and other Sampling Considerations When Sampling for Per- and Poly-Fluoroalkyl Substances (PFAS)*
- State guidance:
 - MA DEP (2018b) Massachusetts Department of Environmental Protection, *Interim Guidance on Sampling and Analysis for PFAS at Disposal Sites Regulated under the Massachusetts Contingency Plan*.
 - Washington Department of Ecology (2016) *Quality Assurance Project Plan; Statewide Survey of Per- and Poly-fluoroalkyl Substances in Washington State Rivers and Lakes*.
 - NH DES (2019b) New Hampshire Department of Environmental Services, *Laboratory Testing Guidelines for Per- and Polyfluoroalkyl Substances (PFAS) at Waste Sites, 2019*

A comprehensive project-specific quality assurance project plan (QAPP) should be created to address PFAS-specific considerations. If a QAPP is not created for a project, the sampling and quality assurance and quality control elements outlined in Section 11.1.6 should be included in site-specific work plans. If regulatory procedures, methods, or guidelines are inconsistent with the needs of a PFAS sampling program, the governing agency should be contacted directly to determine if an exception can be made or an alternate approach is needed. A CSM should be completed as part of the QAPP, including information on previous site uses, PFAS use/manufacturing/handling practices, other possible contaminants and their uses, and/or related remediation activities (for example, granular activated carbon (GAC), in situ treatments, or dig and haul) to determine all possible source areas of PFAS. Because PFAS is not typically analyzed along with other parameters at traditional remediation sites, and analytical methods are only recently becoming standardized, previous or ongoing remediation of other contaminants of concern can add a layer of complexity to a site's geochemistry and the fate and transport of PFAS.

Although some sampling elements (for example, sample bottle, preservation, and hold times) relating to drinking water sampling are defined by USEPA 537.1 and 533, they do not provide all information that is needed to conduct a sampling event for PFAS. Because USEPA methodologies are still evolving for all other media, there currently is no USEPA published information relating to media other than drinking water. As a result, consultants and laboratories have derived their own requirements and protocols for these media, so they have yet to be standardized. It is important that the laboratory/consultant selected has demonstrated the quality assurances (for example, sample hold time/preservation studies, proficiency testing, and laboratory accreditation) necessary to providing credible results from their sampling/analysis requirements and protocols. The USEPA is currently working on guidance for sampling/analysis of PFAS in nonpotable water and solids.

Communication with the laboratory before, during, and after sampling is conducted is critical in ensuring that project needs are met. If a sample is from an area known or suspected to be highly contaminated with PFAS, it is important that this is communicated to the laboratory. Chain of custody should indicate samples that potentially contain a high concentration of PFAS. The laboratory should screen all samples to select the necessary sample preparation procedures and to avoid contamination of their laboratory equipment and contamination of other field samples.

Any water used for field sample blanks (for example, field and decontamination blanks) should be supplied by the laboratory performing the analysis. The laboratory should provide documentation verifying that the supplied water is PFAS-free. "PFAS-free" is the project-defined concentration that associated blank concentrations must be below (for example, less than the

detection limit or less than half the limit of quantitation (LOQ)) to ensure an unacceptable bias is not introduced into the sampling and analysis processes. The QAPP should clearly state the project's definition of PFAS-free. Review of the laboratory's standard definition of "PFAS-free" upfront is necessary to ensure that it meets project needs and is a critical step in laboratory selection for a project. Documentation of verification of PFAS-free water used in sampling should be required to be maintained for data validation purposes.

11.1.2 Equipment and Supplies

Many materials used in environmental sampling can potentially contain PFAS. There is limited published research or guidance on how certain materials used by field staff or in sampling equipment affect sample results (see Denly et al. 2019; Rodowa et al. 2020). However, a conservative approach is recommended to exclude materials known to contain the PFAS that are the target of the analysis from a sampling regimen, and such an approach should be documented accordingly in the QAPP. Obtain and review all Safety Data Sheets (SDSs) before considering materials for use during PFAS sampling, as product manufacturing formulations can change over time. If PFAS are listed on the SDS, it is recommended that piece of equipment/supply not be utilized. Exclusion from the SDS does not necessarily mean the equipment/supply is not contaminated with PFAS. PFAS could have been used not as a component of the equipment/supply, but as a material used in the manufacturing process itself (for example, mist suppressant or mold coating). This can result in the equipment/supply manufactured containing PFAS. If necessary, materials in question can be sampled and analyzed for PFAS, or thorough decontamination and collection of equipment blanks can provide sufficient quality assurances. Ultimately, a sampling program should produce defensible data, and the best way to protect the integrity of samples is to ensure they are not compromised by contaminants originating from sampling equipment or otherwise.

Due to the ubiquitous nature of PFAS, sampling crews must review all materials and sampling protocols to avoid contamination and possible adsorption issues. Materials that may come into contact with samples and therefore could potentially introduce bias include, but are not limited to:

- Teflon, polytetrafluoroethylene (PTFE)
- waterproof coatings containing PFAS
- fluorinated ethylene-propylene (FEP)
- ethylene tetrafluoroethylene (ETFE)
- low-density polyethylene (LDPE)
- polyvinylidene fluoride (PVDF)
- pipe thread compounds and tape.

A conservative PFAS sampling program may additionally restrict materials that are allowed on the sampling personnel or in the staging area. A tiered approach is used for materials restrictions in that case, where the first tier would include restrictions on the sampling materials that will come in direct contact with the sample media, and the second tier would include restrictions on what materials are allowed on sampling personnel or within the staging area.

Examples of published guidance documents identify materials and equipment that can be used in PFAS-focused investigations, as well as materials that should be avoided because they are known or suspected to be potential sources of PFAS are:

- *Bottle Selection and other Sampling Considerations When Sampling for Per- and Poly-Fluoroalkyl Substances (PFAS)* (USDOD EDQW 2017)
- *Interim Guideline on the Assessment and Management of Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS), Contaminated Sites Guidelines*, (Government of Western Australia 2017)
- *Wastewater PFAS Sampling Guidance*, 10/2018 (Michigan Department of Environmental Quality 2018b)
- *General PFAS Sampling Guidance*, 10/2018 (Michigan Department of Environmental Quality 2018a)

Sometimes it is impossible or financially infeasible to eliminate materials that affect PFAS results in samples. For example, these materials might be needed at sites where hazards warrant the use of specific PPE such as Tyvek suits, where PFAS are the secondary or co-contaminant and the primary contaminant requires specific materials for proper sampling, or where the opportunity to collect a sample occurs before a proper sampling program is developed. At PFAS sites where co-contaminants are not a factor, the same PPE is required as at traditional sampling sites (a minimum of nitrile gloves and safety glasses).

11.1.3 Bottle Selection

Sample container recommendations are dependent on the analytical method and should be supplied by the laboratory and laboratory-verified to be PFAS-free, as defined by the QAPP. USEPA 537.1 requires the use of 250 mL polypropylene containers and caps/lids for drinking water sampling; USEPA 533 also requires polypropylene containers and caps/lids but the bottle can be 100-250 mL. Currently, USEPA has not issued guidance or analytical methods for any sample media other than drinking water, but nonpotable water methods guidance is expected to be published in the near future. Depending on the analytical method used or program (for example, state or DOD) requirements, polypropylene or high-density polyethylene (HDPE) bottles with unlined plastic caps are typically used (USDOD EDQW 2017).

Whole Sample Versus Aliquot

Because the concentration level of PFAS in aqueous samples determines whether the whole sample or an aliquot is used in the laboratory preparation, the sampler should collect an additional volume of each sample in a separate container. Then the laboratory can screen the extra sample for high concentrations without affecting the final sample result. For soil or sediment, obtaining a representative subsample in the laboratory is critical, so the entire sample should be homogenized in the laboratory prior to subsampling. Coordinating with the laboratory is crucial to determine the appropriate sample container volumes for environmental media other than drinking water.

Best practices in sample preparation must be used when selecting the size, volume, and representativeness of samples. To minimize effects from analyte sorption on sample containers, the laboratory must analyze the entire sample, including the sample container rinsate (USEPA 537.1 and 533). The project screening or applicable regulatory levels and the expected or potential concentration of the analytes are also relevant. If the sample is known to contain high concentrations (ppm range) of PFAS (for example, AFFF formulations), loss due to adsorption onto the sample container is negligible and therefore the entire sample does not need to be used.

11.1.4 Sample Preservation, Shipping, Storage, and Hold Times

USEPA 537.1 and 533 contain specific requirements for drinking water sample preservation, shipping, storage, and holding times (Shoemaker and Tettenhorst 2020; USEPA 2019f). Currently, there is no USEPA guidance or requirement for other sample media. The USEPA has indicated that draft guidance covering nonpotable water sampling methods will be published in the near future. Until additional information is available, the thermal preservation, shipping, storage, and holding times contained in USEPA 537.1 or 533 should be used for all other sample media except biota. Biota samples (for example, vegetation, fish) should be frozen to limit microbial growth until sample preparation is performed at the laboratory. Microbial growth may result in PFAAs values biased high due to biodegradation of precursor compounds; however, these effects have not been well studied. Note that the chemical preservation required by USEPA Method 537.1, TRIS (Trizma), and USEPA Method 533, ammonium acetate, is added for buffering and free chlorine removal and is applicable to drinking water samples only.

USEPA 537.1 Requirements

- Samples must be chemically preserved with TRIS (Trizma).
- Samples must be chilled during shipment and not exceed 10°C during the first 48 hours after collection.
- When received by the laboratory, samples must be at or below 10°C and stored in the laboratory at or below 6°C until extraction.
- Samples must be extracted within 14 days of collection.

11.1.5 Decontamination Procedures

Sampling equipment should be thoroughly decontaminated before mobilization to each investigation area and between sample locations at each investigation area or as required in the site-specific QAPP. Field sampling equipment, including oil/water interface meters, water level indicators, nondisposable bailers, and other nondedicated equipment used at each sample location requires cleaning between uses. The SDSs of detergents or soaps used in decontamination procedures should be reviewed to ensure fluorosurfactants are not listed as ingredients. Use laboratory-verified PFAS-free water for the final rinse during decontamination of sampling equipment. Decontaminate larger equipment (for example, drill rigs and large downhole drilling and sampling equipment) with potable water using a high-pressure washer or steam. To the extent

practical, rinse parts of equipment coming in direct contact with samples with PFAS-free water. Heavy equipment is best cleaned within a decontamination facility or other means of containment (for example, a bermed, lined pad and sump, or a portable, self-contained decontamination booth). Potable water sources should be analyzed in advance for PFAS, as well as during the sampling event. Wherever possible, rinse equipment with PFAS-free water immediately before use.

An example decontamination procedure is as follows.

- Equipment caked with drill cuttings, soil, or other material will initially be scraped or brushed. The scrapings will be sampled, containerized, and appropriately disposed.
- Equipment will then be sprayed with potable water using a high-pressure washer.
- Washed equipment will then be rinsed with PFAS-free water.
- Decontaminated downhole equipment (for example, drill pipe, drive casing, bits, tools, bailers, etc.) will be placed on clean plastic sheeting (PFAS-free) to prevent contact with contaminated soil and allowed to air dry. If equipment is not used immediately, it will be covered or wrapped in plastic sheeting to minimize airborne contamination.
- Field sampling equipment and other downhole equipment used multiple times at each sample location will require cleaning between uses utilizing a four-stage decontamination process. The equipment will first be rinsed in a bucket containing a mixture of potable water and PFAS-free soap. The equipment will then be rinsed in each of two buckets of clean potable water. Water used for the final rinse during decontamination of sampling equipment will be laboratory-verified PFAS-free water.

Decontamination solutions should be replenished between sampling locations as needed. Spent decontamination fluids should be containerized, properly labeled, and appropriately disposed of according to the investigation-derived waste (IDW) plans addressed in the site-specific QAPP. Heavy machinery or motors should be inspected daily for leaks or problems that may result in an inadvertent release at an investigation area.

11.1.6 Field QC Samples

Field QC samples are a means of assessing quality from the point of collection. Such field QC samples typically include field reagent blanks, source blanks, equipment rinse blanks, and sample duplicates. Collection and analysis of field QC samples are important for PFAS investigations because of very low detection limits and regulatory criteria (ppt), to ensure accuracy and representativeness of the results to the sampled media, and to assess potential cross-contamination due to the ubiquitous nature of PFAS. A sampling program should be designed to prevent cross-contamination and anthropogenic influence. However, the widespread commercial use (historical and current) of PFAS-containing products, and especially their prevalence in commonly used sampling materials and PPE, should inform the sampling program. PFAS sites may also have a wide range of concentrations with varying families of PFAS, as well as co-contaminants. Furthermore, PFAS sites have the potential to be high profile in nature. Therefore, a comprehensive site-specific QAPP addressing DQOs and field QC samples, including frequency, criteria, and procedures, is vital to a PFAS sampling program (see also Section 11.3, Data Evaluation).

When planning QA/QC sample frequency, the risk of cross-contamination should be considered. Cross-contamination can occur from several sources, including field conditions, ineffective decontamination, incidental contact with PFAS-containing materials, and sampling equipment and materials that were manufactured alongside PFAS-containing equipment.

USEPA 537.1 and 533 contain specific requirements for the field QC samples that must accompany drinking water samples to be analyzed for PFAS. These include a minimum of one field reagent blank for each set of samples per site and field duplicates. USEPA specifies the frequency of the field duplicate in terms of extraction batch (one per extraction batch, not to exceed 20 field samples), not collection frequency. Although USEPA methods are not yet available, media other than drinking water also warrant field QC samples, with discussion and rationale provided in the following sections. Table 11-1 provides a list of field QC samples typical to these methods and their typical minimum frequency. Once field QC sample data are obtained, they should be evaluated against the field samples by a person knowledgeable on the DQOs set forth in the site-specific QAPP. For laboratory QC considerations, see Section 11.2, Analytical Methods/Techniques.

Table 11-1. Typical field QC samples

QC Sample	Description	Minimum Suggested Frequency
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QC Sample	Description	Minimum Suggested Frequency
Field reagent blank (field blank)	Laboratory-provided reagent water that, in the field, is poured into an empty sample bottle or a sample bottle containing only preservative (if required)	One per day per matrix per sample set
Source water blank	Water collected from potable water source that is utilized during the sampling processes (such as decontamination and drilling processes)	One per site, preferably prior to sampling event (if possible) and at least once during sampling event
Equipment rinse blank (decontamination blank)	Final rinse of nondedicated sampling equipment with laboratory-verified PFAS-free water	One per day per type of sampling equipment used for each day of sampling and each matrix sampled
Field duplicate	Two samples collected at the same time and location under identical circumstances	One per day per matrix up to 20 samples
Performance evaluation (PE) sample	A sample containing known concentrations of project analytes	One per project per matrix

11.1.6.1 Field Reagent Blank

A field reagent blank (FRB), described in the USEPA 537.1 and 533 for collection of drinking water samples, consists of a sample bottle filled with reagent water and preservatives (same as those used for the samples) in the laboratory, sealed, and shipped to the sampling site along with the sample bottles. An empty sample bottle containing only preservatives (same as those used for the samples) is also shipped along with each FRB into which the sampler pours the preserved reagent water and seals and labels the bottle for shipment along with the samples back to the laboratory for analysis. This ensures that PFAS were not introduced into the samples during sample collection/handling. A laboratory reagent blank is also analyzed in a laboratory setting to ensure the reagent water meets USEPA 537.1 and 533.

Field blanks may also be warranted during collection of sampling media other than finished drinking water. In lieu of using a prepared quantity of laboratory reagent water/preservative solution as for drinking water FRB, a field blank can be prepared in the field using laboratory-verified PFAS-free water (may be equivalent to the laboratory reagent water) and filling an empty sample container in the field, which is then sealed and labeled as a field blank. This sample will be analyzed in the same manner as the normal samples and can indicate whether or not PFAS were introduced during sample collection/handling, and help to account for additional factors, such as introduction of contaminated air particulate.

As discussed above, the frequency of FRB samples for finished drinking water sampling is one FRB for every sample set at each site. A sample set is described in USEPA 537.1 and 533 as “samples collected from the same sample site and at the same time” (Shoemaker and Tettenhorst 2020; USEPA 2019f).

11.1.6.2 Source Water Blank

Large quantities of water may be necessary to carry out a field sampling program for various reasons, including decontamination and certain drilling techniques (Section 11.1.5, Decontamination Procedures). For equipment that may come into contact with samples of any media type, a multistep process is common to adequately prevent cross-contamination. Quantities of laboratory-verified PFAS-free water are generally limited and can be costly. Therefore, potable water sources are typically used in initial decontamination steps. It is imperative that these water sources be sampled and analyzed the same as normal samples prior to and even during a PFAS sampling program to ensure that source water is not contributing to PFAS detections in normal samples.

Collect a sample from the source the same way it is collected for use (for example, if the source water is collected through a hose, collect the source water blank from that same hose). If there are unnecessary fittings or hoses attached for collection of the source water, consider removing them for the duration of the sampling program to avoid contamination of PFAS that may be present in their materials.

Frequency of collection of source water blanks is up to the professional judgment of the project manager, site owner, and other stakeholders. The source water should be sampled at least once prior to starting the field sampling program and once during the sampling event in case the analysis reveals that a different water source must be found. A more conservative

sampling program may include provisions for additional periodic sampling and/or in cases where the conditions of the source water change.

11.1.6.3 Equipment Rinse Blank

Field equipment rinse blanks (ERBs) are those collected by rinsing a piece of field sampling equipment/supplies with laboratory-verified PFAS-free water and collecting the rinse water in a sample container for PFAS analysis. ERB collection is not required by the USEPA 537.1 or 533 and is dependent on the sampling media and methods that are employed at a site. Generally, any equipment that is reused throughout the sampling program, or nondedicated, and must be decontaminated, should have an ERB collected from it. That is, if a piece of equipment is decontaminated, an ERB should be collected from it prior to its next use. Collection of ERBs can be avoided by using all dedicated or disposable equipment where possible. However, many of these options are limited due to the ubiquitous nature of PFAS compounds in many of these equipment materials.

Equipment Rinse Blanks (ERBs)

ERBs can be collected from equipment or supplies prior to the sampling event in cases where PFAS content is unknown or suspected or to verify the cleanliness of nondedicated equipment/supplies (Section 11.1.2).

Field ERB collection frequency is largely up to the professional judgment of the project manager or other stakeholders and is dependent on the sampling media and methods. For instance, ERBs collected from decontaminated soil sampling trowels may only warrant a frequency of once per day, whereas ERBs collected from groundwater pumps may warrant an ERB prior to being deployed down each well due to their more rigorous decontamination procedure and higher contact time with the groundwater being sampled.

11.1.6.4 Field Duplicate

Field duplicate (FD) samples are two samples collected at the same time and location under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analysis from these identical samples helps evaluate the precision of sample collection, preservation, storage, and laboratory methods.

USEPA 537.1 and 533 do not specify the frequency of FD collection for finished drinking water samples; however, they do specify the frequency of preparation (once per extraction batch, not to exceed 20 field samples). A more conservative sampling program may indicate a frequency of one FD per 10 field samples. FD collection frequency should be discussed with stakeholders as necessary and be evaluated as part of the comprehensive site-specific QAPP.

11.1.6.5 Performance Evaluation Sample

A PE sample contains project analytes with known concentrations of PFAS. This sample can be submitted to the laboratory as a single- or double-blind sample. Analysis from this sample provides a positive control from a second source.

11.1.6.6 Additional QA/QC Samples

Quality assurance replicate samples are defined here as co-located samples, taken at the same time and each sent to a different laboratory. These types of samples may not be required in all sampling events. Aqueous QA samples should not be split into two samples from the original container. Analysis from these QA samples provides a measure of interlaboratory variability.

Trip spike samples are laboratory-spiked matrices that are included in the sampling kit sent to the field. These are used to evaluate desorption efficacy of the analytical extraction.

11.1.7 Sampling Procedure

Standard sampling procedures can be used at most PFAS sites. However, there may be some exceptions and additional considerations related to PFAS behavior and issues associated with potential use of PFAS-containing or -adsorbing sampling equipment and supplies, as previously discussed. A site-specific QAPP should contain the standard operating procedures incorporating these considerations and client requirements. Refer to Section 11.1.2 for materials to avoid during sampling and drilling. Consult the supplier to determine if PFAS-free options are available.

Pretesting any equipment or supplies to be utilized is recommended. The analysis of field reagent blanks may also provide useful information for equipment that cannot be pretested. ERBs are recommended to ensure supplies such as bailers, beakers, and dippers are PFAS-free and that decontamination is effective.

11.1.7.1 Drinking Water/Non-Drinking Water Supplies

Sampling a “potable water source,” as defined by the USEPA SDWA (Section 1401(4), August 1998), is conducted according to protocol established in the USEPA Methods 537.1 and 533. This protocol defines sample bottle preparation, sample collection, field reagent blanks, sample shipment and storage, and sample and extraction holding times. The drinking water source is further defined here as a public drinking water supply, as opposed to a private drinking water supply, as it applies to the USEPA 537.1 and 533. The following summarizes the sampling considerations described in this protocol:

- For Method 537.1: Sample bottle is a laboratory-provided 250-mL polypropylene bottle fitted with a polypropylene screw cap. For finished (treated) drinking water sampling only, a preservation agent is provided inside each bottle prior to sample collection. This agent acts as a buffer (TRIS pH 7, 5 g/L) and removes free chlorine from chlorine-treated drinking water supplies.
- For Method 533: Sample bottle is a laboratory-provided 100-250-mL polypropylene bottle fitted with a polypropylene screw cap. For finished (treated) drinking water sampling only, a preservation agent is provided inside each bottle prior to sample collection. This agent acts as a buffer (ammonium acetate, 1 g/L) and removes free chlorine from chlorine-treated drinking water supplies.
- The sample handler must avoid PFAS contamination during sampling by thoroughly washing their hands and wearing nitrile gloves.
- Open the tap and flush the water (approximately 3-5 minutes) to obtain a “fresh” sample. Collect the sample while water is flowing, taking care not to flush out preservative. Samples do not need to be headspace-free. Cap the bottle and, if applicable, shake to completely dissolve preservative.
- Keep sample sealed and place sample on ice for shipment.
- Samples must be chilled during shipment and must not exceed 10°C during shipment.
- Laboratory extraction of the sample must take place within 14 days hold time.

Based on a review of industry experience and guidance, additional considerations for collecting drinking water samples for PFAS analysis are as follows.

- Ideally, the sample should be collected from a tap or spigot located at or near the well head or pump house and before the water supply is introduced into any storage tanks or treatment units. If the sample must be collected at a point in the water line beyond a tank, a sufficient volume of water should be purged to provide a complete exchange of fresh water into the tank and the tap or spigot. If the sample is collected from a tap or spigot located just before a storage tank, spigots located downstream of the tank should be turned on to prevent any backflow from the tank to the tap or spigot. Several spigots may be opened to provide for a rapid exchange of water.
- The sample port for a private water supply well will be opened and allowed to flush for at least 15 minutes, when possible. When sampling from a drinking water well that is not in regular use, purge water until water quality parameters (that is, pH, specific conductance, dissolved oxygen, oxidation-reduction potential, turbidity, and temperature) have stabilized, to ensure formation water (as opposed to stagnant well column water) will be sampled. An adequate purge is achieved when the pH and specific conductance of the potable water have stabilized (for example, within 10% across three consecutive measurements) and the turbidity has either stabilized or is below 10 nephelometric turbidity units. Note: According to USEPA (2013d), pg. 21 “[a] well with an intermittently run pump should, in all respects, be treated like a well without a pump. In these cases, parameters are measured and the well is sampled from the pump discharge after parameter conditions have been met. Generally, under these conditions, 15 to 30 minutes will be adequate.”
- When sampling from a tap, the tap must be protected from exterior contamination associated with being too close to a sink bottom or to the ground. Contaminated water or soil from the faucet exterior may enter the bottle during the collection procedure because it is difficult to place a bottle under a low tap without grazing the neck interior against the outside faucet surface. If the tap is obstructed in such a way that prevents direct collection into the appropriate sample container, it is acceptable to use a smaller container to transfer sample to a larger container. The smaller container should be made of HDPE or polypropylene and should be either new or decontaminated as specified in Section 11.1.5. Evaluation of the transfer container is recommended to ensure that it does not introduce a bias.

- When filling any sample container, care should be taken that splashing drops of water from the ground or sink do not enter either the bottle or cap.
- Leaking taps that allow water to discharge from around the valve stem handle and down the outside of the faucet, or taps in which water tends to run up on the outside of the lip, are to be avoided as sampling locations.
- Disconnect any hoses, filters, or aerators attached to the tap before sampling. These devices can harbor a bacterial population if they are not routinely cleaned or replaced when worn or cracked, and may contain PFAS.

Taps where the water flow is not constant should be avoided because temporary fluctuation in line pressure may cause clumps of microbial growth that are lodged in a pipe section or faucet connection to break loose. A smooth flowing water stream at moderate pressure without splashing should be used. The sample should be collected without changing the water flow.

11.1.7.2 Groundwater

Groundwater PFAS sampling protocols are the same as those for drinking water sampling as discussed above with the following exceptions and/or additional considerations.

- Nonpotable water does not require a chemical preservative. Clean laboratory-provided HDPE or polypropylene bottles are recommended; typically 125 mL to 1L are used.
- Groundwater is typically sampled from a well, and therefore additional equipment is required. Purging and sampling equipment is constructed from a variety of materials. As a result, there are more opportunities for contamination of the sample due to the sampling equipment. For example, pumps, bailers, and stopcocks can contain O-rings and gaskets that may be Teflon, or another fluoropolymer, that can be changed out. The most inert material (for example, stainless steel, silicone and HDPE), with respect to known or anticipated contaminants in the well(s), should be used whenever possible. The various types of purging and sampling equipment available for groundwater sampling are described in ASTM International *Standard Guide for Sampling Ground-Water Monitoring Wells*, D 4448-01 (ASTM 2007) or *Compendium of Superfund Field Operations Methods* (USEPA 1987).
- Do not use dedicated sampling equipment installed in existing wells prior to the PFAS investigation without identifying all materials found within the equipment and reviewing their chemical properties to ensure they are PFAS free. Pumps can be a source of PFAS contamination due to internal components (for example, bladder pumps that contain Teflon components that can be switched out for HDPE). Consult with the equipment vendor to determine if they have PFAS-free alternatives. For circumstances that warrant, such as very deep wells or sites with co-contaminants, samples may be collected in duplicate with and without existing dedicated equipment. If PFAS analyses show that the equipment does not impact results, the equipment may be kept and used long term. However, this determination is dependent upon project-specific requirements and should be allowed by a project manager only with full disclosure to all stakeholders. It may also be acceptable to simply collect an ERB after fully decontaminating equipment containing PFAS components to confirm it does not contribute to groundwater sample concentrations. A site-specific procedure should be outlined in the QAPP.
- In addition to equipment, ensure tubing and bailing twine are PFAS-free.
- Within the context of sample collection objectives outlined in a site-specific QAPP, the sample location in the water column should consider the potential stratification of PFAS in solution and their tendency to accumulate at the air/water interface. For more information on stratification, see Section 5.2.
- Do not filter the sample, as filtration may be a source for contamination (Ahrens L 2009; Arp and Goss 2009) or PFAS may be adsorbed to the filter. If filtration is absolutely necessary, it should be performed in the laboratory, using a validated procedure that includes steps to eliminate the bias that can occur due to sorption issues. As an alternative, laboratory-validated procedures may include centrifuging the sample due to potential filter sorption or contamination issues.

In cases where co-contaminants require use of PFAS materials, sampling events should be separated to avoid contamination from these materials. The PFAS sampling event would be completed first, followed by the sampling event for the co-contaminants. In some cases, it may be acceptable to use the same equipment and concurrent sampling event.

11.1.7.3 Surface Water

Surface water PFAS sampling is conducted in accordance with the traditional methods such as those described in the USEPA's *Compendium of Superfund Field Operations Methods* (USEPA 1987) with the following exceptions and/or additional considerations.

- Within the context of sample collection objectives outlined in a site-specific QAPP, the sample location in the water column should consider the potential stratification of PFAS in solution and their tendency to accumulate at the air/water interface. For more information on stratification, see Section 5.2. If possible, the transfer container will be lowered sufficiently below the water surface but above the bottom sediments.
- Transfer containers, such as beakers or dippers, which may be attached to extension rods, should be used if sample containers have preservatives. Sampling by direct sample container immersion is not recommended.

11.1.7.4 Porewater

Similar in many ways to sampling techniques and equipment used in groundwater sampling for PFAS, porewater purging and sampling involves a variety of materials. The various types of purging and sampling equipment available for porewater sampling are described in *Pore Water Sampling Operating Procedure* (USEPA 2013c). For PFAS sampling, peristaltic pumps with silicon and HDPE tubing are typically used for porewater sample collection, along with push point samplers, porewater observation devices (PODs), or drive point piezometers. Push point samplers and drive point piezometers are made of stainless steel, while PODs consist of slotted PVC pipe and silicon tubing. PODs and drive point piezometers are permanent, or dedicated, sample points typically installed and used for multiple sample events, whereas push point samplers are used for a temporary sampling location. Otherwise, the standard procedure for porewater purging and sampling using a peristaltic pump, as described in the *Compendium of Superfund Field Operations Methods* (USEPA 1987), can be followed.

11.1.7.5 Sediment

Most core and grab sampling devices are constructed of stainless steel. Some core samplers include an HDPE sleeve inserted in the core barrel to retain the sample. Ensure that materials that contact the media to be sampled do not have water-resistant coatings that contain PFAS that are the target of the analysis. Additional PPE may be required for sampling personnel, such as waders and personal flotation devices. Ensure that materials that will potentially contact sampling media do not consist of water-resistant coatings or other PFAS-containing materials or substances. Refer to Section 11.1.2 for typical materials used during sampling and drilling.

11.1.7.6 Surface Soil

For surface soil sampling, refer to Sections 11.1.2 and 11.1.5 for equipment and supplies and decontamination procedures. No additional considerations are recommended for PFAS sampling of surface soil.

11.1.7.7 Subsurface Soil

No additional considerations are recommended for PFAS sampling of subsurface soil.

11.1.7.8 Fish

The species of fish collected, as well as the portion of fish sampled (whole versus fillet), depends on the project goals (for example, ecological risk or human health). Studies have shown that the majority of the PFAS in fish are stored in the organs, not the flesh (Martin et al. 2004) (Yamada et al. 2014). Communicating project objectives to the laboratory is important prior to fieldwork to determine the necessary quantity and quality of tissue, fish handling requirements, laboratory sample preparation (including single fish or composite fish samples, and whole or fillet preparation), and packing and shipping requirements. Fish or other biota samples should be wrapped in HDPE or polypropylene bags.

11.1.7.9 Air Emissions and Ambient Air

Currently, there are no multilaboratory-validated, published sampling methods for PFAS in air emissions (for example, from thermal treatment in manufacturing plants or incinerators). In their absence, sampling and analysis have been performed using modifications of existing USEPA methods. For example, stack testing has been performed in a few states (New Hampshire, New Jersey) using a modified USEPA Method 5 sampling train.

There are currently no USEPA Federal Reference Methods (FRM) or Toxic Organic Methods (TO series) available specifically for the measurement of PFAS compounds in ambient air. In their absence, some sampling and analysis of ambient air has been performed using modified TO methods, such as TO-13A and TO-9. Both of these methods make use of high-volume air samplers fitted with both a particulate filter glass fiber filter/quartz fiber filter (GFF/QFF) and sorbent cartridge for the collection of particulate and gaseous phases, respectively. USEPA TO-13A specifies collection of air samples at a flow rate of approximately 225 liters/minute, resulting in an air volume greater than 300 m³. The solid sorbent used consists of a “sandwich” of polyurethane foam (PUF) and XAD-2 (polymer of styrene divinyl benzene).

PFAS in ambient air have been measured using both active (with actual flow) and passive (gas diffusion) sampling techniques. The majority of techniques have made use of solid sorbents such as PUF, XAD-2, and sorbent-impregnated PUF (SIP). (Finely ground XAD-4 resin is often the sorbent of choice for impregnating the PUF). Active samples also include a particulate filter (glass or quartz fiber) ahead of the sorbent module. To optimize detection limits, high-volume air samples have been used most often.

Detection limits of air and emissions methods can be greatly influenced by PFAS artifacts found in the neat filter, sorbent media, or components within the sampler itself. For example, use of Teflon gaskets in high-volume samplers is not recommended. Field sampling programs must include collection of field blanks as a means of assessing PFAS artifacts present in sampling media and potentially introduced during sample handling in the field. Other quality control measures that should be considered include collection of duplicate or co-located samples and the use of isotopically labeled PFAS. The latter compounds are typically applied/spiked by the laboratory into the sorbent media prior to field deployment. These compounds serve to assess analyte ("native PFAS in air") collection efficiency, breakthrough, and the accuracy of the combined sample collection and analysis method on a sample-specific basis.

Passive samplers should also make use of mass-labeled PFAS as a sample-specific quality control measure to account for native PFAS losses during each sampling event. Volatilization of labeled PFAS during the deployment period provides sampling rates on a site-specific basis and accounts for both temperature and wind influences.

USEPA and European groups (Verein Deutscher Ingenieure [VDI], association of German engineers) are currently evaluating and investigating which sampling methods might be, in principle, the most suitable to capture PFAS and resulting byproducts in all fractions of the emissions (particles, moisture, gas phase). An important consideration is that fluorinated polymers are used in common sampling equipment, which may cause contamination of the samples. For the purposes of PFAS determinations, this material must be replaced.

Stack Emissions

Stationary source, or stack, emissions of PFAS have been measured in North Carolina (NC DEQ 2019a) and New Hampshire (NH DES 2019a) from industrial facilities that synthesized (Chemours, NC) or conducted manufacturing utilizing (Saint-Gobain, NH) PFAS. These test programs confirmed that stack emissions from industrial facilities contribute to ground and surface water contamination (NC DEQ 2019b). As in the case of ambient air measurements, no USEPA FRMs are available specifically for the measurement of PFAS from stationary sources. In these tests PFAS were measured using USEPA SW846 Method 0010 (*Modified EPA Method 5 Sampling Train*) (USEPA 1986), a method designed for measurement of semivolatile organic compounds.

PFAS can be partitioned in stack emissions into several different fractions due to the physical properties of these species. At the elevated temperatures typically encountered in stack emissions the vapor pressure can be sufficiently high that some is present in the gas phase. The lower molecular weight fluorotelomer alcohols (FTOHs) have lower boiling points and so may primarily be present as vapors. PFAS can adsorb to particulate matter, are highly water soluble, and can dissolve in water droplets if present in the stack. To measure these partitioned fractions, the stack effluent is sampled isokinetically (that is, the air enters the probe at the same velocity as it is moving in the stack, to accurately sample particles and droplets) and captured on a heated filter, an XAD-2 sorbent resin tube, and in water impingers. In some test programs a second XAD-2 sorbent cartridge is included in the sample train to determine if breakthrough has occurred. The filter, sorbent cartridge, and water impingers are recovered separately, and the sample train components are rinsed with a methanol/ammonium hydroxide solution.

The four fractions (filter, sorbent, water, and rinse) are extracted as defined in SW846 Method 3542 (*Extraction of Semivolatile Analytes Collected Using SW-846 Test Method 0010*) (USEPA 1996b) and analyzed by a modified version of USEPA Method 537 (Shoemaker and Tettenhorst 2018) utilizing isotope dilution. The more volatile (boiling point < 100°C) PFAS can be sampled by modified USEPA Method 18 (*Measurement of Gaseous Organic Compound Emissions by Gas Chromatography*) (USEPA 2017f), in which the analytes are captured in chilled methanol impingers.

The USEPA Office of Research and Development has been evaluating alternate sampling and analysis approaches for PFAS air emissions (USEPA 2019j). According to the USEPA's *Per- and Polyfluoroalkyl Substances (PFAS) Action Plan* (2/19) (USEPA 2019h), a method for sampling and analyzing PFAS in factory stack air emissions is anticipated in 2020. USEPA has been participating in the testing at Saint-Gobain (NH) and Chemours (NC) by either evaluating alternate sampling methods or performing independent analysis of the stack test samples. As stated in the Action Plan pg. 51, USEPA is "testing and

developing additional methods for possible refinement, including methods to quantify PFAS precursors; Total Organic Fluorine for a general PFAS detection method; and refinement of non-targeted high-resolution mass spectrometry approaches for suspect screening and novel PFAS discovery."

To date, test reports from ten stack tests conducted at Chemours have been published on the North Carolina Department of Environmental Quality website (NC DEQ 2019a). One stack test report from the Saint-Gobain facility has been published on the New Hampshire Department of Environmental Services website (NH DES 2019a). These test reports detail the sampling and analysis methodologies used thus far in measuring PFAS stack emissions.

11.1.7.10 Human Blood, Serum, Tissue

Currently, there is no official or standard method for testing blood, serum, or tissue. Laboratories and the Centers for Disease Control and Prevention (CDC) are in the process of developing best methods. A procedure developed by the CDC's National Center for Environmental Health has been published (CDC 2016). There are also several laboratories advertising this capability; however, the analytical methods and modifications from validated environmental laboratory protocols will not be consistent between these vendors. Human testing is outside the scope of this document; however reference points that could be used for comparison of whole blood or serum results to geometric mean serum levels generated from the U.S. population are included in the ATSDR ToxGuide for Perfluoroalkyls (ATSDR 2018c).

11.1.7.11 Potential High Concentration Samples

The CSM or previous sampling may indicate areas of high concentrations of PFAS for which single-use, disposable equipment is recommended. If single-use is not possible, take additional precautions such as implementing a greater frequency of ERBs and not reusing equipment to sample potentially low PFAS concentration samples. High concentration samples should be segregated during shipping to the laboratory, and clearly identified on the *Sample Chain of Custody*.

Some projects may require the analysis of AFFF product that has been used at the site. All AFFF product samples must be considered high concentration samples. These samples should be segregated from other samples during sampling and shipping to avoid cross-contamination. Notify the laboratory in advance, if possible, to expect serial dilutions so that practical quantitation limits can be met for high concentration samples. High concentration samples should be segregated during shipping to the laboratory, and clearly identified on the *Sample Chain of Custody*. When alerted to potential high concentration samples, the laboratory will complete an initial screen of the sample and proceed with a serial dilution of the sample as necessary.

11.1.7.12 Field Test Kits

Field test kits are available for PFAS but have not been fully evaluated. Although these kits cannot achieve low detection limits, they could be helpful in screening for potential high concentrations of PFAS in the field.

11.2 Analytical Methods/Techniques

11.2.1 Quantitative

11.2.1.1 General

Analytical methods are still evolving for PFAS analysis. Currently, very few methods are multilaboratory-validated and published. Two multilaboratory-validated methods, USEPA 537.1 and USEPA Method 533 have been published for analysis of finished drinking water samples (Shoemaker and Tettenhorst 2020; USEPA 2019f).

- Method 537.1 tests for 18 PFAS analytes (12 PFAAs and 6 other PFAS, including HFPO-DA (a GenX process chemical)). In this method surrogates are added prior to solid-phase extraction (SPE) to assess for analyte loss due to sample preparation. Internal standards are added to the final sample extract to assess instrument performance.
- Method 533 tests for 25 PFAS analytes (16 PFAAs and 9 other PFAS, including HFPO-DA (a GenX process chemical) and ADONA).

Other methods have been published for media other than finished drinking water. Lists of these methods by various categories are provided in external tables (Excel spreadsheet).

- External Table 11-2–Published Method Basics. Provides information on basic principles of each method (media

type, validation status, method type, sample container requirements, holding time, preservation requirements, and analytical instrument.

- External Table 11-3–Published Methods Specifics. Provides more details of the methods such as sample preparation requirements, quantitation scheme, confirmation requirements, quantitation limits, and isomer profile.
- External Table 11-4–Analyte Lists. The method analyte list for each of these methods varies.
- External Table 11-5–Draft Published Methods

Currently, the DOD's *Quality Systems Manual (QSM) for Environmental Laboratories*, Version 5.3, Appendix B, table B-15 (USDOD 2019) provides the most current and comprehensive set of quality standards for PFAS analysis. These performance-based standards outline specific quality processes for sample preparation, instrument calibration, and analysis when working with PFAS. The USDOD (2019), QSM Version 5.3, Appendix B, table B-15 criteria currently require isotope dilution quantitation of PFAS. The isotope dilution method accounts for interferences caused by complex sample matrices and bias introduced by sample preparation and instrument issues.

Significant improvements in the trace level analysis of PFAS in environmental and biological matrices can be attributed to the availability of good chemical standards and their mass-labeled internal standards. There is a need for well-characterized and high-purity branched isomeric standards for the accurate measurement of branched and linear PFAS isomers. Additionally, innovations and availability of instrumentation and laboratory supplies that help to eliminate background contamination are being sought. Such advances include the availability of polyetherketone (PEEK) tubing for solvent lines and use of an additional column to delay the contamination peaks due to impurities in solvents and system components.

Quantification of the branched isomers is often performed using the calibration curve of linear isomers and reported as the total isomers (both linear and branched). Branched isomers interact with adsorbent materials and analytical columns differently than their linear counterparts, which can make analyses of these PFAS challenging, especially if there are no branched stable isotopically labeled analog standards available.

11.2.1.2 Sample Preparation

Although ASTM International provides analytical methods for waters (D7979) and soils (D7968), there are no USEPA-promulgated analytical methods for nondrinking water matrices. Each laboratory creates their own method, and the customer should review and confirm that the laboratory method will meet their needs. Care must be taken to prevent sample contamination during preparation and extraction because the limits of quantitation and detection are 1,000 times below (ppt) those for more routine analyses such as volatiles or semivolatile analysis (ppb). It is recommended that all supplies be checked and confirmed as PFAS-free prior to sample preparation. Intermittent contamination can occur due to vendor or manufacturing changes.

For PFAS analysis, isotope dilution analysis (IDA) requires the use of extraction internal standards (EIS) consisting of isotopically labeled analogs of the PFAS targets when available, to be added to the sample at a designated point in sample preparation or analysis, depending on the sample matrix:

- aqueous samples—added to field samples while in the original container prior to extraction
- solid samples and biota—added after homogenization and subsampling, prior to addition of water or extraction solvent to samples
- serial dilution—added to high concentration samples after final dilution for serial dilution prepared samples

Ensuring a representative sample/subsample for analysis is critical. For aqueous samples the entire sample and rinsate of the sample container received by the laboratory must be extracted by SPE, to recover any PFAS that adhere to the sample container. Sample filtration is not recommended for sample with high particulate content because retention of PFAS onto filters has been noted. Centrifuging is often used to reduce sample particulates. Due to limitations in SPE cartridge capacity, samples containing high concentrations of PFAS (for example, AFFF formulations) may be prepared by serial dilution. These high concentration samples are the only instance when adsorption onto the sample container is not an issue. The laboratory should prescreen aqueous samples using the small volume sample that was received to determine if the sample contains PFAS at concentrations too high for SPE sample preparation and may be prepared using serial dilution techniques.

It is recommended that for soil samples, the entire sample collected be homogenized in the laboratory prior to subsampling.

Solids are typically extracted using solvent, with the resulting extract being further extracted using SPE.

Cleanup procedures (such as ENVI-Carb) should be used on extracts and all associated batch QC samples (for example, method blank and laboratory control samples) when matrix interferences (for example, bile salts, gasoline range organics) could be present. Cleanup procedures should always be utilized for preparation of soil, sediment, and biota. PFAS loss may occur when extracts are evaporated to dryness or at temperature higher than 60°C. Care must be taken to avoid these outcomes.

QC samples should be performed in accordance with the QAPP. Common laboratory QC samples included in PFAS analysis are:

- method blank—(one per prep batch of 20 field samples or fewer) PFAS are ubiquitous and found in many analytical instrument systems, reagents, containers, and common laboratory environments. The method blank is the same media as associated field samples and undergoes the same sample preparation procedure as the associated field samples. It is a vital indicator for the analysis.
- instrument blank—(minimum of one prior to start of daily analysis and after samples exceeding the quantitation range) Instrument blanks must contain internal standards, as they are used to measure background concentrations resulting from instrumentation and supplies and sample carryover.
- sample duplicate —(minimum of one per preparation batch of 20 field samples or fewer) A solid or high concentration sample that cannot undergo SPE is prepared and analyzed in duplicate in a single laboratory to ensure the laboratory's subsampling procedures are capable of achieving a known level of precision as defined in the QAPP.
- lab control sample (LCS)—(one per prep batch of 20 field samples) Must contain all of the project-specific PFAS in the same media as associated field samples and is used to evaluate bias associated with sample preparation as well as analytical processes.
- certified reference material (CRM)—(if available, one per prep batch of 20 field samples or fewer) Unlike LCSs, which contain no matrix interferences, CRMs can be of significant value when dealing with complex matrices such as soil and tissue.
- matrix spike (MS) and MS duplicate (MSD)—(one pair per prep batch of 20 field samples or fewer) An MS/MSD QC pair is not needed if IDA can be used for all of the PFAS of interest because the EIS used account for the influence of matrix interferences. If such standards are not available for a PFAS of interest, an MS/MSD QC pair may be warranted to assess the effects of matrix interference on that specific PFAS.

When IDA is performed or for samples with high concentrations of PFAS, it is recommended that in lieu of an MS and MSD, an LCS duplicate and sample duplicate be prepared. If samples are prepared using serial dilutions, the sample duplicate should be prepared using a different aliquot from the same sample bottle to create a second set of serial dilutions.

11.2.1.3 Sample Analysis

Instrument Type-LC/MS/MS

Currently, the analytical detection method of choice for PFAS analysis is liquid chromatography-mass spectrometry-mass spectrometry (LC/MS/MS), which is especially suited for analysis of ionic compounds, such as the PFASs and PFCAs. Gas chromatography-mass spectrometry (GC/MS) can also be used for PFAS analysis, specifically the neutral and nonionic analytes, such as the fluorotelomer alcohols (FTOHs), perfluoroalkane sulfonamides, and perfluoroalkane sulfonamido ethanols. At this time, LC/MS/MS analysis of PFAS is available, whereas GC/MS analysis has very limited commercial availability for PFAS. LC/MS/MS operated in multiple reaction monitoring (MRM) mode offers a unique fragment ion that is monitored and quantified from a complex matrix. MRM is performed by specifying the mass-to-charge ratio of the compound of interest for fragmentation within the MS/MS. This is facilitated by specifying the parent mass of the compound of interest for MS/MS fragmentation and then monitoring only for product ions. Ions arising from that fragmentation are monitored for by the MS/MS, which yields improved specificity and sensitivity.

Standards Preparation and Storage

Certified analytical standards are available from several manufacturers. Products may have variable purity and isomer profiles, which may compromise the accuracy, precision, and reproducibility of data. Only certified standards of the highest purity available, for example, American Chemical Society grade, can be used for accurate quantitation. Standards containing linear and branched isomers are not commercially available for all applicable analytes. Currently, such standards are available only for PFOS, perfluorohexane sulfonic acid (PFHxS), 2-(N-methylperfluorooctanesulfonamido) acetic acid (NMeFOSAA), and 2-(N-ethylperfluorooctanesulfonamido) acetic acid (N-EtFOSAA). Technical grades that contain branched

and linear isomers are available for other PFAS, but these standards do not have the accuracy needed for quantitation purposes. These standards may, however, be qualitatively useful for verifying which peaks represent the branched isomers. Stock standards of PFAS analytes, internal standards, and surrogate standards supplied in glass ampoules by the manufacturer are acceptable. Manufacturers of the certified analytical standards often provide laboratories storage and shelf life guidance for stock and working standards.

Steps to Help Eliminate Laboratory/Instrument Contamination (Verification of Supplies, Instrument Blanks, Isolator Columns)

Laboratory and instrument contamination is of particular concern for PFAS given that the limits of detection are in the parts per trillion (ppt) range. Additionally, nonpolymer PFAS may be found at trace levels as impurities in some polymer products (3M 1999). PFAS are found in commonly used laboratory items such as polytetrafluoroethylene products (PTFE), solvent lines, aluminum foil, and methanol, which could lead to method interferences and elevated baselines in chromatograms if not checked. USEPA 537.1 recommends that all of the above items must be “less than 1/3 the MRL (minimum reporting limit) for each method analyte under the conditions of analysis by analyzing laboratory reagent blanks.” (Shoemaker and Tettenhorst 2020) pg. 7. USEPA 533 further specifies that the isotopically labeled analogues and isotope performance standards meet this same requirement (USEPA 2019f), pg. 7. The liquid chromatograph can be fitted with an isolator column to separate contamination arising from the solvent delivery system, which allows for quantitation at low detection limits. Guard columns should be used to protect analytical columns.

Ion Transition Selection (Recommended Transitions for Primary and Confirmation Ions, Including Ratio Criteria)

Quantification by LC/MS/MS may be accomplished using a variety of techniques. For relatively simple matrices such as drinking water, USEPA 537.1 quantifies analytes by comparing the product ion of one precursor ion and retention time in samples to calibration standards. For more complex matrices, additional product ions and their ion ratios can be used to distinguish analytes from matrix interference. In an MS/MS system, most analytes can be fractured into more than one ion. By monitoring the area of each ion and comparing the ratio of those area counts, a more definitive identification can be made. This identification allows the analyst to distinguish true target analytes from false positives. This more detailed quantification is not required for drinking water matrices, but it is useful for more complex matrices. It is recommended that two ion transitions from parent to characteristic product ions be monitored and documented for each analyte, with the exception of PFBA and PFPeA. Ion transition ratio criteria should be determined based on information obtained from analysis of standards and used to detect potential bias in sample results. To avoid biasing results high due to known interferences for some transitions, the following are recommended transitions as defined in DOD QSM (2019), Version 5.3, Appendix B, table B-15 (USDOD 2019): PFOA: 413 → 369, PFOS: 499 → 80, PFHxS: 399 → 80, PFBS: 299 → 80, 4:2 FTS: 327 → 307, 6:2 FTS: 427 → 407, 8:2 FTS: 527 → 507, N-EtFOSAA: 584 → 419, and NMeFOSAA: 570 → 419.

Mass Calibration, Calibration Criteria, and Calibration Verification

Mass calibration should be performed at setup, after performing maintenance that is required to maintain instrument sensitivity and stability performance, and as needed based on QC indicators, such as calibration verifications. Mass calibration should be performed according to the manufacturer’s instructions.

USEPA Methods 537.1 and 533 contain requirements for instrument calibration and calibration verification specific for drinking waters. It is suggested that until other USEPA or ISO methods are published, these criteria should be used for all nonisotope dilution/internal standard analyses. The instrument should be calibrated at setup and as needed following initial calibration verification (ICV) or continuing calibration verification (CCV) failure. The lowest calibration point should be a concentration at or below the LOQ. A standard at the LOQ concentration should be analyzed at least daily to document the instrument’s ability to accurately quantitate down to that concentration.

An ICV prepared from a source separate from the calibration standards should be analyzed after each initial calibration and before sample analyses are performed. The minimum frequency for ICV should be once after each initial calibration, prior to sample analyses. At a minimum, CCV should be done prior to sample analysis on days an ICV is not analyzed, after every 10 field samples, and at the end of the analytical sequence. CCVs should rotate in concentration to cover the entire calibrated range of the instrument. For example, as in USEPA 537.1, the calibration acceptance criteria for each analyte are that the lowest calibration point must be within 50–150% of its known value while the other calibration points must be within 70–130% of true known values.

To account for biases resulting from preparation steps, isotope dilution should be used for quantitation. Isotope dilution is a quantitation technique that considers sample matrix effects on each individual PFAS quantitation in the most precise manner possible. This technique quantifies analytes of interest against isotopically labeled analogs of the analytes, which are added to the sample both prior to and after sample preparation. Addition of EIS prior to preparation helps account for loss of analyte during the preparation process and for bias associated with the instrumentation. Calibration criteria for methods using isotope dilution can be found in ISO Method 25101 or DoD QSM Version 5.3, Appendix B, table B-15. Methods using isotope dilution should include isotope analog recovery for each sample and analyte in data reports. Isotope analog recoveries should be reported, and minimum/maximum isotope analog recoveries may be required by specific analytical procedures. Depending on project DQOs, low isotope recovery may indicate that quantitation was inadequate; the data are then reported as estimated values.

Instrument Blanks: When Are They Needed, Criteria, and Corrective Actions to Take

Due to the ubiquitous nature of PFAS, instrument blanks are critical in determining if the instrument is potentially affecting PFAS concentrations in samples. Instrument blanks should be analyzed following the highest calibration standard analyzed and daily prior to sample analysis. The concentration of each analyte should be $\leq \frac{1}{2}$ the LOQ. If instrument blanks indicate contamination following the highest calibration standard, corrective action, such as calibrating with a lower concentration for the highest standard, should be taken. Successful analysis of an instrument blank following the highest standard analyzed determines the highest concentration for which carryover does not occur.

Matrix-Specific Information

Drinking Water

Interferences related to the matrix can be caused by the co-extraction of contaminants from the sample. These matrix interferences can have considerable variation from sample to sample. For example, there are problems associated with free chlorine in chlorinated finished waters and using TRIS (Trizma; for USEPA Method 537.1) or ammonium acetate (for USEPA Method 533) can help overcome some of these issues.

Potential High Concentration Samples: Postspike Verification of Reporting Limit (RL) for Those Reported as <RL.

Samples with concentrations greater than the highest standard will require dilution. As a standard practice, extrapolation beyond the established calibration is prohibited. The sample may be diluted and the appropriate amount of internal standard is added to match the original concentration. The dilution factor must be accounted for in the final concentration calculations.

Postspike verification is suggested for samples prepared by a dilution. Analytes that will have a concentration less than the LOQ in the final dilution should be spiked at the LOQ. Recovery information should be reported with the samples to provide information on the effects of the dilution on quantitation.

11.2.2 Qualitative

Several techniques employing indirect measurement have been developed that more comprehensively assess the range of PFAS contamination at a site. These qualitative techniques are not standardized through a published USEPA method and range in commercial availability. To date, these techniques have not undergone multilaboratory validation. Data from these qualitative techniques may augment the definitive data from quantitative methods.

11.2.2.1 Overview of Qualitative Techniques

Because of the large number of PFAS and their varied structural characteristics, a single targeted method on either LC/MS/MS or GC-MS/MS is unable to quantify all PFAS that may be present in a sample. When the release source is well understood and the types of PFAS present are both known and amenable to regular PFAS analysis methods (for example, LC/MS/MS of ionic PFAS or GC-MS/MS analysis of neutral PFAS), a targeted analytical approach may be sufficient to adequately characterize a release. For releases that are not well understood or consist of multiple sources, alternative ways of measuring PFAS in a more comprehensive but less targeted fashion may be desirable. Additionally, PFAS that are in polymeric form, such as those used in coatings for paper and textiles, are not amenable to LC- and GC-based separation techniques; they may also not be effectively extracted, even with rigorous methods.

Four primary techniques have been developed to characterize unknown PFAS in a sample. These techniques are not

multilaboratory, validated, or promulgated. They are described in more detail in the following sections:

- The total oxidizable precursor (TOP) assay measures PFAA precursors or polyfluorinated compounds that can be converted to PFAAs by LC/MS/MS.
- Particle-induced gamma-ray emission (PIGE) spectroscopy measures elemental fluorine isolated on a thin surface.
- Adsorbable organic fluorine (AOF) paired with combustion ion chromatography (CIC) measures the combusted organofluorine content of a sample as fluoride on an ion chromatograph.
- High-resolution mass spectrometry techniques, such as quadrupole time-of-flight (qTOF) MS/MS, can tentatively identify PFAS structures through library matching or in-depth data analysis.

11.2.2.2 TOP Assay

Technique Description

The TOP assay (or TOPA) converts PFAA precursor compounds to PFAAs through an oxidative digestion. The increase in PFAAs measured after the TOP assay, relative to before, is an estimate of the total concentration of PFAA precursors present in a sample, because not all PFAS present will be subject to quantitation or reaction and some will remain as undetected PFAS. The PFAAs generated have perfluoroalkyl chain lengths equal to, or shorter than, the perfluoroalkyl chain lengths present in the precursors (Houtz et al. 2013; Houtz and Sedlak 2012; Weber et al. 2017; Dauchy et al. 2017).

The TOP assay is a technique developed to estimate oxidizable precursors that can transform to perfluoroalkyl acids (PFAAs) end products that are included in the target analyte list (Houtz et al. 2013; Houtz and Sedlak 2012). A sample is measured using conventional LC/MS/MS to determine baseline levels of PFAAs present in the sample. A separate aliquot of the sample is then exposed to a highly basic persulfate solution and then placed in a sealed container at an elevated temperature (for example, 85°C) to thermolyze persulfate into sulfate radical. At elevated pH, the sulfate radical is scavenged by hydroxide and forms hydroxyl radical, which then converts the free PFAA precursor compounds to PFAAs. The predominant products (that is, > 95% in control experiments) of the precursors are the perfluoroalkyl carboxylates, whether or not the precursors contain sulfonamido or telomer functionalities. After sufficient time has elapsed to convert all the persulfate, the samples are removed from the heated environment (for example, a water bath), brought to room temperature, and neutralized prior to analysis. The additional concentration of PFAAs generated after the oxidation step estimates the concentration of oxidizable PFAA precursors.

The technique can be applied to aqueous (Houtz et al. 2013; Houtz and Sedlak 2012; Houtz et al. 2016; Weber et al. 2017; Dauchy et al. 2017) and solid samples (Houtz et al. 2013). In most cases, samples need to be pretreated prior to oxidation to remove competitive organic compounds. For aqueous samples, dilution may be sufficient, although extraction techniques may be used to further remove matrix effects. Soil samples are extracted prior to persulfate treatment, and the extracts are cleaned with ENVI-Carb prior to treating the evaporated extract. The specific extraction procedure used may impact which PFAA precursors are retained for oxidation. For example, acidic extraction procedures may be required to remove cationic precursor compounds from soils (Barzen-Hanson 2017; Mejia-Avendaño et al. 2017).

Possible Technique Uses

TOP assay may be used to estimate a total concentration of free PFAA precursors in a sample. When measuring strictly a sample post-TOP assay, the total concentration of PFAS measured may be thought of as a conservative measurement of the sample's total PFAS concentration. In some cases, oxidation can be incomplete (Australia Government DOD 2019). The total PFAA precursor or total PFAS concentration is considered conservative for the reasons explained below in Technique Limitations. Because the method depends on a compound containing a perfluoroalkyl group, it is highly specific to PFAS. The chain lengths of the PFAAs generated after oxidation provide an indication of whether the precursors are predominantly short- or long-chained, although the production of a particular C_n (where "n" signifies the number of carbons in the alkyl chain) PFAA is not equivalent to the concentration of PFAA precursors containing the same chain length. However, if significant amounts of PFOA are generated after oxidation, that is an indication that the sample contains a comparable concentration of C₈ or longer PFAA precursor compounds.

TOP assay, the most widely commercially available of the qualitative techniques, is typically accepted as a means of determining PFAS load on remediation substances to estimate the replacement cycle, but not for site characterization.

Technique Limitations

As mentioned above, the TOP assay does not easily differentiate between precursors that contain telomer or sulfonamide functionalities, because all these precursors are chemically oxidized primarily to perfluoroalkyl carboxylates. This is significant because a precursor that would likely form PFOS in the presence of a mixed consortium of aerobic bacteria will convert to PFOA under the conditions of TOP assay. The production of branched perfluoroalkyl carboxylates could be attributed to precursors derived from an ECF-based manufacturing process, but environmental samples may not contain the same distribution of branched and linear isomers as was originally generated from the ECF manufacturing process.

TOP assay results in a mixture of PFCA products upon the conversion of fluorotelomer-based compounds (Houtz and Sedlak 2012). For example, 8:2 FTS was converted to 3% PFNA, 21% PFOA, 27% PFHpA, 19% PFHxA, 12% PFPeA, and 11% PFBA in control experiments. Because of this effect, two limitations arise. First, the production of PFOA, for example, is not equivalent to the C8 precursor concentration, because PFOA can be generated from longer-chain telomer compounds and is only a partial product of C8 telomer products. Second, some shorter chain PFCA products of telomer compounds are not captured. Only 73% of 6:2 FtS was recovered as PFCA products PFBA and longer in control experiments (Houtz and Sedlak 2012). As a result, TOP assay may underquantify short-chain PFAA precursors that are telomer-based. Sulfonamido compounds in control experiments do not exhibit a distribution of products; the C_n precursor forms the C_n PFCA in a 1:1 molar ratio.

TOP assay has not been demonstrated on large molecular weight polymer compounds or newer ether-linked PFAS such as GenX process chemicals; it is unknown if the oxidative process would liberate PFAAs from these types of compounds. Because PFAS polymers have shown limited ability to biodegrade (Russell et al. 2008; Russell et al. 2010) (Washington et al. 2009) relative to low molecular weight free PFAA precursor compounds (Wang, Szostek, Buck, et al. 2005; Lee, D'eon, and Mabury 2010; Wang et al. 2011; Harding-Marjanovic et al. 2015), TOP assay may be similarly ineffective at converting PFAS polymers to free PFAAs. TOP assay cannot be used to measure large molecular weight polymeric PFAS unless they are proven to break down in the assay.

For many samples, TOP assay requires adjustments in dilution, sample preparation, or reagent dosing to achieve complete conversion of PFAA precursors. Standardized quality guidelines are needed to ensure that TOP assay data reflect full conversion of PFAA precursors.

11.2.2.3 PIGE

PIGE is a nondestructive analytical technique that takes advantage of the unique gamma-ray wavelength emission of fluorine when impacted with a proton ion beam. The technique is not compound-specific but able to assess total fluorine content of a variety of materials isolated on a thin surface (0.22 mm) (Ritter et al. 2017). The sample is secured in the instrument and bombarded *ex vacuo* under a 3.4 MeV beam with an intensity of 10 nA for approximately 180 s. Two gamma rays characteristic of the decay of the ¹⁹F nucleus (110 keV and 197 keV) are measured and the responses integrated. Quantification is achieved with comparison to fluorine-based calibration standards.

In the published literature, PIGE has been used to demonstrate total organofluorine concentrations in papers and textiles (Ritter et al. 2017; Robel et al. 2017) and food packaging (Schaidler et al. 2017). It has also been used on an experimental basis to evaluate organofluorine concentrations in extracted water and soils, but those results are not yet available in the peer-reviewed literature.

Possible Technique Uses

PIGE is a rapid screening technique to measure fluorine on surfaces. If a sample does not contain significant amounts of fluoride or can be prepared to remove inorganic fluoride, PIGE can become a technique specific for organofluorine; however, it is not specific for PFAS. It is a proven way to measure total fluorine in matrices containing high concentration of fluorine polymeric material, which is a limitation of both TOP assay and AOF. It also requires relatively minimal sample preparation to analyze fluorine content in commercial products. Sample preparation of environmental samples for PIGE analysis is likely to require a similar level of sample preparation, along with the limitations of extraction techniques, as TOP assay or AOF.

Technique Limitations

Like AOF, PIGE is not specific to PFAS and, depending on the preparation, it is also not specific to organofluorine. The polymeric compounds that PIGE has been used to detect in consumer products may not contain perfluoroalkyl groups or be capable of breaking down to free PFAS.

PIGE also does not provide any differentiation on PFAS perfluoroalkyl chain length present in a sample. Depending on how

the sample is prepared prior to the instrumental analysis, samples may be biased toward measurement of long-chain PFAS, as with TOP assay and AOF.

Extraction methods for PFAS in environmental samples have not yet been demonstrated for this technique. When using SPE to extract environmental aqueous samples prior to PIGE analysis, cartridges that are suitable to hydrophobic and anionic PFAS may not retain positively charged PFAS of interest. For soil samples, the extraction method also determines the PFAS likely retained. However, by using targeted extraction techniques for PFAS in environmental samples, the method becomes much more specific for PFAS.

As with AOF, the range of operating conditions for PIGE has not been standardized and so far the technique has been demonstrated with only one commercial lab.

11.2.2.4 Adsorbable Organic Fluorine or Combustion Ion Chromatography

AOF (Wagner et al. 2013) or extractable organofluorine (Miyake, Yamashita, So, et al. 2007; Miyake, Yamashita, Rostkowski, et al. 2007; Yeung et al. 2008) paired with CIC (AOF/CIC) are complimentary terms for an analysis for fluorine content of environmental samples. In this application, an aqueous sample is passed through a carbon-based sorbent on which the fluorine-containing organics adhere. The carbon sorbent is then combusted at high temperatures that should completely decompose the organics into their elemental constituents. The gaseous stream is passed through deionized water, which is then analyzed for fluorine content (as fluoride) by ion chromatography.

The technique has been demonstrated on human blood samples (Miyake, Yamashita, So, et al. 2007; Yeung et al. 2008) and various environmental aqueous samples (Miyake, Yamashita, Rostkowski, et al. 2007; Wagner et al. 2013; Dauchy et al. 2017; Willach, Brauch, and Lange 2016). Presumably, the method could be adapted to other types of matrices to measure organofluorine in soils or biota. The matrices could be extracted for PFAS, resuspended into an aqueous solution that could adhere to the activated carbon, and then analyzed with CIC. As with TOP assay, the specific extraction procedures would influence whether some or all PFAS are retained and ultimately measured as combusted fluoride product. Alternatively, it is possible that the technique could be used without extraction to directly combust organofluorine-containing products.

Possible Technique Uses

AOF can be used to measure PFAS or other fluorine-containing compounds as a total organofluorine concentration. If the method is available more readily or at a lower cost than LC/MS/MS measurement of PFAS, it can be a quick screening tool to determine if a significant concentration of fluorine-containing compounds is present in an aqueous sample or other sample from which the organofluorine content can be extracted. A detection limit of 0.77 µg/L fluorine (13 µg/L PFOS equivalent) (Willach, Brauch, and Lange 2016). was reported for one laboratory offering the technique, although the detection limit will vary by amount of sample processed and laboratory conducting the procedure.

Technique Limitations

AOF is not specific to PFAS. If a sample contains relatively high concentrations of non-PFAS that contain fluorine (for example, fluorine-containing pharmaceuticals), then the organofluorine may be falsely attributed to PFAS content and bias "total PFAS" concentrations high.

AOF does not provide any differentiation on PFAS perfluoroalkyl chain length present in a sample. Some short-chain PFAS may be unable to sorb to the activated carbon material that is combusted, but this will depend significantly on laboratory-specific procedures.

Extraction methods for PFAS in commercial products and solid samples coupled with this technique have not yet been demonstrated for this technique. Background fluoride concentrations may be challenging to remove from some matrices and would result in samples biased high for total organofluorine that was actually attributable to fluoride.

The range of operating conditions for AOF-CIC has not been standardized. In addition to the limitations mentioned above, some matrices may contain sufficient competitive organics or other materials that coat the activated carbon to prevent complete retention of organofluorine compounds.

11.2.2.5 High-Resolution Mass Spectrometry (qTOF/Orbitrap)

Technique Description

Quadrupole time-of-flight mass spectrometry (qTOF/MS) can be used to determine both the chemical formula and structure

of unknown PFAS in a sample, but analytical standards are required for unequivocal structural identification.

High-resolution mass spectrometry has been used to tentatively identify the molecular formulas and structures of unknown PFAS (Newton et al. 2017; Moschet et al. 2017; Barzen-Hanson et al. 2017). Similar to targeted PFAS analysis, separation techniques such as LC or GC are used to separate compounds in a sample so that individual PFAS can be resolved. The mass is measured using a time-of-flight or other high-resolution detector, and molecular formula are proposed. If an MS-MS technique is used, the fragments of the parent compound can be used to piece together the structural arrangement of the compound. To identify compounds that are specifically PFAS versus other organics present in the sample, compounds with negative mass defects (that is, the accurate mass is slightly less than the nominal mass) can be selected. Fluorine is one of the few elements that has a negative mass defect, and the inclusion of multiple fluorines in a PFAS molecule means that net mass defect of the molecule will likely be negative. Compounds that are either 50 or 100 mass units apart also identify homologous series of PFAS separated by one or two CF₂ groups. MS libraries of previously identified PFAS exist for targeted matching, although they will not definitively identify an unknown compound.

Possible Technique Uses

High-resolution mass spectrometry analysis of PFAS can tentatively identify the structures of unknown PFAS and can also be used, in comparison with analytical standards of known compounds, to semiquantitatively estimate their concentrations. Because accurate identification of compounds using high-resolution MS is a time-intensive and expensive process, a high motivation for knowing the exact PFAS structure, for instance in differentiating forensically between two different sources, may be the biggest driver of its use for PFAS analysis. High-resolution MS is best suited for media in which unknown PFAS are likely to be present in significant concentrations. When many other non-PFAS compounds are present in the sample, the MS signal of competing compounds will likely obscure the signal of PFAS. Sample preparation steps can inadvertently or intentionally select for certain types of PFAS. As user skill and data interpretation time increase, accurate identification of PFAS is likely to improve.

Technique Limitations

High-resolution mass spectrometry cannot definitively identify the exact structure or formulas of PFAS without comparison to reference materials or analytical standards.

Not all PFAS, even if present in a prepared sample, can or will ionize under the conditions to which the instrument is tuned. A skilled instrument operator may be able to adjust the instrument conditions to match the types of compounds expected.

False positives are much more likely to result using high-resolution MS than with TOP assay, AOF, or PIGE. Compounds may be mistakenly identified as PFAS, and if correctly identified, their concentrations may be greatly over- or underestimated when other compounds are used for comparative quantitative purposes.

11.3 Data Evaluation

Evaluation of data involves looking at all the factors that indicate whether the data are:

- precise (agreement between results that are supposed to be similar)
- accurate (how close they are to the true concentrations)
- representative (results characterize the site properly)
- comparable (data compare well to other data)
- complete (all the samples and compounds requested were reported, especially for critical samples that represent a point of exposure, such as drinking water)
- sensitive (nondetect data reported with concentrations below required regulatory or risk level)

These factors are illustrated in Figure 11-1, and guide users through the process of looking at their data (field collection and laboratory information) with a critical eye.

The USEPA has guidance to aid in evaluating PFAS drinking water data generated in accordance with USEPA 537, *Data Review and Validation Guidelines for Perfluoroalkyl Substances (PFASs) Analyzed Using EPA Method 537*, as well as a technical bulletin to aid in the review of PFAS data generated for all other media, *Per- and Polyfluoroalkyl Substances (PFAS): Reviewing Analytical Methods Data for Environmental Samples*. The USDOD EDQW has published PFAS Data Validation Guidelines, for evaluation of PFAS data generated in accordance with the *DoD/DOE Quality System Manual for Environmental Laboratories, Version 5.3* (USDOD 2020).

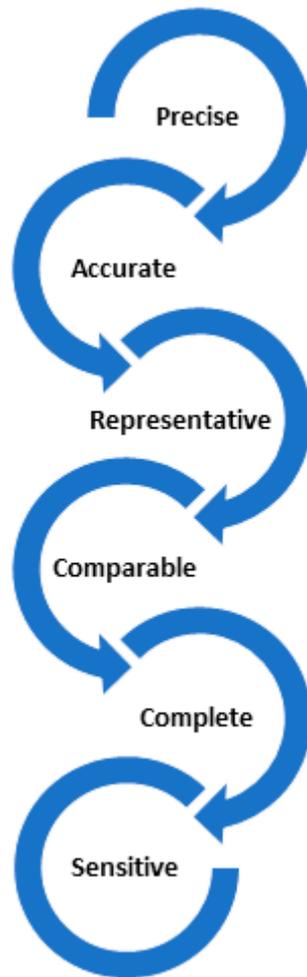


Figure 11-1. Data evaluation factors.

Source: H. Albertus-Benham, Wood Environment & Infrastructure, used with permission.

11.3.1 Presampling Planning

To ensure the usability of the data, communication with the laboratory that is performing the analysis is important. Until there are accepted methodologies for matrices other than drinking water, it is incumbent on the data user to collect information about the methodology to be employed by the lab. Figure 11-2 contains laboratory considerations related to data usability in order to plan a sampling program.



Figure 11-2. Laboratory planning considerations for data usability.

Source: H. Albertus-Benham, Wood Environment & Infrastructure. Used with permission.

The most important goal of data usability is to ensure that the PFAS data generated are usable to meet the stated data needs and that the user understands any limitations in the use of the data due to potential uncertainty or bias. Overall usability of data is judged by evaluating the quality of the results compared to the data quality objectives (DQO) of the project. Therefore, establishing these project DQOs and communicating them to the field sampling team and the laboratory prior to sample collection and sample analysis is vital to ensuring that the correct methods, correct compounds, and adequate sensitivity are reported for your samples.

Throughout the rest of section 11.3, pre-sampling planning will be indicated by these yellow call-outs.

11.3.2 Overall Usability of the Data

Three questions are most important in evaluating data: (1) Have the results exceeded a level of concern?, (2) Do these results make sense?, and (3) Are data of acceptable quality? To judge whether results have exceeded a level of concern, the potential bias or uncertainty in the data should be evaluated along with the sensitivity of the results. At a minimum, it is recommended that a report from the laboratory contains a cover letter (or narrative) explaining sample receipt, analytical methods, and any QC deviations plus data sheets for field samples and QC samples (method blanks, blank spikes), which should also contain results for sample-specific QC (such as internal standard recoveries). Often the most critical data for a project are the non-detects to prove the absence of compounds of concern at specific concentration levels (quantitation limits). Therefore, before evaluating QC associated with your samples, the data should be evaluated to ensure that all compounds required are reported with quantitation limits at or below the project's required sensitivity objective. If this sensitivity is not acceptable, then the data may be of very limited use.

If the compound list reported and quantitation limits are acceptable, then the associated QC results (for example, EIS recoveries, results of blanks, blank spike recoveries, etc.) can be compared to project DQOs to evaluate potential uncertainty in the data. The formal systematic process of this QC evaluation is called data review or validation. The approach to data validation is well documented, for example, see the USEPA *National Functional Guidelines*, January 2017 (USEPA 2017h), (USEPA 2018c) and DOD/DOE QSM 5.3 tables C-44 and C-45, 2019 (USDOD 2019) and beyond the scope of this document; however, evaluation of all of the QC associated with the sampling and analysis of a set of samples will lead to an understanding of the uncertainty in the data.

Some critical QC issues might result in unusable data or concern for project actions. For example, if the data are considered biased low based on low QC results and the sample concentrations are at or near the level of concern or an action level, it may be that the true sample concentration actually exceeded the action level. Conversely, if the sample data are considered biased high based on high QC results and the sample concentrations are near but below the levels of concern or action level,

then there is added certainty that the data do not exceed the action levels.

Once the data have been adequately reviewed for accuracy to determine if there are limitations to their use or uncertainties to be considered during use, the results should be evaluated by answering the following questions:

- Do field duplicates, if performed, agree, indicating acceptable precision for the sampling and analysis?
- Do the data from the current sampling event correlate with historical data?
- Do the data make sense from a temporal point of view?
- Do the data from one sampling point to the next make sense across the project area?

This type of review can point out data trends or areas of concern (for example, interferences with project analytes) that could not be elucidated by looking at a single data point and may lead to overall project changes such as a need to increase sampling density to improve data representativeness, correction of procedures for collecting samples to minimize contamination, changes in methods of analysis to achieve project sensitivity requirements, etc. Following this review, the data user can determine whether the data set is complete and sufficient for project decisions and data uses or whether additional samples need to be collected and analyzed.

Evaluating results may lead to overall project changes such as a need to increase sampling density to improve data representativeness, correction of procedures for collecting samples to minimize contamination, changes in methods of analysis to achieve project sensitivity requirements, etc.

11.3.3 Sensitivity

A reporting limit (RL) or quantitation limit (QL) is the limit of accurate quantitation for a specific analyte in a specific sample after any adjustments have been made for sample amount, dilutions, or percent moisture. Typically, the RL concentration is selected as the lowest nonzero standard in the calibration curve for each analyte. It takes into account the sample size, matrix effects, and any dilutions made during the analysis of that particular sample. Because of varying properties between samples, the RL can vary from sample to sample. The RL should represent the level at which reliable qualitative and quantitative information is routinely reported.

Sensitivity is related to the RL in that sensitivity refers to the capability of a method or instrument to detect a given analyte at a given concentration and reliably quantitate the analyte at that concentration. If a specified analyte is not reported by a laboratory to be in a specified sample, it does not necessarily mean that the chemical is not present; it is an indication that the concentration of the analyte may be below the method sensitivity.

Detected PFAS results between the method detection limit (MDL) and RL (that is, "J" values) can generally be reported as long as all qualitative identification criteria are achieved. Typical RLs for PFAS are as follows:

- common PFAS analytes in aqueous matrices: 2-8 ng/L
- common PFAS analytes in solid matrices: 0.2-2 ng/g

Sometimes even though lower RLs were planned for, the laboratory may have to perform dilutions, which causes the RLs to be elevated. Ensure that the dilution performed by the laboratory was reasonable. If there are elevated concentrations of specific target analytes or interferences, then the dilution is likely justified and the presence of elevated RLs may not be an issue if these other target analytes are present at very high levels.

It is imperative that the RLs (and not the MDLs) for each method are evaluated versus the project screening criteria prior to submitting samples to the laboratory. The RLs should be below the project screening criteria to ensure achievement of project objectives.

If a dilution was performed and it is not obvious why (for example, low concentrations or nondetect results for target analytes), then inquire with the laboratory why the dilution was performed. This could happen due to elevated concentrations of nontarget compounds but should be documented.

The RLs can also be affected by the sample preparation parameters, the mass of solid sample or volume of aqueous sample used in the extraction, or the final volume of the extracts. Typically, laboratories will utilize 100-250 mL for aqueous sample extractions and 1-5 grams for solid sample extractions. Final extract volumes are typically between 0.5 mL and 1.0 mL. If a complex matrix is encountered, the sample sizes may be reduced and/or the final extract volumes may be increased, causing the RL to be elevated accordingly.

11.3.4 Target Analyte Lists

Target analyte lists for PFAS will vary by laboratory and regulatory program. The data user should work with the laboratory to ensure that the correct list is being reported, as dictated by the project objectives. In general, Table 11-4 includes the common PFAS reported by existing laboratories (Excel file). The selected list may be dependent upon project objectives, as well as the potential source of PFAS contamination (for example, AFFF, landfill, chromium electroplating).

The data user should work with the laboratory to ensure that the correct list is being reported, as dictated by the project objectives.

11.3.5 Linear and Branched Isomers

It is also important to note that PFOS and PFOA (and other PFAS as well) contain a mixture of linear and branched isomers, which can be significant when the laboratory is quantifying these chemicals. Very few standards are available for branched isomers. If branched isomers are not included in the sample quantitation by the lab, the resulting concentrations will be underestimated.

In general, all laboratories should be reporting the sum of the linear and branched isomers for PFHxS, PFOS, PFOA, NMeFOSAA, and N-EtFOSAA because these are the PFAS for which both linear and branched analytical standards exist. In the absence of a standard that includes branched isomers, only the peak associated with the linear isomer is integrated. As more analytical standards become available, more PFAS will be reported as linear and branched in the future.

Figure 11-3 shows an example of the integration performed correctly and incorrectly. It is the responsibility of the data user to ensure that the contracted laboratory is performing the integration of the target PFAS to include both linear and branched isomers. This requires upfront communication with the laboratory and a possible independent review of the laboratory raw data by a qualified chemist/data user to verify the integrations were properly performed.

Ensure that the contracted laboratory is performing the integration of the target PFAS to include both linear and branched isomers.

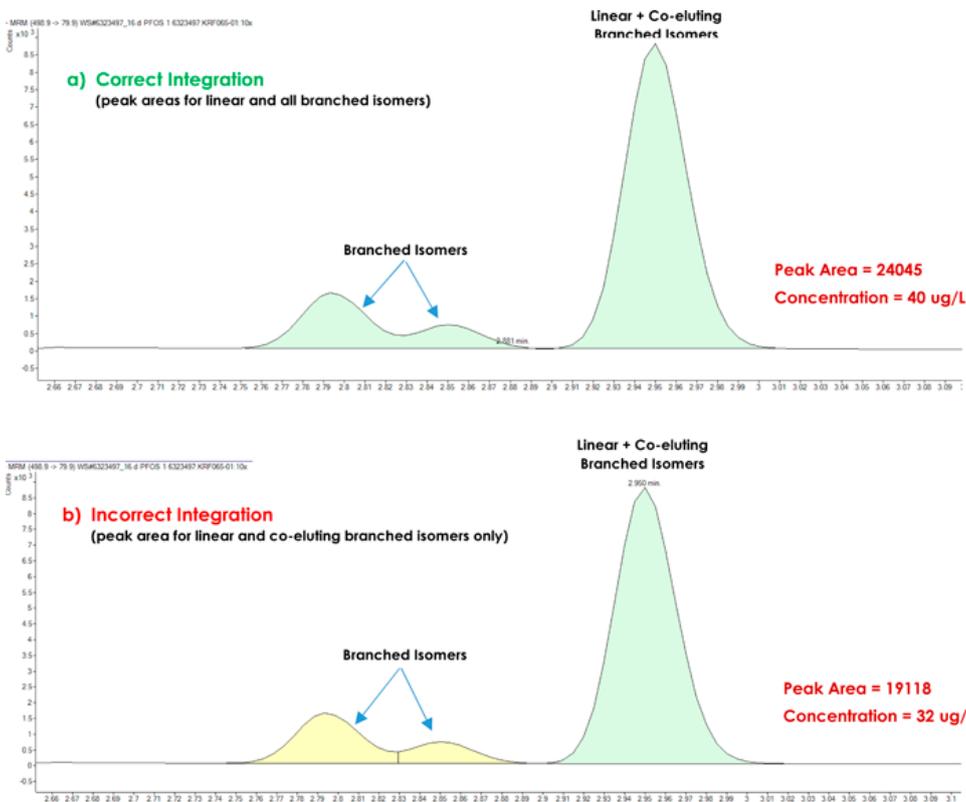


Figure 11-3. LC/MS/MS data illustrating a) complete integration of linear and branched PFOS, and b) partial integration of PFOS. Discrepancies in concentration will depend on the fraction of branched versus linear PFAS present, but in the current example PFOS concentrations in b) were 20% lower than in a).

Source: Bureau Veritas Laboratories, Mississauga, Ontario, Canada. Used with permission.

11.3.6 Isotope Dilution Standard Results and Surrogates

The isotope dilution technique involves quantitation of a compound of interest using a labeled isotope of that very compound. A variety of isotopically labeled analogs (for example, carbon-13 isomers of the compounds of interest) are added to a sample prior to extraction or prior to analysis when extraction is not required. These isotopically labeled analogs are sometimes referred to as surrogates or as extracted internal standard analytes as defined in the DOD/DOE (2019) QSM 5.3 and function from a data usability standpoint as both a surrogate standard (calculation of the recovery of the standard) and as an internal standard (used in the calculation of the target compounds)(USDOD 2019). Generally, the number of isotopically labeled analogs used in the isotope dilution technique matches the number of target compounds and exceeds the number of surrogates used in nonisotope dilution procedures. For example, Method 537.1 uses three surrogates for 18 target compounds, while isotope dilution attempts to use an isotopically labeled analog for each compound being reported. Internal standards are also added to the sample or extract immediately preceding analysis. For nonisotope dilution analyses, quantitation of the target compounds and surrogates is performed relative to these injection internal standards. The results from the nonisotope dilution technique report concentrations of the target compounds and recovery results for surrogates and it is up to the data user to determine the impact (that is, bias) of the extraction and analysis on the sample results (that is, results are not recovery-corrected).

For the isotope dilution methods, quantitation of the target compounds is performed relative to the response of the isotopically labeled analog, which should recover in a manner similar to how the nonlabeled compounds recover. Effectively, the sample data are recovery-corrected for losses that might have occurred during sample processing. The isotope dilution recovery correction procedure greatly improves the accuracy of the analysis and is considered to be an improvement over other techniques for the analysis of complex samples for analytes requiring high sensitivity. Chemical standards manufacturers are working to make a wider variety of labeled isotope compounds available to further improve accuracy of the methods for all compounds under investigation (for example, fluorotelomers, precursors, various isomers of carboxylates and sulfonates).

Acceptance criteria or control limits for surrogate and isotopically labeled analog recoveries are either developed by the laboratory or dictated by the requirements of the project (for example, QAPP-specified criteria, regulatory criteria, or method criteria). Poor recovery of surrogates in complex matrices is common; however, if a project requires ongoing analysis of a problematic matrix, the laboratory should perform method development to improve recovery, if possible (for example, change in cleanup procedures, change in the transition ions monitored, etc.). If the recovery for a surrogate is below criteria in a sample for nonisotope dilution techniques, compounds associated with this surrogate may be biased low. If surrogate or EIS recovery is very low (for example, < 10% recovery), nondetects associated with the surrogate or EIS may be false negatives and should not be used for project decisions.

In the case where an isotope dilution extract is analyzed and requires re-analysis at a high dilution, the sample extract may be re fortified with labeled isotope compounds for adequate response. In reporting the final data, the isotope recovery results from the initial analysis should not be used to adjust the data from the secondary dilution analysis. The result from this scenario is no longer quantitated from an isotope dilution but is calculated from an internal standard calculation and should be noted as such in the case narrative.

11.3.7 Blank Contamination

As a consequence of the ubiquitous nature of PFAS, samples that may not contain PFAS can become contaminated if they come into contact with samples or materials containing PFAS. The types of blanks commonly used to evaluate contamination are field-based blanks and lab-based blanks. Field-based blanks include field reagent blank (field blank), source water blank, and equipment rinse blank. Lab-based blanks include method blank, lab reagent blank, and instrument blank. Reagent, field, trip spike, and method blanks are prepared and analyzed using the same procedures as for the field samples. Instrument blanks are analyzed periodically to verify the instrument is clean for analysis of subsequent samples.

The reagent blank is used to evaluate the potential PFAS contamination from the reagent water source used to generate the field-based and lab-based blanks. A systematic review of all of the blank results compared to the associated field sample results (the group of samples associated with the field-based and lab-based blanks or the analytical batch of samples associated with a specific method blank) must be made

The possible sources of contamination that may occur during field collection activities and sample preparation and analysis and the recommended procedures to minimize contamination have been previously addressed in Section 11.1.

to determine whether the field sample results are accurate. For example, if the reagent water source is nondetect for PFAS, then contamination found in the field-based blanks indicates potential contamination of the associated field samples from the sample bottle itself and/or during collection, handling, or transport to the laboratory.

However, if a lab-based blank is also contaminated, the contamination observed in the field-based blanks may have been due to sample handling at the laboratory. If the conclusion of this systematic blank data review is that an associated sample result may have been contaminated, then the sample result is considered to be biased high or may be a false positive, depending on the magnitude of the blank contamination compared to the field sample result. A general rule of thumb is that if sample contains a contaminant within 5x the concentration in the associated blank, the results may be biased high or result in a false positive in the sample (USDOD 2019).

11.3.8 Duplicate Results

Laboratory replicates are two separate aliquots of the same sample put through the entire sample preparation and analytical procedures. Field duplicates are two separate samples collected at the same location at the same date and time. Laboratory replicates may be performed in lieu of an LCS duplicate or MSD. It should be noted that sometimes laboratories report the results of laboratory replicates performed on samples that are from a different project (that is, batch QC); if the laboratory replicates reported are not from a sample at the site of interest, then these results should not be used in the evaluation of sample data.

During data evaluation, the relative percent difference of each detected analyte versus the acceptance limits should be reviewed. The acceptance limits should be provided within the laboratory report and are either regulatory- or method-specific. The acceptance limits may have been provided in a QAPP, or may be laboratory-generated. When both results are < 2x the RL, the potential uncertainty increases and therefore the acceptance criteria may need to be adjusted.

Review regulatory or method-specific acceptance limits with the laboratory, whether from a QAPP or laboratory-generated.

- If both results are < 2x the RL, relative percent difference criteria can be doubled.
- If one result is detected and one result is not detected, then the evaluation will depend on whether the detected result is > 2x the RL or not. If one result is > 2x the RL and the other result is nondetect, then the variability is considered unacceptable and there may be potential uncertainty in the results for this sample.

Variability in laboratory replicate and field duplicate analyses could be from the sampling process, possibly due to an inefficient homogenization procedure in the field. It could also be from the laboratory aliquoting process or it could be due to heterogeneity in the sample matrix. The effect on project objectives will depend on the screening criteria and how far above or below these criteria the results are. If the results are close to the criteria with significant variability, this may require collection of more samples to better represent the location. If results are significantly above or below the screening criteria with high variability, it may not adversely affect the ultimate decision-making process.

11.3.9 Acid Versus Anion Form of PFAAs

The data user must be aware of the form of PFAS the laboratory is reporting when comparing to project screening criteria. PFAS are typically formulated as acids, but they are present in the environment and in humans in the anionic form. The differences in names used are the result of the different names for the acid form and the anion form of the chemical (see also Section 2.2.3.1). For example, when perfluorobutanoic acid (PFBA) disassociates and loses its hydrogen in water, it becomes the anionic form (perfluorobutanoate). This becomes more important when looking at physical and chemical properties of these chemicals, because whether they exist as an acid, an anion, or a salt (cation) will affect how they behave in the environment. Typically, laboratories are reporting the acid form of the perfluorocarboxylic acids and the anionic form of the perfluorosulfonates.

Some target PFAS, such as PFHxS and PFOS, are not available as acids, but rather as their corresponding potassium or sodium salts (K⁺ or Na⁺). These salts are acceptable starting materials for the stock standards provided the measured mass is corrected for the salt content according to the equation below. Note that this correction will result in a minimal change to the mass of the acid but still must be performed for consistency and comparability with other results to ensure the data user that the correct form of PFAS is represented in the final concentration.

$$mass_{acid} = measured\ mass_{salt} * (MW_{acid} / MW_{salt})$$

MW_{acid} = molecular weight of PFAA

MW_{salt} = molecular weight of purchased salt

CAS numbers will change depending on if the acid or anion form of the PFAS is reported (Table 11-6).

Table 11-6. Example of CAS number differences between acid and anion

Chemical	CAS number
PFOA: Perfluorooctanoate (anion)	45285-51-6
PFOA: Perfluorooctanoic acid (acid)	335-67-1

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12 Treatment Technologies

The PFAS Team developed a training module video with content related to this section, it is the Treatment Technologies video.

This section provides information about treatment technologies for PFAS in environmental media. Treatment technologies for PFAS in environmental media are still evolving and it is prudent to use caution in implementing long-term remedies. Selection of remedial actions should prioritize protection of drinking water supplies and human health, with consideration of other objectives (such as reducing risk to ecological receptors and environmental resources, liability, source area mass, mass flux, generation of PFAAs from precursors). At some sites, it might be reasonable to take short-term site stabilization actions with the intent of applying more robust and cost-effective technologies as these are developed.

The treatment technologies described in this section are organized by degree of development and implementation, as well as current confidence in the technology based on peer-reviewed literature and the professional judgment of the authors. The levels are field-implemented technologies, limited application technologies, and developing technologies.

Section Number	Topic
12.1	Overview
12.2	Field-Implemented Liquids Treatment Technologies
12.3	Field-Implemented Solids Treatment Technologies
12.4	Incineration
12.5	Limited Application and Developing Liquids Treatment Technologies
12.6	Limited Application and Developing Solids Treatment Technologies
12.7	Integrated Remedial Solutions
12.8	Sustainability of PFAS Treatment
12.9	Improving Evaluation of PFAS Treatment Technologies

12.1 Overview

Treatment technologies exploit a contaminant's chemical and physical properties to immobilize, remove, or destroy the contaminant. The stability and surfactant nature of PFAS make many treatment technologies ineffective, including those that rely on contaminant volatilization (for example, air stripping, soil vapor extraction) or bioremediation (for example, biosparging, biostimulation, bioaugmentation). Even aggressive technologies such as thermal treatment and chemical oxidation require extreme conditions beyond typical practices (for example, extreme temperatures, high chemical doses, extreme pH) to be effective or partially effective in destroying PFAS.

Treatment technologies can be employed either ex situ or in situ. For example, when groundwater is extracted via pumping from wells and treated, this would be considered an ex situ approach. In contrast, when treatment materials are injected into the subsurface to immobilize contaminants in groundwater under the surface, this would be considered an in situ approach. Because existing treatment technologies have generally shown to be inadequate, the unique chemical properties of PFAS often require new technologies or innovative combinations of existing technologies.

A range of unproven technologies exist for treatment of either liquids or solids that may be performed either in situ or ex situ. However, the most demonstrated technologies for treating PFAS in liquids are limited to the use of ex situ technologies.

Full-scale treatment of PFAS-impacted liquids or solids is currently limited to sequestration technologies that remove or bind PFAS but do not destroy them. Sorption using granular activated carbon and ion exchange media has been proven effective at full scale (see Table 12-1, provided as separate PDF, for references). Transformation or destruction technologies, including bioremediation, chemical oxidation, chemical reduction, and thermal technologies, are currently being tested. This section discusses both proven and emerging treatment technologies for liquids (waters, leachates, or other liquid wastes) and solids (soil, sediment, or other solid wastes).

The treatment technologies described in this section are organized by degree of development and implementation, as well as current confidence in the technology based on peer-reviewed literature and the professional judgment of the authors. Three levels of implementation/confidence are defined as follows:

- *Field-implemented technologies*—Technologies that have been demonstrated under full-scale conditions at multiple sites, by multiple practitioners and multiple applications, and are well documented in practice or peer-reviewed literature. Stakeholder concerns about the effectiveness of certain treatment technologies, including the testing and analytical approaches to measure efficiency, are presented in Section 13.1.20.
- *Limited application technologies*—Technologies that have been implemented on a limited number of sites, by a limited number of practitioners, and may not have been documented in peer-reviewed literature. These limited application technologies for liquids and solids are contained in the technology comparison Tables 12-1 and 12-2 (provided as separate PDF) and discussed in Section 12.5 and Section 12.6.
- *Developing technologies*—Technologies that have been researched at the laboratory or bench scale, but have not been field demonstrated. Often, these results are reported by only one group (for example, one university, practitioner, or vendor) or lack detailed validation of the treatment effectiveness or mechanisms. Experimental techniques to treat PFAS are under development, but only those technologies that have some level of publicly available documentation demonstrating effectiveness are included here.

“Treatment” versus “Remedial Action”

The term “treatment” refers to the application of certain technologies to specific impacted media to achieve desired remedial action goals or objectives.

As defined in the Superfund Amendments and Reauthorization Act (SARA), a “remedial action” is the actual construction or implementation phase of a site cleanup. Remedial action has a broader context that includes concepts surrounding targeted clean-up levels and monitoring but also addresses issues related to administrative elements, long-range planning, and remediation/restoration.

Technology Selection

Selecting a technology to meet treatment targets is dependent on:

- an understanding of PFAS fate and transport
- a well-prepared conceptual site model
- proven remediation technologies
- defined (and achievable) treatment targets
- a stable regulatory environment.

The technology evaluations presented herein provide data for PFAS removal. This information varies widely among technologies and the data provided are based on the reported test conditions and results. Ultimately, the feasibility of a technology to meet applicable regulatory guidance values and standards often depends on site-specific conditions.

Currently in the United States, the regulatory standards for PFAS treatment are primarily driven by drinking water mitigation and focused on a small subset of PFAS. PFOS and PFOA are the only two compounds with federal regulatory guidelines

(USEPA 2016c, d), and most regulatory discharge criteria for PFAS focus on PFOS and PFOA. Some states have guidelines, and several have regulatory criteria for additional PFAS, but precursor and short-chain PFAS are generally not considered in regulations or guidance, although that is changing. The technology evaluation information presented here provides data about all PFAS tested for a given technology. This information varies widely among technologies. Additional information on regulations is provided in Section 8.

12.1.1 Factors Affecting Technology Selection

Selection of a remedy, with confidence that treatment targets can be achieved, depends on a number of key factors, including the ability to reliably define the nature and extent of contamination, the availability of proven remediation technologies, and the capacity and tools to measure progress and compliance with desired regulatory criteria. A well-prepared CSM requires adequate information and is also fundamental to understanding and presenting the rationale and justification for the selected remedy.

Moreover, proven remediation technologies are limited in capacity and demonstrated ability to meet chosen treatment targets. The comprehensive discussions contained herein reveal many questions and uncertainties that must be addressed.

Factors affecting PFAS remedy selection include:

- **characteristics of PFAS.** The wide-ranging chemical and physical characteristics of PFAS affect the treatment effectiveness. Key factors include recalcitrance to common technologies due to the strength of the carbon-fluorine bond, ionic state (anionic, cationic, and zwitterionic), types of ionic groups (sulfonate or carboxylate), lipo- and hydrophobicity, chain length and branching, partitioning coefficients, phase behavior, volatility, solubility, acidity, total PFAS mass, and total concentration.
- **changes in PFAS properties.** Naturally occurring processes or remedial actions for other (commingled) contaminants, such as chlorinated solvents and petroleum hydrocarbons, can affect PFAS distribution and mobility in groundwater (McGuire et al. 2014). Example changes include:
 - The alkyl functional group of some PFAA precursors may be more readily subject to chemical or biological transformation than the fully fluorinated aliphatic chain (PFAAs).
 - Partial degradation of the carbon-carbon bonds in the aliphatic chain reported for some chemical remedies generates short-chain PFAS, which may be more mobile (Guelfo and Higgins 2013).
 - Modifications in aquifer properties (for example, redox or pH) during remediation of commingled contaminants results in a conversion of some precursors to the more stable and mobile PFCAs (McKenzie et al. 2015; McKenzie et al. 2016).
- **co-contaminants, organic matter, and geochemistry.** The presence of co-contaminants, total organic carbon, natural organic matter, minerals, and anions can significantly affect remediation. Some technologies that are designed and implemented to treat PFAS co-contaminants may transform perfluoroalkyl acid (PFAA) precursors into more stable perfluorocarboxylic acids (PFCAs) (McKenzie et al. 2015).
- **community acceptance.** Stakeholders, including community members, are often faced with trade-offs in terms of cost, level of cleanup, and residual contamination as part of remediation efforts.

For those directly engaged in assessing the suitability of PFAS treatment technologies, a structured process for systematic evaluation is currently under development via a SERDP-funded project (ER18-1633). The project focuses on five lines of evidence to evaluate technology performance and will provide resources to identify relevant information and data gaps and address key questions necessary for that assessment. Additional information is provided in Section 12.8.

12.1.2 Section Organization

The information presented in the following sections reflects the availability of performance results published, presented, or posted to the internet. Those technologies that have been implemented in the field at multiple sites, by multiple parties, and have peer-reviewed documentation of performance are discussed in Section 12.2 and Section 12.3. Projects funded by SERDP and the Water Research Foundation (WRF) are also highlighted. This section discusses the following key elements for each of these field-implemented technologies:

- *treatment description*—background and development of technology
- *treatment mechanism*—separation, sorption, or destruction
- *state of development*—applications and degree of commercial availability
- *effectiveness*—documented treatment effectiveness on PFAS and common co-contaminants along with water quality considerations and pretreatment need and options

- *design/operating considerations* –critical or unique operational or design needs
- *sustainability*–footprint, community enhancement, and cost.

Treatment case studies are presented in Section 15.2. Note that air treatment technologies are not included in this section because the current research is limited to liquid and soil treatment technologies and air exposures are not presently a regulatory priority.

12.2 Field-Implemented Liquids Treatment Technologies

These technologies have been implemented in the field by multiple parties at multiple sites and the results have been documented well in the peer-reviewed literature. The liquid treatment technologies in this section may be applied to a variety of PFAS-impacted media, including drinking water (regardless of source), surface water, groundwater, wastewater, or landfill leachate. At this time, all technologies that are considered “field-implemented” are ex situ treatment systems, meaning PFAS-impacted water is extracted and treated. Although some of the technologies described in this section have been applied in situ, they are not considered field-implemented at this time. Not all technologies would be appropriate for all applications. Site-specific evaluation is necessary to identify the best technology alternative for a given treatment media or scenario.

12.2.1 Sorption Technologies

Sorption technologies have been used for both ex situ and in situ water treatment applications. In situ applications are not covered in this section, because they are still considered “limited application or developing technologies” as defined in this document. Multiple sorption media types may be used in series for ex situ applications to optimize overall concentration reduction and removal capacity. Adsorption and ion exchange are two “sorption” mechanisms by which PFAS can be removed from water. Adsorption is a physical mass transfer process that uses Van der Waals and/or other weak ionic forces to bind the entire PFAS molecule to the surface areas of the adsorptive media. Ion exchange is the exchange of ions of the same charge. Ion exchange targets and binds to the hydrophilic ionized or functional end of the molecule (for example, the sulfonate in PFOS) while releasing an equivalent amount of an innocuous ion (for example, chloride) into the treated water. A number of influent water parameters can therefore be expected to impact the sorption efficiency for a specific PFAS compound. These include pH, ionic strength, the nature and concentrations of organic co-contaminants present (including naturally occurring organic matter [NOM]), competing inorganic ions normally present (for example, sulfate, nitrate, bicarbonate, and chloride), and any suspended solids or potentially precipitating impurities (for example, iron, manganese, calcium carbonate) that can foul and degrade the performance of the media. Pretreatment steps may be necessary to optimize the performance of such media, including coagulation, precipitation, filtration, pH adjustment, or oxidant removal. Ion exchange media used for PFAS removal from water use both the adsorption and ion exchange mechanisms. The use of two or more different media in series can be considered if the expected increase in overall removal efficiency can be used to justify the increased equipment cost.

Life cycle cost assessments can be used to compare the long-term cost-performance benefits of various sorption media types. Spent media management can be an important cost component. Common options used at the time of publication for spent media management are off-site disposal by thermal destruction (via commercial incineration or cement kilns), reactivation/regeneration for reuse, and landfilling.

Incineration and thermal reactivation/regeneration offer the possibility of destruction of PFAS waste streams, though incineration has received recent attention due to possible incomplete combustion and by-product generation and is the topic of current study to better understand the fate of PFAS. Incineration is discussed in Section 12.4.

Key Cost Considerations for Sorption Media Selection

- PFAS mix and competitive species
- pretreatment needs
- influent concentrations
- flow rate
- discharge criteria
- media change-out criteria
- media disposal

Related Ongoing Research Funded by SERDP (ER) and Water Research Foundation (WRF)

- ER18-1395 Electrically Assisted Sorption and Desorption of PFASs
- ER18-1417 Molecular Design of Effective and Versatile Adsorbents for Ex Situ Treatment of AFFF-Impacted Groundwater
- ER18-1052 Remediation of PFAS Contaminated Groundwater Using Cationic Hydrophobic Polymers as Ultra-High Affinity Sorbents
- ER18-1306 Combined In Situ/Ex Situ Treatment Train for Remediation of Per- and Polyfluoroalkyl Substance (PFAS) Contaminated Groundwater
- ER18-5015 Removal and Destruction of PFAS and Co-contaminants from Groundwater via Groundwater Extraction and Treatment with Ion-Exchange Media, and On-Site Regeneration, Distillation, and Plasma Destruction
- ER18-B3-5053: Evaluation and Life Cycle Comparison of Ex-Situ Treatment Technologies for Poly- and Perfluoroalkyl Substances in Groundwater
- WRF 4913: Investigation of Treatment Alternatives for Short-Chain PFAS

12.2.1.1 Granular Activated Carbon (GAC)

Treatment Description: GAC is an effective sorbent media for organics that has historically been used to reduce contaminants in a variety of water treatment applications. The information contained in this section describes ex situ GAC treatment in which water is extracted and transferred from the source of contamination and directed through the treatment system.

Treatment Mechanism: Removal of PFAS by GAC is a physical mass transfer process (refer to Section 12.2.1) from the aqueous phase onto solid media that does not involve or trigger any form of chemical degradation or transformation.

State of Development: GAC is an established water treatment technology proven to effectively treat long-chain PFAS (such as PFOS, PFOA, and PFNA). The application of GAC as a treatment technology for PFAS removal has been practiced for over 15 years at more than 45 military installations, as well as several industrial sites and publicly owned treatment works (Forrester 2018) involving private and municipal drinking water supplies.

Effectiveness: The following references were used to support the treatability effectiveness discussion presented below for long-chain PFAS by GAC: Appleman et al. (2013); Burdick et al. (2016); Cummings (2015); Dickenson (2016); Ochoa-Herrera and Sierra-Alvarez (2008); Szabo (2017) and Woodard, Berry, and Newman (2017). These references also include more comprehensive bibliographies if further details are needed on specific topics or studies. Literature and supporting column studies have shown that newly placed GAC can reduce effluent concentrations for PFAS listed in USEPA Method 537.1 (Shoemaker and Tettenhorst 2018) to below analytical detection limits until initial breakthrough begins to occur. The adsorption removal mechanism is not expected to transform precursors (for example, telomer alcohols) to terminal PFAS as would be the case when using advanced oxidation/reduction technology. Because GAC is generally used to treat many common groundwater contaminants, it is capable of also treating most organic co-contaminants that may be present, with the primary impact being increased GAC consumption due to greater loading per unit of time, which may require more frequent change-outs.

Individual PFAS have different GAC loading capacities and corresponding breakthrough times (often defined as the number of bed volumes treated prior to detection in the effluent) (Eschauzier et al. 2012). GAC removal capacity for PFOS is greater than PFOA, but both can be effectively removed (McCleaf et al. 2017). In general, shorter chain PFAS have lower GAC loading capacities and faster breakthrough times, but could be effectively treated if changeout frequency is increased. Figure 12-1 provides an example of removal curves and breakthrough information for a number of PFAS performed at a specific influent concentration based on vendor-supplied column studies.

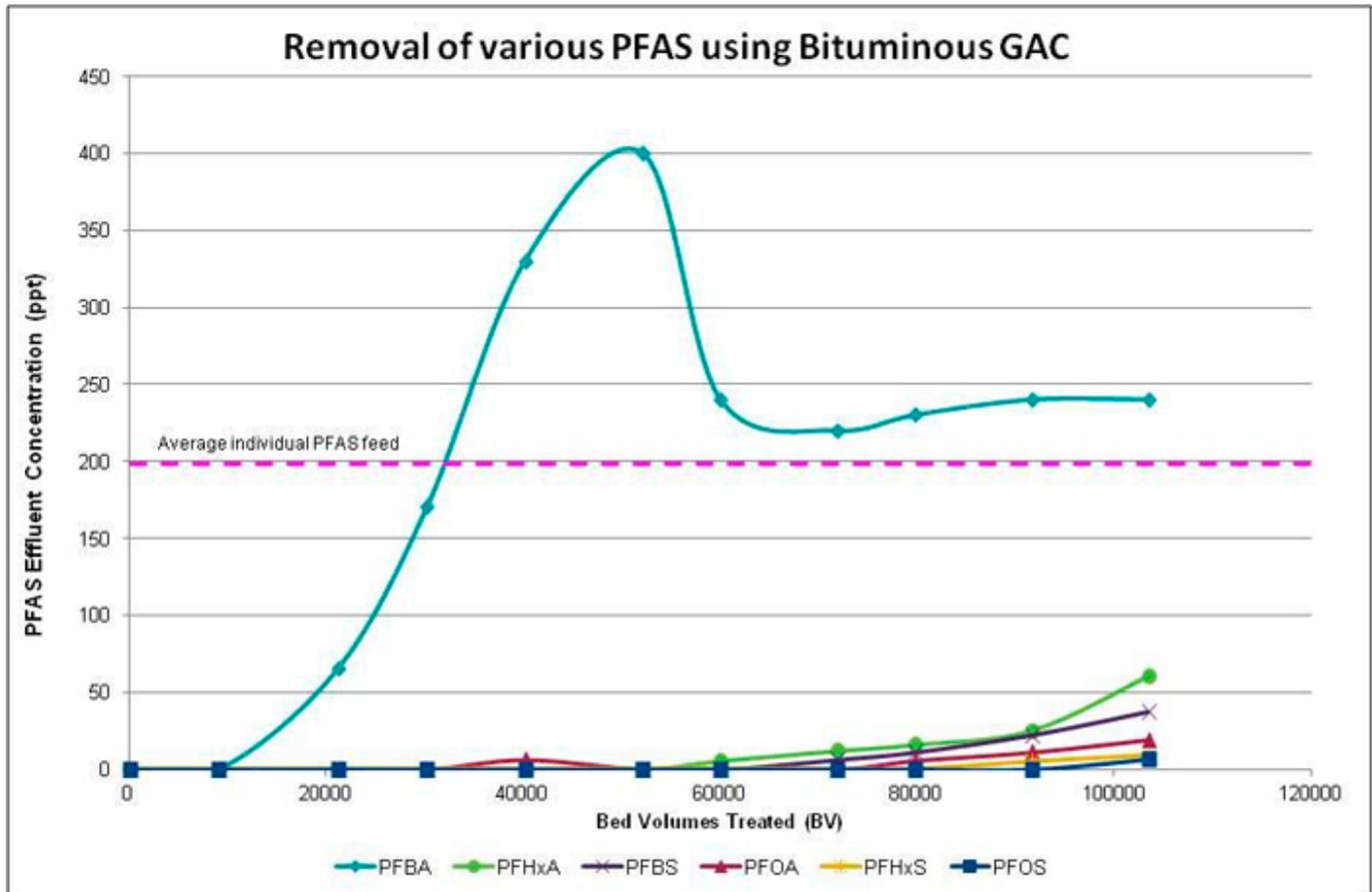


Figure 12-1. Example GAC removal curves at specific influent concentration (15-minute empty bed contact time).

Source: Used with permission from Calgon Carbon Corporation.

More studies are needed to confirm GAC treatment effectiveness for shorter chain PFAS or to identify complementary technologies/materials to supplement GAC removal capability. This may include studying the influence on sorption site competition from PFAS precursors that are often not quantified during the GAC system design. Recent accelerated column tests by vendors have shown the successful removal of a variety of PFAS, including the butyl (C4), pentyl (C5), and hexyl (C6) compounds (Appleman et al. 2013; Dickenson 2016; Brewer 2017). Functional groups also impact the ability of GAC to adsorb PFAS compounds. Compounds with sulfonate and sulfonamide groups are more readily adsorbed than those with carboxylates (Appleman et al. 2013; Dickenson 2016). Studies currently in the developmental stage involve the use of other materials that can modify GAC surfaces to improve removal capabilities. Mixtures of powdered activated carbon, kaolinite, and amorphous hydroxide have been tested at the bench- and pilot-scale and have shown high removal rates for shorter chain PFAS in raw AFFF-impacted groundwater (Chiang 2017; Kempisty, Xing, and Racz 2018).

Most GAC full-scale treatment system case studies to date are based on treatment of PFOA and PFOS in the impacted drinking water sources. As such, limited information is available regarding the treatment of other PFAS. The full-scale drinking water systems demonstrate that PFOA and PFOS can be removed to below analytical detection limits until breakthrough occurs. More information is available in Table 12-1 posted as a separate PDF. Treatment of groundwater impacted with PFAS from an AFFF release area contaminated with PFAS such as fire training areas (FTAs) may require complex pretreatment and more frequent change-outs (higher influent concentrations compared to influent for drinking water treatment systems) and higher operation and maintenance (O&M) costs.

Design/Operating Considerations: Laboratory treatability tests (for example, rapid small-scale column testing (RSSCT) and accelerated column test (ACT)) are useful for evaluating treatability and determining initial design parameters. Larger scale pilot demonstrations are recommended to establish site-specific design parameters such as adsorption bed depth; GAC consumption rate to meet a given treatment objective; empty bed contact times (EBCTs); projections of breakthrough (based on bed volumes treated); and corresponding change-out frequency/costs. Column studies can also be used to compare loading capacity/breakthrough performance for different types of GAC (for example, different materials, preparation methods, and pore size distributions) offered by various vendors. These studies should always use site water to

ensure that the effects of site-specific geochemical characteristics are assessed. Alternative analytical screening methods, for example, total oxidizable precursor (TOP) Assay (Section 11.2.2.2) and particle induced gamma ray emission (PIGE) (Section 11.2.2.3), can be used to better estimate potential total mass load during the GAC remedial design phase. Field performance of GAC systems often varies significantly from that predicted in the RSSCT and other bench tests. Proper monitoring is critical to demonstrate that the desired performance is being achieved, especially at system start-up and following media change-out events.

Temporary and permanent GAC systems can be rapidly deployed and require minimal operator attention, if intensive pretreatment is not needed. The GAC media are placed in packed-bed flow-through vessels generally operated in series (lead-lag configuration). EBCTs of 10-15 minutes per vessel are typical. PFAS breakthrough is monitored by testing the water, at a minimum, between the lead and lag vessels. Additional sampling ports can be added (for example, at 25%, 50%, and 75% of the depth of the media). When breakthrough exceeds identified change-out criteria, the lead bed is taken offline and the spent GAC is removed and replaced with either new or reactivated GAC. The spent media are disposed off site by thermal destruction or can be thermally reactivated for reuse. Treatment can be continuous if the lag bed is used as the lead bed while the media in the latter are changed out. Figure 12-2 depicts a simple process flow diagram for a GAC treatment system.

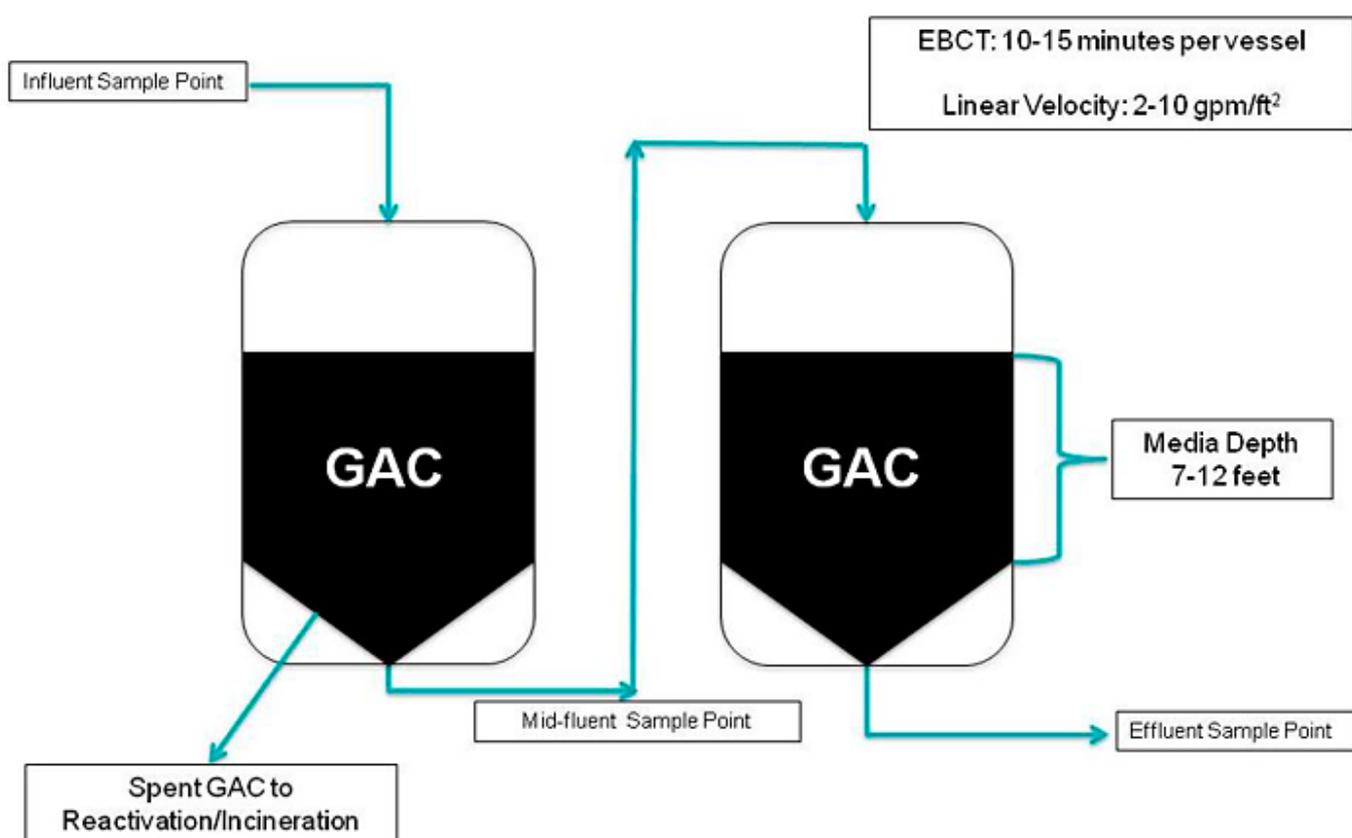


Figure 12-2. Typical GAC treatment system process flow diagram.

Source: Used with permission from Calgon Carbon Corporation.

Various GAC base materials (for example, bituminous coal, lignite coal, coconut shells) can be used for adsorption, though bituminous coal-based GAC has been used for the majority of existing sorption treatment systems for PFAS and current data show that bituminous-based products are more effective for PFAS removal (McNamara et al. 2018; Westreich et al. 2018). Specialized GAC formulations and coconut-based GAC can also be effective. Media selection and life cycle cost will depend upon a number of factors, including PFAS and co-contaminant concentrations, media availability, and pricing.

GAC treatment applications will evolve as analytical methods improve and regulatory concerns encompass an increasing number of PFAS. Shorter chain PFAS exhibit faster breakthrough times as mass loading rates increase (Appleman et al. 2013), so particular attention needs to be given to these compounds if their removal is required. Alternative design optimization approaches or use of other technologies in combination with GAC (for example, ion exchange (IX) resins discussed in Section 12.2.1.2) can address high O&M costs that can be incurred for GAC treatment involving high influent PFAS concentrations, especially if shorter chain PFAS must be removed. As discussed in Section 12.2.1.2, specialty single-

use and regenerable IX resins have been developed that have higher loading capacities for shorter chain PFAS. GAC and IX can also be used in series to optimize removal capacity and minimize O&M costs, generally with GAC ahead of IX to remove non-PFAS organics and longer carbon chain PFAS, followed by IX to remove the shorter carbon chain PFAS. This approach has been implemented in the field and is presented in a case study in Section 15.2.2.1.

Spent GAC that contains PFAS can be thermally reactivated and reused, which may result in a lower cost media replacement option versus new GAC. However, some regulatory agencies may not allow the use of reactivated GAC for drinking water systems. NSF/ANSI standards require that the use of reactivated GAC for drinking water systems involve only media generated by the treatment system owner/operator and cannot include a mixture of GAC that originated from other sources. The management of spent media should be planned during the life cycle assessment phase and be documented as the treatment system is executed. Commercial facilities are available for thermal reactivation of spent GAC, which currently are not available for other sorption media and can offer a potential life cycle cost benefit for spent media disposal. Based on vendor feedback (Mimna 2017), commercial thermal GAC reactivation is performed at higher operating temperatures than steam or nitrogen regeneration systems, and may be capable of complete desorption and destruction of PFAS from spent GAC (Watanabe et al. 2016; Yamada et al. 2005). However, similar to incineration, additional studies are needed to investigate the fate of PFAS in the GAC reactivation process.

Sustainability: GAC ex situ PFAS water treatment systems have unique sustainability considerations as well as considerations in common with other ex situ PFAS sorption media water treatment systems (treatment complex construction, utilities, water collection and pumping, and discharge infrastructure). Major sustainability considerations unique to GAC systems are associated with:

- raw material collection and transportation
- GAC manufacturing and transportation
- larger media vessels relative to IX due to longer EBCTs
- larger treatment complex size due to larger vessels
- spent media transportation followed by reactivation, destruction, or disposal.

Multiple resources are available for performing sustainability assessments for sorption remedial designs (Amini et al. 2015; Choe et al. 2013; Choe et al. 2015; Dominguez-Ramos et al. 2014; Favara et al. 2016; Maul et al. 2014; Rahman et al. 2014; Ras and von Blottnitz 2012).

12.2.1.2 Ion Exchange Resin

Treatment Description: IX is an effective sorbent for other contaminants and has historically been used for a variety of water treatment applications (for example, nitrate, perchlorate, arsenic). To date, IX for PFAS removal from water is limited to ex situ applications.

IX resin options for removal of PFAS include single-use and regenerable resins. Single-use resins are used until breakthrough occurs at a pre-established threshold and are then removed from the vessel and currently disposed of by high temperature incineration or by landfilling, where permitted. Regenerable resins are used until breakthrough but are then regenerated on site using a regenerant solution capable of returning the full exchange capacity to the resin. Temporary and permanent IX systems can be rapidly deployed.

Related Ongoing Research Funded by SERDP (ER) and Water Research Foundation (WRF):

- ER18-1027 Ex Situ Treatment of PFAS Contaminated Groundwater Using Ion Exchange with Regeneration
- ER18-1063 Regenerable Resin Sorbent Technologies with Regenerant Solution Recycling for Sustainable Treatment of PFASs
- ER 18-5015 Removal and Destruction of PFAS and Co-Contaminants from Groundwater via Groundwater Extraction and Treatment with Ion-Exchange Media, and On-site Regeneration, Distillation, and Plasma Destruction
- ER 18-1306 Combined In Situ/Ex Situ Treatment Train for Remediation of Per- and Polyfluoroalkyl Substance (PFAS) Contaminated Groundwater
- ER18-5053: Evaluation and Life Cycle Comparison of Ex-Situ Treatment Technologies for Poly- and Perfluoroalkyl Substances in Groundwater
- WRF 4913: Investigation of Treatment Alternatives for Short Chain PFAS

Treatment Mechanism: Removal of PFAS by IX is a physical mass transfer process from the aqueous phase onto solid

media that does not involve any form of chemical degradation or transformation. IX resins with positively charged functional groups can readily remove negatively charged PFAS compounds from water by forming ionic bonds (the sulfonic and carboxylic acid heads of PFOS and PFOA are negatively charged at the typical range of pH values found in natural water). Simultaneously, the hydrophobic end of the PFAS structures can adsorb onto the hydrophobic surfaces of the IX resins. This dual removal mechanism can exhibit higher selectivity versus other sorption media that function largely by adsorption alone.

State of Development: Ion exchange technology has been used since the late 1930s for common water treatment processes like softening, demineralization, and selective contaminant removal. The development and use of selective resins for PFAS removal is relatively new but already well established. As of 2019, a limited number of regenerable IX systems have been installed in full-scale applications after successful pilot testing. Collection of data on longer term treatment and on-site regeneration of the IX resin is ongoing at a case study site (Section 15.2.2.2). In general, the removal capacity of the single-use resin is higher than that of regenerable resin, and single-use resin can be more fully exhausted in a lead-lag vessel configuration than regenerable resin. The relative efficiency of regenerable and single-use resins depends upon PFAS and co-contaminant influent concentrations and treatment goals.

Effectiveness: Selective IX has been demonstrated to reduce concentrations for a broad suite of PFAS at the bench and field scale for influent concentrations as high as 100s of parts per billion (ppb) total PFAS to below analytical detection limits in effluent (Kothawala et al. 2017; McCleaf et al. 2017; Woodard, Berry, and Newman 2017). The affinity of such resin for common subgroups of PFAS generally follows the order PFSA > PFCA. Within each subgroup, affinity increases with increasing carbon chain length, and are not necessarily sequential (that is, longer chain PFCA may be adsorbed better than shorter chain PFSA).

In general, IX resin systems being used for PFAS removal are not installed with the intention of removing co-contaminants. Co-contaminants (including organic and inorganic compounds) may significantly reduce the removal capacity of IX for PFAS, although this depends on the selectivity of the IX resin. Because of the variability in resin behavior, as well as groundwater chemistry, influent characterization is needed to assess potential pretreatment options to remove co-contaminants. Pretreatment is necessary to preserve resin capacity for PFAS removal, particularly in the context of remediation where complex co-contaminant chemistry is expected. Pretreatment needs for drinking water applications may be simpler or not required.

Single-use PFAS-selective IX resins are well-suited to treat low-concentration PFAS such as is typically encountered in potable water treatment systems, where media change-out would be infrequent. Figure 12-3 provides an example of removal curves and breakthrough information for a number of PFAS at the specified influent concentrations (in the legend) based on vendor-supplied data for a full-scale single-use system.

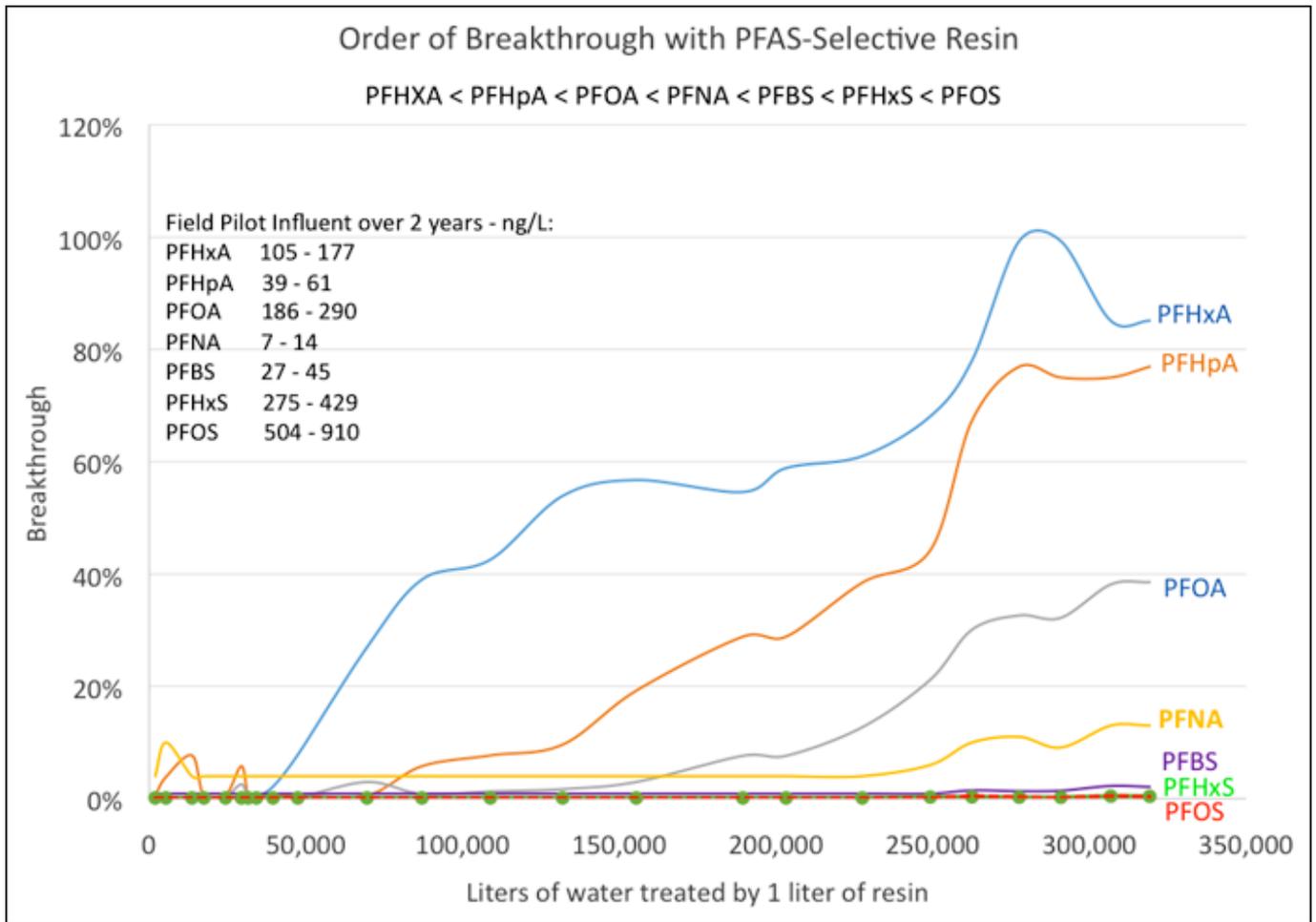


Figure 12-3. Example of IX removal curves at specific influent concentrations (2.5-minute EBCT).

Source: Used with permission from Purolite Corporation.

Regenerable resins are better suited for removal of higher concentration PFAS where the savings realized from reusing the treatment media outweighs the cost of frequent replacement of nonregenerable media. Depending on the treated water discharge goals, evaluation of regenerable resin could be warranted once influent concentrations exceed 10 ppb total PFAS, such as would be encountered in groundwater remediation at or near PFAS release areas. Regenerable resins can be more efficient for treating higher ppb influent levels of PFAS where the cost of the regeneration system may pay for itself over time as compared to disposal and replacement cost for single-use resin. An example of typical breakthrough curves for regenerable resin system is shown in Figure 12-4. On the graph the y-axis is sample concentration/original concentration (C/C_0), also note the influent PFAS concentrations (in the legend) in Figure 12-4 are higher (reported in ppb) than presented in Figure 12-3 (reported in ppt). Additional details on a regenerable resin system are provided in a case study in Section 15.2.2.2. The cost effectiveness for regenerable resin systems increases significantly when a central regeneration facility can be shared amongst multiple PFAS removal systems. The application of single-use versus regenerable resins must be evaluated on a site-specific basis.

Example Breakthrough Characteristics
 Regenerable IX Media - 2.5 min EBCT; Total PFAS ~ 90 ppb

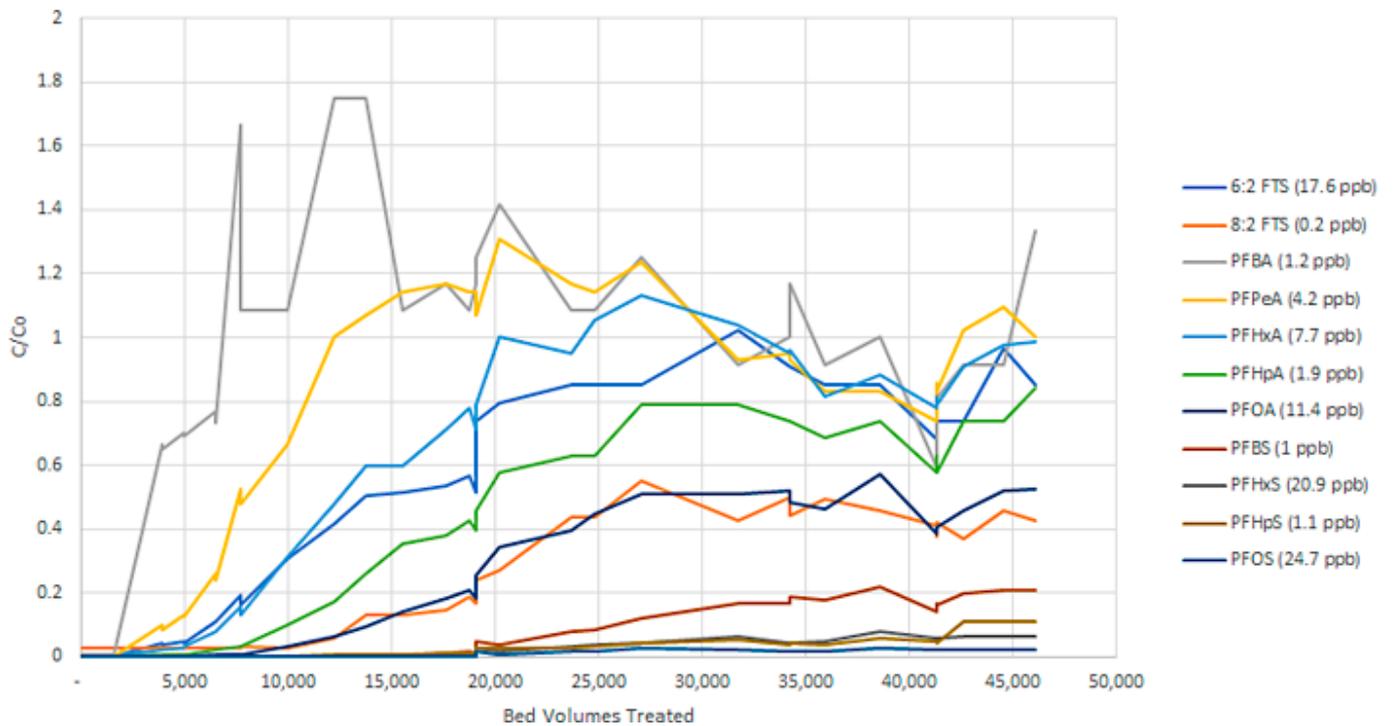


Figure 12-4. Example of regenerable IX removal curves at specific influent concentrations (2.5-minute EBCT).

Source: Used with permission from ECT2.

Design/Operating Considerations: IX treatment systems are configured similarly to GAC systems. Refer to Section 12.2.1 for a description of GAC systems that also applies to IX systems. Figure 12-5 depicts a simple process flow diagram for a single-use IX treatment system.

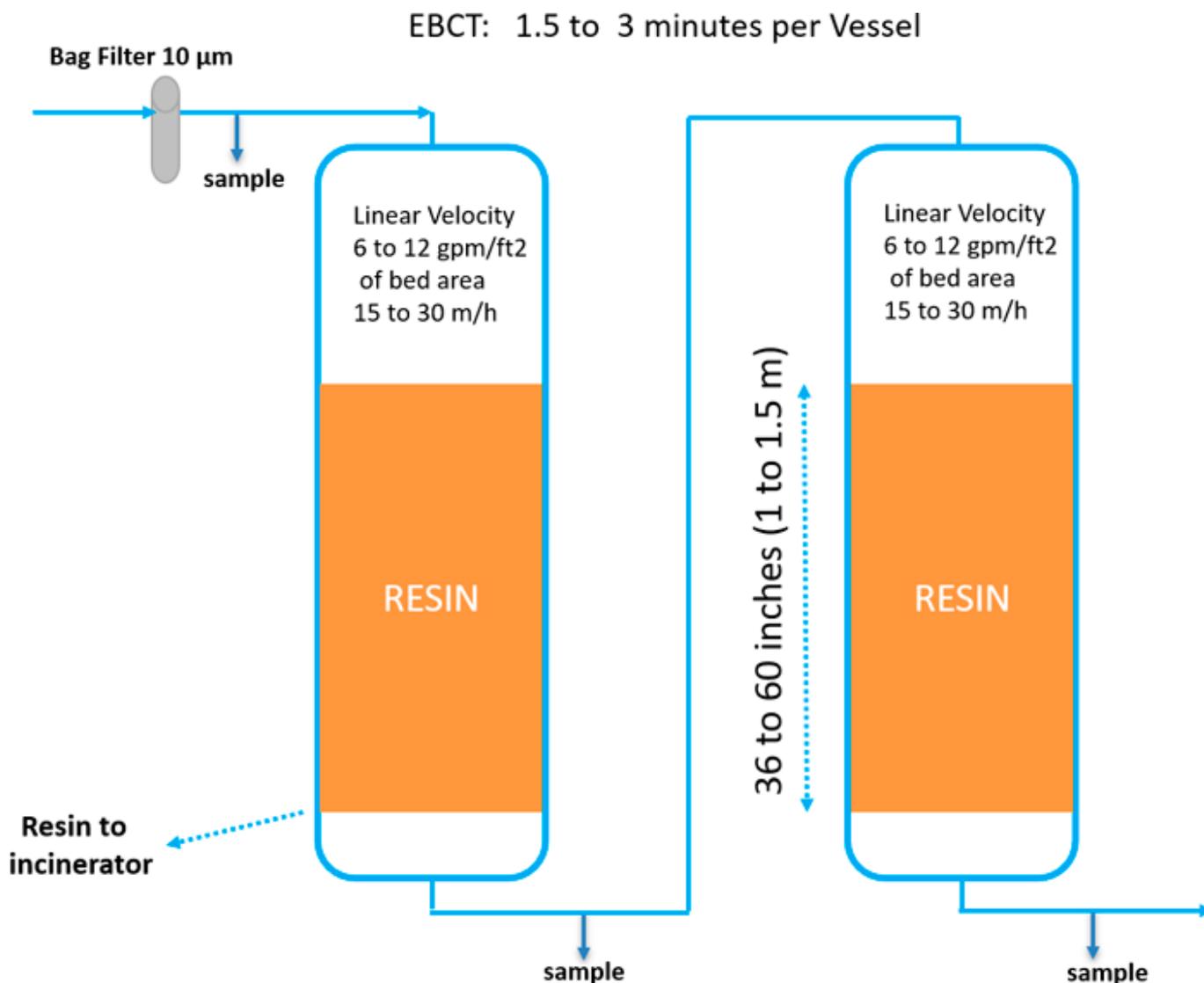


Figure 12-5. Single-use IX process flow diagram.

Source: Used with permission from Puralite Corporation.

IX technology features include:

- high selectivity—single-use IX resins can be used to selectively target more mobile PFAS (for example, shorter chain PFAS), although results will depend on water chemistry
- greater capacity, faster kinetics, and lower EBCT compared with GAC, resulting in smaller vessel size and potentially less frequent media change-out
- ability to consistently reduce PFAS to low ppt levels
- simultaneous removal of ionic co-contaminants
- for regenerable resins, the possibility of reduced operating and disposal costs as compared to single-use IX.

Selective IX requires a relatively short EBCT of 1.5–5 minutes per vessel of resin (Boodoo 2017), hence smaller resin volumes and smaller, less costly treatment vessels for a specific application. Selective IX resins have shown high operating capacities when removing trace levels of PFAS (for example, 200,000–300,000 bed volumes; refer to Figure 12-5), resulting in fewer change-outs of spent IX resin and reduced O&M costs.

Selective IX resins show much higher selectivity for PFAS compounds than for common anions in water such as sulfate (SO_4^{2-}), nitrate (NO_3^-), chloride (Cl^-), and bicarbonate (HCO_3^-). However, these common anions are generally present in water at about three orders of magnitude higher than PFAS and will be the main competitors for the ion exchange sites on the resin. As such, they will largely determine the operating capacity of such resins. The choice between single-use and regenerable resins will in part be determined by the expected service period before the resin must be either replaced (single-use) or regenerated.

Regenerable IX resin can be reused for many years if protected from contact with strong oxidizing agents, foulants, and chemical/mechanical stresses. To date, insufficient operating data are available for PFAS regenerable systems to understand the long-term durability of regenerable resin because the first regenerable IX systems were installed in 2018. IX regeneration is a chemical process. The only field-demonstrated regeneration method capable of fully restoring PFAS removal capacity is a proprietary process using a solvent-brine solution, where the brine dislodges the ionic head of the PFAS molecule and the solvent desorbs the fluorinated carbon chain (or “tail”) from the IX resin (Woodard, Berry, and Newman 2017; Amec Foster Wheeler 2017). For a regenerable IX system, it is possible to concentrate the regenerant solution and reuse it by distillation (Nickelsen and Woodard 2017). The distillate residue then contains a concentrated PFAS waste that can be super-loaded onto specialized resin to create a small volume of solid waste that can be managed by off-site disposal or potentially through on-site destruction using other technologies currently under development and discussed in Table 12-1 (provided as separate PDF) (for example, plasma or electrochemical destruction).

Sustainability: Resin ex situ PFAS water treatment systems have unique sustainability considerations in addition to those shared with other ex situ PFAS sorption media water treatment systems. Major sustainability costs unique to resin systems are associated with;

- raw material collection and transportation
- resin manufacturing and transportation
- regeneration of multiple-use resin
- generation, use, and disposal or destruction of regeneration residuals
- spent single-use and, eventually, multiple-use media transportation followed by destruction or disposal.

12.2.2 Reverse Osmosis (RO)

RO is a technology used to remove a large majority of contaminants (including PFAS) from water by pushing the water under pressure through a semipermeable membrane as described below. The most common membrane module configuration is spiral-wound, which consists of flat sheet membrane material wrapped around a central collection tube.

Treatment Description: RO membranes are effective in removing most organic and inorganic compounds from water solutions. In recent years, new polymer chemistry and manufacturing processes have improved efficiency, lowering operating pressures and reducing costs. As a result, RO membranes are increasingly used by industry to concentrate or remove chemicals. RO is commonly used around the world in household drinking water purification systems, the production of bottled mineral water, self-contained water purification units (for example, for branches of the U.S. military), and industrial applications (for example, water supply to cooling towers, boilers, and deionized water). The largest application of RO is in desalination.

Treatment Mechanism: RO removes compounds from water solutions by passing pressurized water across a semipermeable membrane. Treated water (permeate) passes through the membrane and the rejected water (concentrate) is collected for disposal or discharge, depending on the nature of the compounds present.

State of Development: RO has been studied in bench-scale studies and pilot plants for wastewater and drinking water applications, offering the opportunity to compare both treatments operating simultaneously (Tang et al. 2006; Tang et al. 2007; Flores 2013; Glover, Quiñones, and Dickenson 2018; Dickenson 2016; Merino et al. 2016; Appleman 2014; Snyder 2007). This allows for an understanding of the effectiveness of traditional drinking and wastewater treatment methods alongside PFAS-specific technologies.

Effectiveness: Pretreatment is important when working with RO membranes. Membranes are highly susceptible to fouling (loss of production capacity) because some accumulated material cannot be removed from the membrane surface. Therefore, effective pretreatment to remove suspended solids is a necessity for any RO system. Pretreatment technologies would be specific to the RO feedwater quality.

RO removal of PFAS from various waters (for example, semiconductor wastewater, drinking water, surface water, and reclaimed water) has been studied and several studies have combined RO with nanofiltration (NF). NF is discussed in Section 12.4.3. PFOS removal > 99% was achieved using four different types of membranes over a wide range of feed concentrations (0.5–1,500 ppm [mg/L]) (Tang et al. 2006). Another study by Tang et al. (2007) tested five RO and three NF membranes at feed concentrations of 10 ppm PFOS over 4 days. The PFOS rejection and permeate flux performances were > 99% for RO and 90–99% for NF (note that 99.9993% removal would be required to reduce 10 ppm to the USEPA health advisory of 70 ppt). The use of RO and NF as advanced drinking water treatments is still limited, but both technologies have

been shown to be successful for the removal of longer chain (> C5) PFAAs (Loi-Brügger et al. 2008; Tang et al. 2006).

Thompson et al. (2011) studied the fate of perfluorinated sulfonates (PFSAs) and carboxylic acids (PFCAs) in two water reclamation plants that further treat water from wastewater treatment plants (WWTPs) in Australia. One plant (Plant A) used adsorption and filtration methods alongside ozonation; the other (Plant B) used membrane processes and an advanced oxidation process to produce purified recycled water. At both facilities, PFOS, perfluorohexane sulfonate (PFHxS), perfluorohexanoate (PFHxA), and PFOA were the most frequently detected PFAS. Comparing the two reclamation facilities, Plant A showed some removal during the adsorption/filtration stages. Overall, however, Plant A failed to completely remove PFOS and the PFCAs shorter than PFNA in chain length. All PFAS present were removed by RO at Plant B from the finished water to concentrations below detection and reporting limits (0.4–1.5 ng/L).

Design/Operating Considerations: This section refers to design and operating considerations for both RO and NF systems. In the process of planning and implementing a membrane filtration system, there are several important issues that affect system design and operation and could impact system performance and thus PFAS removal. These issues include membrane flux, water quality, and temperature.

- **Membrane Flux:** One of the major challenges in the application of membrane technology is fouling (significant flux loss due to continuous accumulation of colloidal and organic matter, precipitation of inorganic salts, and/or microbial growth). There are several ways to avoid fouling: (1) changing operating conditions, (2) modifying the membrane, and (3) modifying the feed by adding antifoulants prior to filtration system (pretreatment) (Roux et al. 2005). Adequate pretreatment and appropriate membrane selection can slow the fouling rate, but the membrane cleaning is an essential step in maintaining the performance of the membrane process. Membrane replacement is a necessary part of plant operation to maintain the quality of the produced water (Abdul-Kareem Al-Sofi 2001). Although there are a number of cleaning techniques, such as physical or chemical or a combination of both, only the chemical cleaning methods are widely used by NF and RO industries for membrane cleaning and regeneration. Spent cleaning solution may contain PFAS and would need to be managed properly.
- **Water Quality:** Because water quality can have a significant impact on membrane flux, feedwater quality is also a primary design consideration for membrane filtration systems. Poorer water quality will require lower fluxes, which in turn increase the necessary membrane area and required number of modules, adding to both the cost and the size of the system. However, pretreatment can often improve feedwater quality at a lower cost than additional membrane area.
- **Temperature:** Like other water quality parameters such as turbidity and total dissolved solids (TDS) (for NF/RO systems), the temperature of the feedwater also affects the flux of a membrane filtration system. Water becomes increasingly viscous at lower temperatures; thus, lower temperatures reduce the flux across the membrane at constant transmembrane pressure or alternatively require an increase in pressure to maintain constant flux. Because rejection decreases as membrane pores expand at higher temperatures, more leakage of PFAS across the membrane could occur at higher operating temperatures.

Sustainability: The environmental footprint for this technology includes energy source and consumption during treatment system operation, as well as manufacturing/disposal of pretreatment/treatment media (examples may include solids from upstream precipitation/coagulation or microfiltration, used cartridge filters, and worn RO membrane modules) and cleaning solutions to maintain the membrane. RO requires power for high-pressure pumps and the management of concentrate, which can be energy-intensive.

An issue inherent to contaminant removal by membrane processes is the disposal of the PFAS-enriched concentrate, which must be carefully considered. Development of effective treatment methods for the concentrate entails evaluating significant parameters, such as volume generated, concentration, characteristics of the feedwater, and operational conditions, and using well-verified analytical methods to detect trace amounts of contaminants. Recycling concentrate to main treatment units is not the only option, and further research on integrated treatment systems must be performed (Joo and Tansel 2015). The reject stream will contain PFAS-enriched concentrate, which needs to be appropriately managed through treatment, permitted discharge, or disposal.

12.2.3 Drinking Water Applications

Remedial actions for PFAS-impacted drinking water from private wells and municipal supplies can include providing alternative drinking water sources, such as bottled water, new nonimpacted source wells or surface water, point of entry

(POE) treatment (also referred to as POET), and point of use (POU) treatment. POE treats water as it enters a home or building (for example, immediately after a pressure tank for a private well system) and POU treats water at one or more specific locations (for example, at a kitchen faucet where water is typically directly ingested or used for cooking). POE systems provide “whole supply” treatment while POU provides selected usage point treatment.

NSF International has developed a testing method and protocol, P473: Drinking Water Treatment Units-PFOA and PFOS, to verify the ability of a water treatment device to reduce PFOA and PFOS to achieve the USEPA health advisory levels of 70 ng/L (NSF International 2018). This method does not evaluate the removal of other PFAS or other organics, metals, and nonorganic compounds that also may adversely impact water supplies. Current systems with this certification are mainly small-scale POU systems such as sink faucet filters, refrigerator water filters, and pour-through filters. It should be recognized that although this certification exists, it is not required. This means that other POU systems as well as POE systems (larger well head or large public-serving systems) may not be certified under NSF P473 but may be acceptable for treatment of PFOA and PFOS. Public serving system components are required to be certified through NSF 61, which certifies that they are acceptable for potable water use. Treatment for PFAS in these systems typically uses adsorbents, GAC (Section 12.2.1.1) or IX (Section 12.2.1.2) or RO (Section 12.2.2).

12.3 Field-Implemented Solids Treatment Technologies

Field-implemented technologies are those that have been implemented in the field by multiple parties at multiple sites and the results have been documented well in the peer-reviewed literature. The technologies in this section may be applied to a variety of PFAS-impacted media, including soil, sediments, or sludge. Site-specific evaluation is always needed to identify the best technology alternative for a given treatment scenario. As with water treatment, solids treatment can be performed ex situ (for example, excavation or dredging) or in situ (for example, injection or reactive capping). At present, field-implemented solids treatment has been performed almost entirely ex situ. There are currently two known field-implemented technologies for treating soil contaminated with PFAS: sorption/stabilization and excavation/disposal.

12.3.1 Sorption and Stabilization

Treatment Description: Amendments are added to the soil and sediment to reduce the potential for PFAS to mobilize from soil and sediment to groundwater and surface water. For sorption purposes, PFAS-adsorbing materials (for example, activated carbon) can be applied through in situ soil mixing or ex situ stabilization (for example, pug mill mixing) to reduce the leachability of PFAS from contaminated soil/sediment through physical and/or chemical bonding.

Sorption and stabilization (considered “immobilization” or “chemical fixation” technologies) is a relatively quick, simple, and low-cost (relative to off-site disposal) way to reduce ongoing PFAS contamination transport to waterways and groundwater from source zones. The main disadvantage is that these technologies do not destroy the contaminants, but rather bind or immobilize them. For some amendments, established test methods have shown the binding to be stable over the long-term (see below).

Treatment Mechanism: Amendments adsorb or stabilize PFAS to reduce their release from soil. This occurs primarily through electrostatic interactions between the negative charge on the PFAS functional group and the positive charges on the sorbent and hydrophobic interactions between the amendment and the electronegative carbon-fluorine chain on the PFAS. Typical amendments that have been demonstrated in the field include activated carbon and composite materials such as a blend of aluminum hydroxide, kaolin, and carbon specifically designed to treat anionic, cationic, and zwitterionic long- and short-chain PFAS (Kempisty, Xing, and Racz 2018).

State of Development: Sorption and stabilization techniques using carbon-based amendments are considered field-implemented technologies. Various amendments have been applied to soil/sediment both in situ and ex situ. Different delivery methods for amendments, such as injection or in situ mixing (ISM), may provide different results depending on geology and objectives. Carbon amendments have been modified to enhance their sorption of PFAS. One patented amendment consists of activated carbon enhanced with amorphous aluminum hydroxide, kaolin clay, and other proprietary additives (USEPA 2017p). This amendment has been used to immobilize PFAS-impacted soil at field-scale in Australia and Europe and at laboratory-scale in the United States. In 2015, a large-scale project involved the ex situ treatment of 900 tons of PFAS-impacted soil from an airport site in Australia (Stewart 2017).

Effectiveness: Carbon- and mineral-based sorption and stabilization techniques vary in their effectiveness according to site conditions, PFAS types, and mixing approaches. The PFAS characteristic that determines sorption is length of carbon-fluorine chain, with longer chains having increased sorption (Xiao, Ulrich, et al. 2017).

Some specifically designed amendments have the ability to bind short- and long-chain compounds using different mechanisms (Stewart, Lawrence and Kirk 2016). The carbon component binds to the hydrophobic backbone of longer chain PFAS, while the negatively charged functional groups of the PFAS anions bind electrostatically to the positively charged surfaces of aluminum hydroxide. Furthermore, the amorphous form of aluminum hydroxide presents a relatively high surface area of positive charges, and the pKa of around 9.1 means that these surfaces remain positively charged over a wide environmental pH range (~pH 3 to pH 9.1). The kaolin component contains some negatively charged surfaces that theoretically have the ability to sorb PFAS cations and zwitterions (Stewart, Lawrence and Kirk 2016; Kempisty, Xing, and Racz 2018). However, standard analytical methods do not quantify cations and zwitterions, and actual field performance on these PFAS compounds is generally undemonstrated.

The charge on the PFAS compounds affects sorption (for example, cations sorb more readily than zwitterions and anions). Aquifer and soil chemistry also affect the sorptive ability of PFAS onto the amendments. High organic content in soil can reduce effectiveness (NGWA 2017). Low pH, the presence of polyvalent cations in the soil, or treatment amendment also increases sorption, retardation, and metals precipitation. An independent study at the University of Adelaide, Australia, showed that environmental ranges of pH and ionic strength did not adversely affect the binding of a specialized amendment to PFOA (Lath et al. 2018). Co-contaminants also play a role in the effectiveness of PFAS sorption. A recent review article (Li, Oliver, and Kookana 2018) showed that the organic carbon component of natural soils and sediments plays less of a role in PFAS sorption than once thought; the mineral component of the soil/sediment and the pH conditions play a more important role in PFAS adsorption.

A patented amendment consisting of activated carbon blended with amorphous aluminum hydroxide, kaolin clay, and other proprietary additives has been field-implemented and was used to successfully immobilize 28 PFAS analytes in more than 14 different contaminated soils in a lab-based trial from fire training grounds across Australia (Stewart and MacFarland 2017). At average addition rates of around 2.5-5%, PFOS and PFOA in soil leachates were reduced by 95% to >99% following a 48-hour treatment process.

Sorption and stabilization do not destroy PFAS, and these technologies have not been implemented for enough time to demonstrate long-term stability of amendments for PFAS. However, in independent studies, the Multiple Extraction Procedure (MEP; USEPA Method 1320) has been used to successfully demonstrate the simulated long-term stability of immobilized PFAS in amended soils (Stewart and MacFarland 2017). The MEP is designed to simulate 1,000 years of acid rain conditions in an improperly designed sanitary landfill. In another independent study, the accumulation of PFAS in earthworms and plants was reduced by >90% in soil treated by carbon-based immobilization compared to untreated soils (Bräunig 2016; Kempisty, Xing, and Racz 2018). The amended soil can be mixed with concrete and other stabilizers to improve performance; however, the concrete increases pH and may influence binder performance (Ross et al. 2018).

Design/Operating Considerations: To establish design and application parameters for implementation of sorption and stabilization technology in soils, it is necessary to perform site-specific laboratory and/or pilot treatability tests. Information and quantity of amendment material required (dose rates) for materials can be determined with either simple beaker or jar-type lab treatability tests. These studies are most applicable if site soils and water are used to ensure that the effects of site-specific geochemical characteristics are assessed. Once the dose of amendment material is determined, field pilot studies are often conducted to validate lab data and design for full-scale implementation.

For in situ soil mixing, the amendments are added to soils at the design dose or application rate under controlled conditions with specific types of equipment designed to perform mixing. In situ soil mixing can be performed on soils in place with a wide range of standard construction equipment, including excavators, large diameter augers, and in situ blenders. In addition, with in situ soil mixing, soils can be removed and mixed in equipment such as a pug mill or other similar mixing systems.

After implementation of in situ soil mixing, it is important to perform postconstruction quality assurance and quality control to verify design endpoints. This may include leachability (Toxicity Characteristic Leaching Procedure (TCLP), USEPA Method 1311; Synthetic Precipitation Leaching Procedure (SPLP), USEPA Method 1312; or Multiple Extraction Procedure (MEP), USEPA Method 1320), hydraulic conductivity (ASTM D5084), and strength tests (various).

Sustainability: The environmental footprint for sorption and stabilization includes emissions from earthwork equipment, manufacturing, and transporting amendment material. This footprint can be smaller than excavation if the treated soil is reused on site. Community impacts include hindrance of redevelopment due to land use restrictions. However, if the land use is not expected to change, such as on active government-owned aviation or military sites, stabilization with

amendments and reuse of the soil may be a viable and cost-effective approach.

Resources are available for performing a sustainability assessment for sorption and stabilization remedial design, relating to other contaminants (Goldenberg and Reddy 2014; Hou et al. 2016; Kuykendall and McMullan 2014).

12.3.2 Excavation and Disposal

Treatment Description: This approach involves removing contaminated soil/sediment for off-site disposal. The contaminated material is disposed of at a permitted landfill, then the excavated area is filled with clean backfill. Treatment with stabilizing agents can reduce PFAS leachability from excavated soils and should be considered prior to landfilling. Sometimes, excavated soil/sediment can be treated on site using the sorption and stability approach or thermal treatment (as discussed in the next section) followed by soil reuse or off-site disposal.

Treatment Mechanism: This method is intended to remove PFAS from the source location. Transportation and disposal in a lined landfill is an option for excavated soil; however, leachate management should be a consideration at these facilities.

Soil ContainmentThe focus of this section is to summarize the state of various remediation technologies. Containment is not listed as a specific technology but is commonly utilized for other contaminants and may be suitable for PFAS depending on site-specific conditions.

Containment could include capping to prevent infiltration or exposure, construction of a slurry wall (or similar isolation barrier), addition of sorptive media to prevent migration, or landfill disposal (discussed further in this section and in Section 2.6.3.1). Containment options will depend on site-specific considerations, nature of PFAS materials, and local regulatory requirements.

State of Development: Soil excavation and disposal is a well-demonstrated, proven technology. However, PFAS have been reported in landfill leachate (Lang et al. 2017), although the source for PFAS in leachate may be consumer product waste containing fluorochemicals. In some states, the leachate is not analyzed or regulated for PFAS. Disposal of PFAS waste to landfills potentially adds to the PFAS contaminant load in the landfill leachate. Some nonhazardous waste landfills do not accept PFAS waste.

Effectiveness: Excavation and disposal of PFAS-contaminated soil effectively removes a source area that may otherwise serve as a continuing source of groundwater contamination but does not result in destruction of the PFAS unless the soil is incinerated. Disposal of PFAS-impacted soils or wastes into unlined landfills should be avoided as unlined or improperly lined landfills can be sources of PFAS to the environment.

Design/Operating Considerations: Difficulties in finding landfills willing to accept the waste, coupled with rapidly changing regulations regarding whether PFAS are hazardous or not, make this option less straightforward than one would expect. Case-by-case inquiries to landfill facility owners is likely the best course of action. Overall, issues related to disposal of PFAS in landfills are similar to issues commonly encountered with other contaminants. See Section 2.6.3, Solid Waste Management, for additional discussion on this topic.

Sustainability: The environmental footprint for excavation and disposal includes earth-moving equipment emissions, transporting contaminated soil and backfill, and resource extraction (such as borrow area fill material) of backfill material. Incineration of the contaminated soil and investigation-derived waste (IDW) is energy-intensive and remains a topic of current study to better understand the fate of PFAS, see Section 12.4.

Truck hauling traffic affects the local community by creating additional traffic congestion, noise, and particulate matter emissions. The cost for this approach is high, but the solution is generally permanent and for smaller treatment volumes may be cost-competitive. Guidance is available for performing a sustainability assessment for an excavation and disposal remedial design (Cappuyns and Kessen 2013; Goldenberg and Reddy 2014; Söderqvist et al. 2015; Song et al. 2018).

12.4 Incineration

Treatment Description: Incineration is defined as destruction (mineralization) of chemicals using heat. Heat is applied directly to the PFAS-contaminated solids (soil/sediment/spent adsorbents/waste) or liquids (water/wastewater/leachate/chemicals). Vaporized combustion products can be captured (precipitation, wet scrubbing)

and/or further oxidized at elevated temperature.

State of Development: Incineration is a mature technology that has been used for various solid and liquid wastes.

Effectiveness: Incineration is one of only a few technologies that can potentially destroy PFAS. However, at the time of publication, this is an active area of research to evaluate effective destruction temperatures and treatment time, the potential to generate products of incomplete combustion, stack gas analyses, deposition onto land, and other risk factors.

Design/Operating Considerations: Waste incinerators are fixed facilities. Federal and state permits dictate the materials processed, core incinerator operations (for example, temperature and time, turbulence), and control of process air, liquid, and solid wastes. Permit and design/construction similarities reduce the operational and performance differences between individual incinerators.

When considering waste disposal options, transportation costs, energy costs, regulatory approvals, and final disposition of process waste residues should be evaluated, as these differ among incineration facilities.

Sustainability: The environmental footprint for incineration includes transportation and supplemental fuel for the incineration process. Incineration of contaminated soil, liquid wastes, and IDW is energy-intensive and PFAS emissions, including potential PFAS combustion byproducts, from incinerators are currently not well understood (USEPA 2020e). Truck hauling traffic affects the local community by creating additional traffic congestion, noise, and particulate matter emissions. The cost for this approach is high, but the solution may be cost-competitive for smaller treatment volumes.

12.5 Limited Application and Developing Liquids Treatment Technologies

The treatment technologies presented in this document are provided in a hierarchy defined in Section 12.1, which is based on level of implementation and confidence derived from widespread, well documented implementation. The three development levels include field-implemented technologies, limited application technologies, and developing technologies. Both in situ and ex situ technologies are included. It is not always clear if a limited application or developing technology may be effective in situ, ex situ, or both; therefore, further distinction is not made in this section.

The field-implemented technologies described in the preceding sections have been applied at multiple sites and are well documented in the available literature. In addition to these well-demonstrated technologies, many technology approaches have been tested in academic and other research laboratories at the bench scale or have progressed as far as field pilot tests or limited field applications. These limited application technologies are briefly summarized Table 12-1 for liquids, Table 12-2 for solids (provided as a separate PDF), and appropriate references are provided. Additional information is provided in the following summary sections.

12.5.1 Sorption Summary

12.5.1.1 In Situ Remediation with Colloidal Activated Carbon

Colloidal activated carbon (CAC) consists of colloidal-sized particles (2 microns diameter on average) in aqueous suspension (the consistency of black-colored water), which can flow into aquifer flux zones upon gravity-feed or low-pressure injection. After injection, CAC particles will attach strongly to the aquifer matrix, where they can act as passive sorbents for organic contaminants, including PFAS. This sorption mechanism is detailed in the Section 12.2.1. Due to the small size of the particles, the kinetics of PFAS sorption on colloidal carbon are much faster than can be achieved with GAC, resulting in higher removal efficiencies (Xiao, Ulrich, et al. 2017). The primary function of injectable CAC is to immobilize contaminants and prevent their further horizontal and vertical migration in groundwater, thereby eliminating the risk to downgradient receptors. By flowing CAC into the flux zones of an aquifer, contaminants moving through the aquifer, as well as those contaminants back-diffusing from lower permeability zones, are captured and taken out of solution.

CAC may be injected in situ using a grid pattern in source zones to immobilize contaminants, or it may be injected in a transect pattern perpendicular to the width of a plume to mitigate contaminant flux. Direct push or vertical wells can be used to inject CAC into the subsurface. The longevity will be dependent upon PFAS composition, rates of mass discharge, presence of co-contaminants, and groundwater geochemistry.

McGregor (2018) discussed the in situ injection of CAC at a site in central Canada to mitigate mass flux of PFOS and PFOA from the source zone. Fire training exercises were carried out at the site in the 1970s and 1980s. Prior to CAC injection,

PFOS and PFOA were measured in groundwater monitoring wells at concentrations up to 1,450 ng/L and 3,260 ng/L, respectively. Monitoring wells at the site were screened in a shallow, thin silty sand overburden unit at depths of approximately 5–10 feet below ground surface. CAC was injected into the source zone at low pressure through temporary wells installed using direct push technology. Postinjection core sampling indicated that CAC was measured at distances of up to approximately 15–20 feet from the injection wells.

Carey et al. (2019) performed modeling with respect to the above site to predict the theoretical longevity and performance of the CAC. The study noted that longevity of performance could be extended by increasing the CAC dose, increasing the thickness of the treatment zone perpendicular to flow, or by additional injection upon breakthrough.

12.5.1.2 Coated Sand

Polymer-coated sand is an adsorbent material that has high affinity for organic contaminants. Cyclodextrin molecules are polymerized by a cross-linking agent and form inclusion complexes with many organics. The adsorbent material has two components: (a) polymer coat (active component that removes the contaminants) and (b) support base (inactive component); the combination of both provides an adsorbent with high selectivity and mechanical stability.

Related Ongoing Research Funded by SERDP:

- ER18-1652 Destruction of PFAS and Organic Co-Contaminants in Water and Soil Present in Investigation-Derived Waste at DoD Sites Using Novel Adsorbent and Ultrasound

The adsorbent showed similar performance in removing PFOA and PFOS as GAC, but one of the key features of this technology is the high regenerability of the adsorbent (filter) for reuse (Bhattarai, Manickavachagam, and Suri 2014). Another important feature of the technology is that it can remove other organic pollutants such as chlorinated solvents (for example, trichloroethene (TCE), perchloroethylene (PCE), hexavalent chromium, and others (Badruddoza, Bhattarai, and Suri 2017). Surface modification has been shown to improve the adsorption of PFOS (Zhou, Pan, and Zhang 2013) by using organic polymeric surfactants.

12.5.1.3 Zeolites/Clay Minerals (Natural or Surface-Modified)

Zeolites are naturally occurring aluminosilicate compounds that are widely used in chemical separation and purification due to their high surface area and small uniform pore size among other properties (Tao et al. 2006). Zeolites are also being increasingly considered as a medium for the sorption of various pollutants, including cationic heavy metals, ammonium, and some volatile organic compounds, due to the aforementioned properties, as well as their high ion exchange capacity and low cost (Delkash, Ebrazi Bakhshayesh, and Kazemian 2015). Clay minerals, including natural and surface-modified (see below), are also used as adsorbents and are similar to zeolites in composition but have different crystalline or chemical structure.

Both zeolites and clay minerals can be used *ex situ* (that is, pump and treat) by being placed in packed-bed flow-through vessels or *in situ* via injection into aquifers. *In situ* applications are currently lacking in study or field application.

Zeolite and clay minerals use both ion exchange and adsorption mechanisms to remove PFAS from water. For removal of PFAS, these natural materials have been shown to be inferior to activated carbon or ion exchange resins (Du et al. 2014). However, synthetic processing of zeolite can create highly siliceous material (Baerlocher 2007) or can incorporate cationic surfactants into the surface structure (aka surface-modified zeolites-SMZ) (Jiménez-Castañeda and Medina 2017). One study indicated that engineered zeolites with a high Si/Al ratio were effective at adsorption of PFOS, presumably due to hydrophobic interactions rather than ion exchange (Ochoa-Herrera and Sierra-Alvarez 2008). Surface-modified clay materials are broadly considered organoclays.

Most available literature is limited to academic laboratory experiments (Ochoa-Herrera and Sierra-Alvarez 2008; Punyapalukul et al. 2013; Zhou, Pan, and Zhang 2013; Zhou et al. 2010). Du et al. (2014) and Arias Espana, Mallavarapu, and Naidu (2015) provided comprehensive literature reviews. Two modified clay-based adsorbent products are identified as being used in field pilots or small-scale field trial applications (Arias (Arias et al. 2013) et al. 2013; (Arias Espana, Mallavarapu, and Naidu 2015) to treat PFOA and/or PFOS.

High silica materials, such as H-form synthetic mordenite (HSM) and Y-form sodium zeolite (NA-Y80), and hydrotalcite clay provided adsorption capacities that were equivalent or exceeded powdered activated carbon (PAC). Surfactant-modified clays also performed as well as or better than PAC. It should be noted that none of these studies were conducted in flow-through column experiments, so applicability to *ex situ* treatment systems cannot be assessed. Arias Espana, Mallavarapu, and Naidu (2015) stated that organoclays, clay minerals, and highly siliceous materials have fast kinetics (0.4–3 hr to reach

equilibrium), making them suitable for remediation applications.

12.5.1.4 Biochar

Biochar is a hybrid word rooted in the words “biomass” and “charcoal.” Biochar is a carbon-rich porous solid that is synthesized by heating biomass, such as wood or manure, in a low oxygen environment (Ahmad et al. 2014). This material has primary applications for carbon sequestration, improvement of soil fertility, and most recently as an adsorbent for pollutant removal. Biochar is characterized to have high affinity for organic contaminants, which is dependent on both the pore structure and the surface functional groups of the biochar material (Guo et al. 2017).

Some of the key factors controlling the properties of biochar (for example, pore size composition and hydrophobicity) include the temperature of pyrolysis and biomass feedstock, among others. In many respects, the properties of biochar are similar to but generally lower than those of GAC for sorptive purposes.

The available literature is limited to academic laboratory batch experiments on the bench-scale (Chen et al. 2011; Inyang and Dickenson 2017; Kupryianchyk et al. 2016; Rahman et al. 2014; Xiao, Ulrich, et al. 2017), with one published study reporting pilot-scale column operation (Inyang and Dickenson 2017).

12.5.2 Precipitation/Coagulation/Flocculation Summary

Precipitation/coagulation/flocculation is a common pretreatment approach used in wastewater treatment plants for removing various particles and dissolved constituents. Coagulants, either commodity or proprietary chemicals, can be added to water (conventional technology) or generated by anode-cathode reactions of metal plates inserted into the water (electrocoagulation). Common examples include:

- inorganic cationic coagulants (for example, alum, iron-based)
- commodity (for example, polyDADMAC) and specialty (for example, Perfluorad) polymers
- electrochemical precipitation

Coagulants assist in the formation of solids. Flocculation is typically conducted by adding a soluble polymer and slowly mixing to allow the particles to agglomerate and grow. Upon solid formation, constituents such as PFAS can be physically incorporated into, or sorbed onto, the flocculated particulate (which is known as co-precipitation). The precipitated solids are then separated from the water by sedimentation and/or filtration processes. The solid material containing the PFAS requires disposal, see Table 12-2 for solids (provided as a separate PDF). See Section 12.3.2 for solids disposal options.

Current literature documents only bench-scale study results on treating PFAS via precipitation, flocculation, or coagulation; therefore, this is considered a partially developed technology. Evaluations have focused on conventional commodity chemical coagulation (for example, aluminum or ferric salts) and nonconventional coagulation (for example, proprietary chemical coagulants or electrocoagulation). Pilot- and full-scale applications have not been documented in the United States (Birk 2017).

Nonconventional precipitation (for example, electrocoagulation or advanced chemical precipitants) has shown more potential for direct PFAS treatment, but has very limited data. High-affinity cyclodextrin polymer has been tested in bench-scale reactors and was found to have superior removal capacity to GAC (Xiao, Ling, et al. 2017).

Related Ongoing Research Funded by SERDP:

- ER-2425 Development of a Novel Approach for In Situ Remediation of PFC-Contaminated Groundwater Systems
- ER18-1026 Rational Design and Implementation of Novel Polymer Adsorbents for Selective Uptake of PFASs from Groundwater

Electrocoagulation reactors, which range from basic to very sophisticated designs, have been reported to be highly efficient, compact, relatively low cost, and completely automatable (Baudequin et al. 2011; Lin et al. 2015). Recent studies have found that PFAAs, such as PFOA and PFOS, can be quickly sorbed on the surface of zinc hydroxide particulates generated by electrocoagulation (Lin et al. 2015).

12.5.3 Nanofiltration (NF)

NF is a form of membrane technology that is pressure-driven and shown to be effective in the removal of PFAS (Tang et al. 2007). This method of filtration provides high water flux at low operating pressure (Izadpanah and Javidnia 2012).

Nanometer-sized membrane pores are used to remove compounds in a process similar to RO, but NF does not remove smaller ions such as chloride and sodium. The most common membrane module configurations are spiral-wound (consisting of flat sheet membrane material wrapped around a central collection tube); however, hollow fiber NF modules may also be available for applications with higher fouling potential.

Available data on the removal of PFAS via NF consist of laboratory-scale tests performed on flat sheet membrane coupons (laboratory-scale sections of the membranes to be tested) and one full-scale drinking water treatment plant using an NF treatment train. Therefore, variations in performance due to fouling, flux, and concentration distributions in standard spiral-wound membrane configurations have not been characterized (Boo et al. 2018).

NF membranes tested include the DuPont (formerly Dow FilmTec) membranes NF-270, NF-200, and NF-90, and the SUEZ (formerly GE Water & Process Technologies) DK membrane. Reported rejections were generally > 95% for PFAS with molecular weights ranging from 214 grams per mole (g/mol) to 713 g/mol, though some compounds had lower rejections (PFPeA at 70% and perfluorooctane sulfonamide at 90%) (Steinle-Darling and Reinhard 2008; Appleman et al. 2013). Effective full-scale removal of PFAS by NF membranes was confirmed based on nondetectable PFAS concentrations (<4 ng/L) in NF permeate (Boiteux 2017). Salt passage for PFOS was reported to range from < 1% for the tighter NF-90 membrane to about 6% for the looser NF-270 and DK membranes (Tang et al. 2007). As mentioned in Section 12.2.2, an appropriate disposal or treatment of the membrane concentrate stream needs to be considered, especially the application of high-pressure membranes for inland communities.

12.5.4 Redox Manipulation Summary

Redox manipulation includes chemical oxidation and reduction technologies. These have been summarized in more detail in Nzeribe et al. (2019). Chemical oxidation for PFAS is a technology approach that is achieved via the delivery of liquid, slurry, or gaseous oxidants to transfer electrons from a reactive oxidant species to a target (PFAS) and affect the cleavage of atoms in the PFAS molecular structure. Carboxylic or sulfonic group “heads” (functional groups) of PFAS are commonly more susceptible to redox transformation than the fluorinated carbon chain “tails.” There is currently a lack of robust evidence of defluorination via chemical oxidation processes. The mechanisms involving multiple species of free radicals that trigger PFAS oxidation are not well understood. PFAA precursors are also known to be oxidized to form persistent and terminal PFAAs without further oxidation (Houtz and Sedlak 2012; Anumol et al. 2016). Consequently, care should be taken to monitor site and plume conditions and understand potential formation and transport of transformation products.

Additional mechanistic studies are needed to develop chemical oxidation as a feasible PFAS remediation approach and to further assess factors that may promote or limit this technology. Common oxidants that have been documented to treat PFAS and other organic contaminants (for example, chlorinated solvents) include ozone, catalyzed hydrogen peroxide, and persulfate, as discussed further below.

12.5.4.1 Ozone-Based Systems

Ozone can be coupled with other oxidants such as hydrogen peroxide and persulfate to promote the generation of a suite of aggressive free radicals capable of degrading PFAS. An ozone-based system was implemented for the treatment of PFAS in a single field-scale test by Eberle, Ball, and Boving (2017) using combined ozone and activated persulfate.

The main pathway and mechanism behind the ozone-based system tested by Eberle, Ball, and Boving (2017) is unknown, as detailed mechanistic studies have not been performed. However, they suggested that PFAS reduction in groundwater after treatment was not limited to partial degradation, but it is possible that sorption also had a role to play in the declining aqueous PFAS concentration. They postulated that activated persulfate could lead to a decline in pH, thereby increasing sorption of PFAS to soil due to increased protonation.

This approach has been partially demonstrated in one field-scale setting, and results are encouraging for application using ex situ or in situ approaches. However, because there is an absence of supporting mechanistic data, it is likely that other factors could come into play that may promote or limit this technology.

The application of the ozone-based system for the treatment of PFAS has also been evaluated in bench studies (Lin, Panchangam, et al. 2012; Kerfoot 2014; Huang et al. 2016; Eberle, Ball, and Boving 2017). Lin, Panchangam, et al. (2012) used an ozone system without and inclusive of hydrogen peroxide addition in an alkaline environment, and Kerfoot (2014) used hydrogen peroxide and ozone bubbles for a bench-scale test of groundwater from a monitoring well foam firefighting site in Canada. Huang et al. (2016) combined ozone with photolysis to produce hydroxyl radicals and photogenerated electrons.

In the field demonstration, PFAS concentrations in groundwater were reduced by 21–79% after treatment. Also, an initial pilot test at a fire training area using ozone and peroxide has shown removal of 98.5% and 92.3% for PFOS and PFOA, respectively, in groundwater and over 80% for PFOS on saturated soil with proportional release of fluoride (Kerfoot 2016).

In bench-scale studies, Eberle, Ball, and Boving (2017) decreased PFAS by 99.9% using PFAS-contaminated site groundwater and spiked deionized water. Eberle, Ball, and Boving (2017) also reported that the system was not sensitive to other groundwater organics. Kerfoot (2014) reported 89.8% removal of PFOS and > 80% for other PFAS (PFPeA 89.8%, PFHxA 86.2% and PFHxS 98.1%). These studies, however, do not confirm destruction through mass balance and analysis of byproducts.

Each of these approaches and test conditions used different water matrices and starting concentrations. It is difficult to state whether current regulatory levels can be achieved in practice with these technologies, but in general they appear to be effective as a polishing technology to achieve low part-per-trillion treatment requirements.

12.5.4.2 Catalyzed Hydrogen Peroxide (CHP)-Based Systems

CHP is one of the strongest oxidant systems used in environmental remediation. It involves reaction of hydrogen peroxide with a catalyst to predominantly generate hydroxyl radicals. Some CHP systems produce nucleophiles and reductants, including superoxide and hydroperoxide (Mitchell et al. 2014). Common catalysts include transition metals such as iron (Fenton and Fenton-like reaction) or manganese, chelated metals, and naturally occurring minerals (for example, (Watts et al. 2005; Teel et al. 2007).

Hydroxyl radicals attack the alkyl groups of both PFCAs and PFSAs, but do not attack the perfluoroalkyl chain. As a result, PFCA and PFSA precursors are transformed to PFCAs of related perfluorinated chain length (Bruton and Sedlak 2017). Mitchell et al. (2014) demonstrated that superoxide and hydroperoxide (which are nucleophiles and reductants generated as a reaction in CHP but are not chemical oxidants) generated in alkaline pH CHP systems mineralize PFOA but did not elucidate a mechanism.

Bench-scale testing has been successfully demonstrated. Field deployment of hydroxyl radical-based CHP systems may be limited due to decomposition of PFAS precursors to PFOA and other PFCAs as unreactive transformation products (Bruton and Sedlak 2017).

CHP systems that predominantly generate hydroxyl radicals partially transform PFAAs to their PFCAs of related perfluorinated chain length, which are not further transformed (Houtz and Sedlak 2012; Bruton and Sedlak 2017). Systems that generate superoxide and hydroperoxide have been demonstrated at the bench test level to mineralize PFOA (Mitchell et al. 2014), but effectiveness with other PFAS is unknown.

12.5.4.3 Activated Persulfate

Persulfate anion ($S_2O_8^{2-}$) is activated to generate reactive radical species, primarily sulfate radicals (2.6 volts, or V) and hydroxyl radicals (2.7 V). Methods to activate persulfate include transition metals, high pH, and heat activation (Siegrist, Crimi, and Simpkin 2011). Hydroxyl radicals are the predominant radicals formed at high pH conditions (Furman et al. 2011), while at acidic pH there is greater yield of sulfate radicals (Siegrist, Crimi, and Simpkin 2011).

PFCAs are attacked by sulfate radicals under acidic conditions, initiating a decarboxylation reaction, where cleavage of the carbon-to-carbon (C-C) bonds occurs between PFCAs and the carboxyl group (-COOH), forming unstable perfluoroalkyl radicals (C_nF_{2n+1}) (Hori et al. 2010; Lee et al. 2012; Yin et al. 2016). A stepwise series of decarboxylation and hydrogen fluoride (HF) elimination reactions continues to form shorter chain PFCAs until all PFCAs are mineralized to fluoride and carbon dioxide. PFSAs such as PFOS are unreactive with sulfate radicals (Park et al. 2016; Bruton and Sedlak 2017). Hydroxyl radicals attack the alkyl groups of both PFCAs and PFSAs, but do not attack the perfluoroalkyl chain. As a result, PFCA and PFSA precursors are transformed to PFCAs of related perfluorinated chain length (Bruton and Sedlak 2017). Under alkaline pH conditions the sulfate and hydroxyl radicals are reactive with the alkyl groups but similarly unreactive with the perfluoroalkyl chain, which is the basis of the TOP method (Houtz and Sedlak 2012).

Related Ongoing Research Funded by SERDP:

- ER-2423 In Situ Treatment Train for Remediation of Perfluoroalkyl Contaminated Groundwater: In Situ Chemical Oxidation of Sorbed Contaminants (ISCO-SC)
- ER201729 Field Demonstration to Enhance PFAS Degradation and Mass Removal Using Thermally Enhanced

Persulfate Oxidation Followed by Pump-and-Treat

- ER18-1545 Innovative Treatment of Investigation-Derived Waste Polluted with Per- and Polyfluoroalkyl Substance Contaminants and Other Co-Contaminants.

Activated persulfate under acidic conditions has proven effective for PFOA (PFCAs) with nominal 100% degradation, but PFOS is not transformed. Sulfate radicals and hydroxyl radicals generated by alkaline persulfate activation transform PFCA and PFSA precursors to PFCAs of related perfluorinated chain length (Bruton and Sedlak 2017).

12.5.4.4 Sonochemical Oxidation/Ultrasound

The sonochemical process relies on the propagation of acoustic waves in liquids at frequencies ranging between 20 kHz and 1,000 kHz (Furuta et al. 2004), which results in cavitation. Operating parameters such as frequency (Campbell and Hoffmann 2015), power density (Hao et al. 2014), solution temperature, sparge gas, and initial concentration of PFAS (Rodriguez-Freire et al. 2015) play a significant role in the sonochemical degradation and defluorination rate of PFAS.

Sonochemical degradation occurs via two mechanisms: localized thermal treatment and free radical destruction (Rayaroth, Aravind, and Aravindakumar 2016). During cavitation, cyclic formation, growth, and collapse of microbubbles result in an intense increase in temperature and pressure (5000 Kelvin (K) and 2000 atmosphere (atm)), along with the generation of free radicals (Furuta et al. 2004; Chowdhury and Viraraghavan 2009).

Sonochemical oxidation has been successfully applied for rapid degradation of PFAS to fluoride (F⁻), sulfate (SO₄²⁻) and carbon dioxide (CO₂). Vecitis et al. (2008) reported a complete recovery of SO₄²⁻ and >90% defluorination of PFOA and PFOS with initial concentrations of 0.24 μM and 0.20 μM, respectively, for a field-scale application to treat groundwater from below a landfill. At bench scale, sonolysis has been reported in the literature as one of the most effective treatment processes for PFAS-contaminated water, because they almost immediately mineralize to SO₄²⁻, CO₂, carbon monoxide (CO), and F⁻ after cleavage of their C-C/C-S bond. Studies have reported >90 percent degradation and defluorination for PFOA and PFOS (Moriwaki et al. 2005; Vecitis et al. 2008; Cheng et al. 2008, 2010). Gole et al. (2018) demonstrated removal and defluorination of AFFF in a 91-L sonolytic reactor.

12.5.4.5 Photolysis/Photochemical Oxidation

A thorough review of photolysis/photochemical oxidation technology for PFAS decomposition is reported in Wang, Yang, et al. (2017). Chen, Zhang, and Liu (2007) and Giri et al. (2011) reported removal of PFAS by direct photolysis at 185 nm. Hori et al. (2004) and Chen, Zhang, and Liu (2007) reported that direct photolysis at 254 nm alone is not very effective because PFAS do not absorb light at wavelengths >220 nm due to their chemical structure. Chemical reagents/catalysts such as Fe³⁺, S₂O₈²⁻, TiO₂, heteropolyacid photocatalyst (H₃PW₁₂O₄₀), CO₃²⁻, and IO₄⁻ when combined with ultraviolet (UV) (>220 nm) light can effectively decompose PFAS (Hori et al. 2005; Chen and Zhang 2006) (Zhang, Pan, and Zhou 2016; Hori et al. 2007; Wang et al. 2008; Cao et al. 2010). This is due to generation of strong and reactive oxidative species such as OH[•], H[•], CO₃^{•-} and PFAS-Fe complexes. Photochemical oxidation of PFAS is said to be dependent on the light source (UV or vacuum ultraviolet), initial concentration of PFAS, environmental matrix, temperature, pH, and type of reagent used (Lin, Panchangam, et al. 2012; Giri et al. 2012; Lyu et al. 2015b, a; Xu et al. 2017).

Related Ongoing Research Funded by SERDP:

- ER18-1595 A Combined Photo/Electrochemical Reductive Pathway Towards Enhanced PFAS Degradation
- ER18-1513 Effective Destruction of Per- and Polyfluoroalkyl Substances in Water by Modified SiC-Based Photocatalysts
- ER18-1515 A Cost-Effective Technology for Destruction of Per- and Polyfluoroalkyl Substances from DoD Subsurface Investigation-Derived Wastes
- ER18-1599 Pilot Scale Assessment of a Deployable Photocatalytic Treatment System Modified with BiPO₄ Catalyst Particles for PFAS Destruction in Investigation-Derived Wastewater

The major degradation pathways involved in the photochemical oxidation of PFAS are direct photolysis and free radical reactions. The C-C bond between PFAS is cleaved with the COOH group to form perfluoroalkyl radicals (Hori et al. 2003; Hori et al. 2008), which then react with water and undergoes hydrogen fluoride elimination to form shorter chain compounds. These then undergo hydrolysis to form subsequent shorter PFAS (losing CF₂ units). During direct photolysis, the C-C and C-S

bonds of PFAS are broken by photoelectrons to generate perfluoroalkyl radicals and carbon dioxide (Wang, Yang, et al. 2017).

12.5.4.6 Electrochemical Treatment

Electrochemical treatment occurs via anodic oxidation; a variety of materials have been used as anodes. The treatment effectiveness of PFOS and PFOA using different anodes can vary significantly. Most research on PFAS, particularly PFOS and PFOA removal, has been conducted using a boron-doped diamond (BDD) electrode due to its mechanical, chemical, and thermal stability (Trautmann et al. 2015; Schaefer et al. 2017). Some other electrodes, such as lead dioxide (PbO₂), titanium oxide (TiO₂), titanium suboxide (Ti₄O₇), and tin oxide (SnO₂), also have the ability to treat PFAS-contaminated water (Ochiai et al. 2011; Zhou et al. 2012) (Zhao, Gao, et al. 2013; Liang 2017; Liang et al. 2018). Operating conditions and parameters such as pH (Lin, Niu, et al. 2012) } (Zhou et al. 2012), current density, electrolyte type (Song et al. 2010; Zhuo et al. 2012), electrode distance (Lin, Niu, et al. 2012), initial PFAS concentration, and temperature are important factors that influence electrochemical oxidation of PFAS (Niu et al. 2016).

Electrochemical treatment proceeds via direct and indirect anodic oxidation (Radjenovic and Sedlak 2015; Niu et al. 2016; Schaefer et al. 2018). In direct electrolysis, contaminants are adsorbed onto and degraded directly at the electrode, while in indirect electrolysis, contaminants are degraded in the bulk liquid in reactions with oxidizing agents (that is, hydroxyl radicals) formed at the electrode (Radjenovic and Sedlak 2015).

Bench-scale studies have shown success in the degradation and defluorination of PFAS, including short-chain, long-chain PFAAs as well as PFAA precursors (Chiang 2018). Electrochemical oxidation of precursors may lead to the transient generation of perfluorinated carboxylates (Schaefer et al. 2018). Ultimately, fluoride is released, with typical recoveries ranging from 60 to 80%; the fate of the remaining fluoride is unknown, but studies have suggested that losses due to volatile perfluorinated alkanes may occur. Currently, technology has not been tested for PFAS-laden water with low PFAS concentrations. However, it has been tested as a stand-alone technology for PFAS concentrations at ppb levels and as a destruction technology to destroy concentrated PFAS waste streams generated from other treatment technologies such as ion exchange resin and ozofractionation (Liang et al. 2018; Chiang 2018). It has been partially demonstrated as an ex situ treatment of PFAS. But in situ application is also being considered and funded in the SERDP program. The issue of perchlorate formation as a byproduct during electrochemical oxidation of PFAS has been addressed by Schaefer et al. (2017) using a biological treatment polishing step. The issue can also be minimized by not using sodium chloride as the electrolyte (Chiang 2018).

The technology has been demonstrated via bench studies and pilot-scale reactor to be very effective for treatment of short-chain, long-chain PFAAs, as well as most commonly detected PFAA precursors in spike water systems and several remediation-derived waste streams laden with high PFAS concentrations.

Related Ongoing Research Funded by SERDP:

- ER-2424 Investigating Electrocatalytic and Catalytic Approaches for In Situ Treatment of Perfluoroalkyl Contaminants in Groundwater
- ER-2718 Synergistic Treatment of Mixed 1,4-Dioxane and PFAS Contamination by Combining Electrolytic Degradation and Electrobiostimulation
- ER18-1320 Electrochemical Oxidation of Perfluoroalkyl Acids in Still Bottoms from Regeneration of Ion Exchange Resins
- ER-2717 A Novel Reactive Electrochemical Membrane System for Treatment of Mixed Contaminants
- ER18-1491 Reactive Electrochemical Membrane (REM) Reactors for the Oxidation of Perfluoroalkyl Compound Contaminated Water

12.5.4.7 Solvated Electrons (Advanced Reduction Processes)

Advanced reduction processes (ARP) has been investigated for the reductive degradation of groundwater contaminants. ARP involves the combination of activation methods such as ultrasound, ultraviolet, microwaves, and electron beam with reducing agents (reductants) such as ferrous iron, sulfide, sulfite, iodide, and dithionite to generate very reactive reducing radicals and the hydrated electrons (e⁻aq) that mineralize contaminants to less toxic products (Vellanki, Batchelor, and Abdel-Wahab 2013). The reducing hydrogen radical (H[•]) and the hydrated electron are strong reductants that react easily with halogenated organic compounds (Buxton et al. 1988). ARP-induced degradation rates depend on initial solution pH and

reductant concentration (Vellanki, Batchelor, and Abdel-Wahab 2013). Bentel et al. (2019) described insights gained from a structure-activity relationship analysis of the mechanisms involved in the reaction of solvated electrons with PFAS.

The degradation pathway of PFAS using ARP differs from that of oxidizing agents in that the hydrated electron (Song et al. 2013) cleaves the C-F bond adjacent to the functional group of the PFAS rather than the C-C or C-S bond. Qu et al. (2014) proposed that hydrated electrons lead to the reductive cleavage of the C-F bonds, resulting in fluorine elimination from PFOA. Furthermore, they proposed that under UV irradiation, cleavage of the C-C bond between the COOH group and the perfluoroalkyl group occurred as shorter chain intermediates were detected in solution. Qu et al. (2014) therefore concluded that two reactions are responsible for the reductive defluorination of PFOA: (1) direct photolysis by UV irradiation, and (2) photoreduction by hydrated electrons.

Reductive processes have proven feasible for degradation of most PFAS, especially PFOS. It should be recognized that electrons will be scavenged by oxygen, nitrate, and chlorides, and this should be considered for treatment application. Recent research using UV-activated sulfite demonstrated effective generation of hydrated (aka solvated) electrons. Laboratory tests showed >50% defluorination of both PFOS and PFOA within 24 hours (Strathmann 2018).

Related Ongoing Research Funded by SERDP:

- ER-2426 Quantification of In Situ Chemical Reductive Defluorination (ISCRD) of Perfluoroalkyl Acids in Ground Water Impacted by AFFFs
- ER18-1526 Complete Reductive Defluorination of Poly- and Perfluoroalkyl Substances (PFASs) by Hydrated Electrons Generated from 3-Indole-acetic-acid in Chitosan-Modified Montmorillonite

12.5.4.8 Plasma Technology

Plasma technology is a promising destructive PFAS treatment technology. Plasma is formed as a result of an electrical discharge from the addition of sufficient energy to gas (Jiang et al. 2014) and is classified into two major groups based on temperature and electronic density: thermal plasma (local thermal equilibrium) and nonthermal plasma (nonequilibrium plasma) (Bogaerts 2002). Due to lower energy requirements and selectivity, nonthermal plasma is most often used in water treatment processes (Jiang et al. 2014). In water treatment plasma applications, electrical discharges can be discharged above the liquid surface, directly to the liquid, or in the form of bubbles in liquids (Locke, Lukes, and Brisset 2012) (Stratton et al. 2017). These electrical discharges diffuse in liquids to initiate various chemical and physical effects, including high electric fields, intense UV radiation, shock waves, and formation of strong oxidative and reductive reactive species (H^{\bullet} , O^{\bullet} , OH^{\bullet} , H_2O_2 aqueous electrons, H_2 , O_2 , O_3), which are effective for the treatment and removal of contaminants (Lukes, Appleton, and Locke 2004; Lukes et al. 2005; Stratton et al. 2017).

Determination of plasma treatment mechanisms and degradation pathways for PFAS is currently a research focus, and several mechanisms and pathways have been proposed. Takeuchi et al. (2013) proposed that the main reaction pathway for PFOA by plasma treatment is by thermal cleavage of the C-C bonds resulting in direct decomposition to gaseous products without formation of shorter chain PFCAs. Others have proposed that PFAS decomposition is due to conversion to unstable radicals during interaction of PFAS with the most energized ions in the plasma (Hayashi et al. 2015; Obo, Takeuchi, and Yasuoka 2015), or with positive ion(s) generated by the plasma (Yasuoka, Sasaki, and Hayashi 2011) at the bubble gas-liquid interface. The unstable radicals produced during PFAS decomposition can result in a sequential loss of one carbon within the chain.

Plasma effectively degrades PFAS in a relatively short period of time (30-minute treatment) in both synthetic water and groundwater. It has been reported that plasma treatment provided 90% degradation of PFOA and PFOS, with only about 10% of the destroyed PFOA and PFOS being converted to shorter chain PFAAs (Stratton et al. 2017). The degradation rate is not affected by the presence of co-contaminants. This is an environment-friendly technology, because there is no demand on pressure or temperature and it does not require significant input of chemicals. Plasma also generates a broad range of reactive species.

Related Ongoing Research Funded by SERDP:

- ER18-1306 Combined In Situ/Ex Situ Treatment Train for Remediation of Per- and Polyfluoroalkyl Substance (PFAS) Contaminated Groundwater
- ER18-1624 Plasma Based Treatment Processes for PFAS Investigation-Derived Waste

- ER18-1570 Application of Non-Thermal Plasma Technology for the Removal of Poly- and Perfluorinated Substances from Investigation-Derived Wastes
- ER18-5015 Removal and Destruction of PFAS and Co-contaminants from Groundwater

12.5.4.9 Zero-Valent Iron (ZVI)/Doped-ZVI

ZVI is an inexpensive groundwater remediation technology. It is the most commonly used reductant for in situ groundwater remediation. It is a strong reducing agent capable of successfully reducing major groundwater contaminants such as chlorinated solvents. Recently nanoscale zero-valent iron (nZVI) has had increased attention due to its higher reactivity, surface area, and potential in situ injectability compared to the micro-sized ZVI.

In general, the removal of PFAS by ZVI in reductive processes involves the mass transfer of contaminants to the ZVI surface, and their adsorption and reaction (transformation of contaminants into less toxic/nontoxic species) on the ZVI surface, followed by the desorption and mass transfer of byproducts into solution (Arvaniti et al. 2015). Because the reduction of contaminants by ZVI is a surface-mediated electron transfer process, the surface properties of ZVI influence contaminant reactivity. (Arvaniti et al. (2015)) found that PFOS removal using Mg-aminoclay-coated nZVI occurred via adsorption of PFOS to the ZVI surface followed by reduction. A similar decomposition mechanism for PFOS using ZVI in subcritical water was reported by Hori et al. (2006), who suggested that adsorption of PFOS onto ZVI played a major role in PFOS decomposition, as fluoride was detected in the treatment solution after treatment.

This technology is highly effective for the removal of PFOS, reacts relatively quickly, and has proven feasible for degradation of most PFAS.

12.5.4.10 Alkaline Metal Reduction

Alkaline metal reduction involves the use of alkali metals (that is, the reductant) to reduce organic compounds to their anion radical. Reductive degradation of branched PFOS has been reported with vitamin B₁₂ as a catalyst and Ti(III)-citrate or nanosized zero-valent zinc as a bulk reductant (Ochoa-Herrera et al. 2008; Park, de Perre, and Lee 2017) where degradation rates increase with increasing solution pH, bulk reductant dose, and temperature.

The degradation pathway of PFAS by alkali metal reduction as postulated by Ochoa-Herrera et al. (2008) suggests that destruction of branched PFOS isomers occurs via chemical reductive dehalogenation. Park, de Perre, and Lee (2017) suggested that the ability of vitamin B₁₂ to reduce branched PFOS isomer and not linear is because the branched PFOS isomers possess greater electron density differences that are absent in linear PFOS isomers. Bench-scale studies have shown success for branched PFOS isomers and have proven to be efficient (greater than 70% removal; see (Ochoa-Herrera et al. 2008)). In situ applications have not been tested. Removal and defluorination are lower for PFHxS relative to PFOS. Polyfluorinated sulfonate intermediates (C₅-C₈) are the final products (Park, de Perre, and Lee 2017).

12.5.5 Biodegradation Summary

A limited number of studies have tested microbial degradation of PFAS and many conflicting reports exist, all suggesting that more work needs to be performed to fully understand the biotic transformations of these compounds.

Microbial degradation of PFAS has been observed to occur only with polyfluoroalkyl substances (Butt, Muir, and Mabury 2014), which contain some carbon-hydrogen bonds instead of C-F bonds (Buck et al. 2011). Recent research documented the aerobic biotransformation of fluorotelomer thioether amido sulfonate (FtTAoS) over a 40-day period to produce 4:2, 6:2, and 8:2 fluorotelomer sulfonate (FTS), 6:2 fluorotelomer unsaturated carboxylic acid (FTUCA), 5:3 fluorotelomer carboxylic acid (FTCA), and C4 to C8 perfluorinated carboxylic acids (Harding-Marjanovic et al. 2015). An unintended consequence of biologically mediated transformations is the conversion of precursors (polyfluorinated) to perfluorinated compounds.

PFOA and PFOS have been shown to be resistant to microbial biotransformation under a variety of growth conditions (Liu and Mejia Avendaño 2013). However, other PFAS, including chemicals in AFFF with nonfluorinated alkyl groups (polyfluorinated substances), are likely amenable to biotransformation. Most recently, defluorination of PFOA and PFOS were observed using an ammonium oxidizing autotroph (Huang and Jaffé 2019). Upon addition of PFOA or PFOS (0.1 mg/L and 100 mg/L, respectively) to the A6 culture, shorter chain perfluorinated products and acetate were observed. Incubations with hydrogen as a sole electron donor also resulted in the defluorination of up to 60% of PFOA and PFOS during 100-day incubations, while total fluorine (organic plus fluoride) remained constant. Reductive defluorination of perfluoroalkyl substances may be possible, as observed when using vitamin B12 and Ti(III)-citrate (Ochoa-Herrera et al. 2008). There are no known reports of biotransformation occurring under aerobic and anaerobic conditions.

A limited number of studies have tested microbial degradation of PFAS and many conflicting reports exist, all suggesting that more work needs to be performed to fully understand the biotic transformations of those compounds.

Research on the fungal degradation of PFAS has been ongoing due to the wide spectrum of substrate reduction catalyzed by extracellular ligninolytic enzymes. Experiments with white-rot fungus showed limited degradation of PFOA in microcosm studies under certain conditions (Tseng 2012). The innovative delivery of fungal enzymes for PFAS treatment requires further research.

The biodegradation of PFAS has been reported in a few studies as described above and in the following: 8:2 FTOH (Wang et al. 2009), 6:2 FTOH (Liu, Wang, et al. 2010), 6:2 FTSA (Wang et al. 2011), and N-ethyl perfluorooctane sulfonamidoethanol (Rhoads et al. 2008; Rhoads et al. 2013). Recently the PFOA-degrading strain YAB1 was isolated from soil that had been impacted by perfluorinated compounds through acclimation and enrichment culture, where perfluorooctanoic acid (PFOA) was amended as the sole carbon source (Yi et al. 2016). This strain was preliminarily identified as *Pseudomonas parafulva* based on colony morphology, physiological and biochemical features, and 16S rRNA gene sequencing. Using shaking flask fermentation, the maximum tolerable concentration of YAB1 on PFOA was found to be 1,000 mg/L, and the optimal PFOA concentration for the growth of YAB1 was 500 mg/L. After 96 hours of culture, the PFOA degradation rate was 32.4%. When 1 g/L glucose was added to the inorganic salt culture medium, the degradation rate increased to 48.1%. Glucose was the best exogenous carbon source for the degradation of PFOA (Yi et al. 2016).

Related Ongoing Research Funded by SERDP:

- ER-2422 Bioaugmentation with Vaults: Novel In Situ Remediation Strategy for Transformation of Perfluoroalkyl Compounds
- ER-2127 Remediation of Perfluoroalkyl Contaminated Aquifers using an In Situ Two-Layer Barrier: Laboratory Batch and Column Study

12.5.6 High-Energy Electron Beam (eBeam)

High-energy electron beam (eBeam) is a high efficiency, flow-through, nonthermal, chemical-free technology that utilizes electron accelerators to generate large numbers of highly energetic electrons from electricity (Cleland 2011; Pillai and Shayanfar 2016). The technology has been commercialized globally for pasteurizing foods, sterilizing medical devices, cross-linking polymers, and eliminating insects and pests from fresh produce (Cleland 2011; Pillai 2016; Pillai and Shayanfar 2016; Zembouai et al. 2016). It provides a form of ionizing irradiation that does not involve the use of radioactive isotopes. The amount of energy from eBeam that is absorbed by an irradiated material per unit mass is called dose. The absorbed dose during eBeam treatment depends on the type and thickness of the material, the beam power, and the length of time the material is exposed to the electron beam (Waite 1998).

eBeam is applicable for use on soil and liquid matrices for many purposes: disinfection of sewage sludge (Praveen et al. 2013; Waite 1998); remediation of heavy hydrocarbon-contaminated soils (Briggs 2015); and remediation of volatile organic compounds (VOCs) and semivolatile organic compounds in liquid wastes such as groundwater, wastewater, and landfill leachate (USEPA 1997b). During irradiation of water, three primary reactive species are formed: solvated electrons and hydrogen radicals, which are strong reducing species, and hydroxyl radicals, which are strong oxidizing species. This creates both advanced reduction and oxidation processes without the addition of any chemicals. The absolute concentration of radicals formed during irradiation is dose- and water quality-dependent, but it has been measured at greater than millimolar (mM) levels in potable, raw, and secondary wastewater effluent (Waite 1998).

Researchers at Texas A&M University recently demonstrated defluorination of PFOA in aqueous samples by eBeam technology (Wang et al. 2016). The study measured defluorination efficiency as a function of molar concentration of free fluoride ions and initial

Related Ongoing Research Sponsored by SERDP:

- ER18-1620 Ex Situ Remediation of Investigation-Derived Wastes containing PFAS by Electron Beam Technology

molar concentration of PFOA to be treated. Final defluorination efficiencies ranged from 34.6 to 95% under various increasing concentrations of nitrate, alkalinity, and fluvic acid. The defluorination is possibly due to the formation of aqueous electrons and the formation of secondary radicals (Wang et al. 2016). An additional study further demonstrated eBeam-mediated defluorination of PFOS and PFOA with decomposition efficiencies of 95.7% for PFOA and 85.9% for PFOS in an anoxic alkaline solution (pH = 13). Radical scavenging experiments indicated that the aqueous electron and hydrogen radical were important in the eBeam degradation of PFOA and PFOS (Ma et al. 2017). Further evaluation of this technology for treating other PFAS (polyfluorinated precursors and other long- and short-chain PFAAs) in soil and water, as well as testing over a range of concentrations, will be necessary to further understand treatment performance potential and to identify any deleterious byproducts.

12.5.7 Surface Activation Foam Fractionation

The surfactant nature of PFAS make them prone to accumulation at surface interfaces. Surface activation foam fractionation (SAFF) is a process that generates fine air bubbles rising through a narrow water column. PFAS that accumulate at the top of the column as foam are vacuumed off for separate disposal. Using hundreds of columns, PFAS is progressively stripped out until drinking water standards have been achieved. The process reduces the volume of PFAS-contaminated water. The base technology was developed and built in Australia and is currently operating at full-scale for the Australian Department of Defence, Army Aviation Centre Oakey (AACO) base near Toowoomba, Queensland. The AACO water treatment plan was commissioned on May 13, 2019 and treats 66,000 gpd.

A small one-day field trial in Williamstown, New South Wales, has also been applied in situ in an existing downhole groundwater monitoring well using compressed air introduced at the base of the well and harvesting of PFAS-rich foam at the top of the well (Phillips et al. 2018). This trial demonstrated that $\geq C6$ PFAS molecules could be removed from the treatment well annulus where hydrogeology could replenish the treatment well with a continuous supply of impacted groundwater. Further research to optimize the downhole foam fractionation engineering design is warranted.

12.5.8 Deep Well Injection

A potential alternative to treatment may be the use of on-site or off-site underground injection waste disposal wells for liquids containing PFAS. This approach eliminates discharges to surface water and groundwater, which could be a consideration given the present climate of varying discharge limitations for PFAS. Class I wells, as defined by USEPA, are acceptable for both hazardous and nonhazardous liquid wastes (USEPA 2019a). The USEPA has published guidance on the requirements for the use of injection wells, which include siting, construction, operation, monitoring, testing, record keeping, reporting, and closure (USEPA 2019a). The USEPA has also studied the risks associated with underground injection wells (USEPA 2001), and these risks should be considered for the use of underground injection wells for PFAS-laden water. This option may be most attractive as a disposal option for high concentration liquids, such as RO reject water, anion exchange regeneration fluids, wastewater from manufacturing sites, and landfill leachate.

12.6 Limited Application and Developing Solids Treatment Technologies

The treatment technologies presented in this document are provided in a hierarchy defined in Section 12.1, based on level of implementation and level of confidence in the technology from peer-reviewed literature and extent of documented performance. The three development levels include field-implemented technologies, limited application technologies, and developing technologies. Where appropriate in the text both in situ and ex situ technologies are discussed. However, it is not always clear if a limited application or developing technology may be effective in situ, ex situ, or both, thus further distinction between in situ and ex situ is not made in this section. Table 12-2 (provided as separate PDF) presents limited application and developing technologies for solids, which may be applicable to soil, sediments, biosolids, or other solid

media, including PFAS-laden materials (for example, GAC, resin, scrubbers, filters). Thermal treatment warrants further discussion as a limited application technology because it has been field-demonstrated at multiple sites by multiple practitioners but has not been well documented in peer-reviewed literature.

12.6.1 Sorption and Stabilization/Solidification

Limited application and developing materials being demonstrated or developed for sorption and stabilization include minerals (for example, organically modified clays) or stabilization agents (for example, Portland cement). Stabilization/solidification through mixing with cementitious materials (for example, Portland cement or other amendments) can be applied to encapsulate PFAS-impacted soil/sediment to restrict PFAS leaching or migration. In situ solidification is always performed with soils in place, and it is necessary to use specialized equipment and maintain careful control over the addition of amendments and water content. In situ solidification is intended to yield a high-compressive-strength monolith that has low permeability. A bench-scale study (Söregård, Kleja, and Ahrens 2019) indicated that solidification using a binder (combination of Portland cement, fly ash, and ground granulated blast-furnace base slag) at a ratio of 9:1 reduced leaching for 13 out of 14 PFAS (except for PFBS). Introducing additional additives (for example, activated carbon, surface-modified clays) at a 2% concentration can further reduce leaching of PFAS in solidification-treated soil.

12.6.2 Thermal Treatment

Thermal treatment is defined as mobilization or destruction, or both, of chemicals using heat. This can be accomplished by thermal desorption or thermal destruction. Heat is applied directly to the PFAS-contaminated soil/sediment.

Ex situ thermal treatment has been demonstrated (450–954°C) at field pilot-scale studies by a few technology vendors and is considered a partially demonstrated technology (Endpoint Consulting 2016; Enviropacific 2017; Colgan et al. 2018; Grieco and Edwards 2019). The effectiveness depends upon the ability to deliver heat to achieve sufficient and evenly distributed temperature at field scale cost-effectively. The pilot studies conducted have reported >90% removal of PFAS from soil when high heat has been applied.

In addition, lower temperature thermal desorption has been demonstrated to be effective for PFAS at 350–400°C on the bench scale. During a recent proof of concept laboratory bench test, 99.99% removal of PFAS from soils was demonstrated while heating the target volume to 400°C (Crowover et al. 2019; DiGuseppi, Richter, and Riggle 2019).

No documented examples of in situ thermal treatment for PFAS-impacted soil have been identified. However, the ex situ testing at 350–400°C suggests that these temperatures are sufficient for desorption of PFAS and therefore in situ treatment is potentially feasible for PFAS. In situ thermal treatment for PFAS is an energy-intensive treatment method. Its environmental footprint includes the energy source and consumption during treatment system operation, as well as manufacturing and installation of heating system materials.

At bench, pilot, and field scales, limited data sets are available and data gaps still exist mainly regarding fate of PFAS and air emissions (Lassen et al. 2013; USEPA 2020e). Another concern is the volatilization of hydrogen fluoride, which could pose serious health and safety issues and could compromise equipment components. Hydrofluoric acid and other non-PFAS off-gas concerns can be managed through conventional off-gas treatment systems (scrubbers). Although air emissions from the thermal treatment of PFAS have not been thoroughly studied at the field scale to date, PFAS destruction via high temperature air incineration and subsequent acid-gas scrubbing is a common practice during carbon reactivation (Mimna 2017).

Related Ongoing Research Funded by SERDP:

- ER18-1501 Hydrothermal Technologies for On-Site Destruction of Site Investigation Wastes Contaminated with Per- and Polyfluoroalkyl Substances (PFASs)
- ER18-1556 Small-Scale Thermal Treatment of Investigation-Derived Wastes (IDW) Containing Per- and Polyfluoroalkyl Substances (PFAS)
- ER18-1572 Evaluation of Indirect Thermal Desorption Coupled with Thermal Oxidation (ITD/TO) Technology to Treat Solid PFAS-Impacted Investigation-Derived Waste (IDW)
- ER18-1593 Demonstration of Smoldering Combustion Treatment of PFAS-Impacted Investigation-Derived Waste
- ER18-1603 Field Demonstration of Infrared Thermal Treatment of PFAS-Contaminated Soils from Subsurface Investigations

12.7 Integrated Remedial Solutions

The information above focuses on in situ and ex situ technologies available to treat (that is, destroy, stabilize, or remove) PFAS in water and soil. There are also nontreatment remediation approaches that may be employed at PFAS sites, including source zone or plume containment or mass flux reduction, excavation and off-site disposal, underground injection, and institutional controls. These approaches can be used alone or together with one or more treatment methods. This discussion provides some examples of remedial strategies that incorporate multiple approaches.

12.7.1 Combined Technologies for Treatment of PFAS and Co-Contaminants

In a drinking water context, PFAS removal may be an isolated treatment objective without interference from co-contaminants; treatment may include a single technology such as GAC. However, for groundwater remediation, particularly associated with PFAS release/source areas, PFAS compounds are typically present with other contaminants. For example, plumes emanating from former fire training areas may consist of PFAS in addition to petroleum hydrocarbons and chlorinated solvents that require different treatment approaches. Natural groundwater geochemistry, such as high metals or organic carbon concentration, can reduce PFAS treatment technology effectiveness and efficiency. A combined remedy approach, using multiple technologies simultaneously or in series, is generally required to optimize PFAS removal in these situations.

For example, McGregor (2018) documented a case study in which CAC was successfully injected to mitigate the mass flux of PFOS and PFOA from a source zone at a site in Ontario. At the same time, a slow-release oxygen amendment was injected to facilitate the aerobic biodegradation of petroleum hydrocarbons that co-occurred with PFAS in one part of the site. This is also an example of applying combined remedies in different areas of the site.

In some cases, the remediation of co-contaminants has affected the fate of PFAS compounds in plumes. Precursor compounds may be transformed in situ to PFCAs or PFSAs through aerobic biological transformation or transformed in situ to PFCAs through chemical oxidation. For example, (McGuire et al. 2014) presented a case study of an AFFF release site where oxygen infusion is believed to have resulted in accelerated transformation of precursors to PFHxS and PFCAs in part of the plume. This indicates that it is important to consider the potential influence of co-contaminant remediation on PFAS transformation or transport.

12.7.2 Addressing Source Areas and Plume with Multiple or Combined Remedies Using Multiple Types of Treatment Alternatives

It may be necessary at some sites to address both mass flux from source areas into groundwater and to contain or control plume migration.

The most commonly used plume containment alternative for PFAS plumes involves groundwater extraction with ex situ treatment. Options for reduction in mass flux leaving a source zone are partly discussed in the (ITRC 2008) Enhanced Attenuation of Chlorinated Organics guidance manual, although many of these are applicable to PFAS sites also. Mass flux reduction strategies for PFAS sites may include:

- injecting CAC to mitigate flux from the source zone (McGregor 2018), or at one or multiple locations within a groundwater plume
- capping part of a site to reduce infiltration through a PFAS source zone above the water table
- excavating shallow soil (although this may not have much benefit if there is a PFAS source zone below the depth of excavation)
- engineering management of surface water runoff to mitigate nonpoint sources at or upgradient of a site (ITRC 2018b)
- upgradient interception/diversion of groundwater to reduce the flux through a source zone below the water table.

12.7.3 Combined Technologies for Efficient PFAS Treatment

Because ultimate destruction of PFAS requires high-energy processes, combining practices that concentrate PFAS followed by destruction offers an opportunity for more efficient and cost-effective treatment. Examples of concentration processes that enable follow-on destruction include, but are not limited to:

- pump and treat using a regenerable ion exchange resin

- foam fractionation
- membrane separation
- reverse osmosis

Examples of destructive processes that are able to destroy separated waste, many of which are under development or have had limited application to date, are provided in Sections 12.5.4 and 12.5.6. Incineration is an example of another destructive technology which is a demonstrated full-scale application, though incineration has received recent attention due to possible incomplete combustion and/or by-product generation and is the topic of current study to better understand the fate of PFAS, see Section 12.4.

12.8 Sustainability of PFAS Treatment

Federal and state environmental protection agencies have published myriad green remediation best management practice fact sheets and guidance documents covering a variety of remediation topics and emphasizing the minimization of environmental cleanup footprints (USEPA 2012d, 2018b), including methods to quantify the environmental footprint (USEPA 2019g). The best management practice fact sheets for excavation and surface restoration, implementing in situ thermal technologies, and (more generally) materials and waste management may offer supplemental sustainability information to that already included alongside the remediation technologies presented within this section (USEPA 2008, 2012c, 2013b).

Applying such a framework for PFAS cleanup projects, the environmental impact drivers for PFAS cleanup technologies that should be considered include the life cycle environmental footprint of all facets of the cleanup, including project site preparation; installation of the remedy; materials, equipment, and energy used to operate the remedy; waste materials generated by the cleanup technology; and demolition and deconstruction of the remedy. In alignment with greener cleanups, green and sustainable remediation recommends the “the site-specific employment of products, processes, technologies, and procedures that mitigate contaminant risk to receptors while making decisions that are cognizant of balancing community goals, economic impacts, and environmental effects” (ITRC 2011b)2011(ITRC 2011a, p. 3). Economic and quality of life impacts to the community can be alleviated by early incorporation of green and sustainable remediation best management practices, including meaningful stakeholder engagement, creation of employment opportunities, and advancement of the local community’s skill set to help manage treatment systems and public outreach (USEPA 2012b). Lastly, climate change vulnerability and adaptation measures of remedial technologies should also be considered to ensure resiliency in the implemented remedial action (USEPA 2013a, 2014a).

In alignment with sustainability principles, performance of early and meaningful risk communication can assist professionals in raising the community’s awareness of environmental hazards, empowering community participation in risk reduction measures, and increasing the quality of life for the community impacted by contamination and related risk management activities (USEPA 2007). Several environmental and public health regulatory agencies have prepared information documents to assist professionals in performing effective risk communication for PFAS sites (for example, see (ATSDR 2018a).

In addition, a communication plan can be developed to assist with information dissemination and stakeholder engagement (Emmett et al. 2009). Section 14 provides further in-depth guidance on risk communication planning and performance. A risk communication toolbox is also being developed to help decision makers through the planning process and provide tools to assist with meeting performance metrics at each planning step. Additional guidance on stakeholder concerns and engagement is provided within this document in Section 13.

12.9 Improving Evaluation of PFAS Treatment Technologies

Significant effort has been completed with respect to reviewing and compiling comparative information on PFAS treatment technologies. In a number of instances, proponents of innovative treatment technologies have claimed success in removing or destroying PFAS with limited confirmation of performance. For example, removal mechanisms may not have been proven, byproducts may not have been measured, and the effect of the technology in actual environmental matrices, at environmentally relevant concentrations, on PFAS mixtures, or with co-contaminants present may be unknown.

To guide future assessments and investments in developing PFAS treatment technologies, a SERDP project has prepared suggested lines of evidence, recommended metrics, and decision tools to assess the effectiveness of PFAS treatment technologies. These lines of evidence and decision-making tools can be used to identify priorities and next steps to advance a given technology, assess whether a technology is ready for field demonstration, and identify key areas of uncertainty regarding technology performance.

Further SERDP-funded work (ER18-5053) is focused on developing a comprehensive assessment framework for ex situ PFAS treatment technologies and generating data to compare established and emerging approaches on a life cycle assessment and costing basis.

Related Ongoing Research Funded by SERDP:

- ER18-1633 Lines of Evidence to Assess the Effectiveness of PFAS Remedial Technologies
- ER18-5053 Evaluation and Life Cycle Comparison of Ex Situ Treatment Technologies for Per- and Polyfluoroalkyl Substances (PFASs) in Groundwater

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13 Stakeholder Perspectives

This section identifies the concerns of stakeholders who have been or may be affected by PFAS contamination. In this section, we summarize many of the concerns that have been expressed by local communities, tribes, and environmental groups. Evaluation of exposure levels and potential human health consequences are of paramount concern to stakeholders.

Section Number	Topic
13.1	Stakeholder Concerns
13.2	Specific Tribal Stakeholder Concerns
13.3	Stakeholder Resources

The term “stakeholder” is defined broadly by ITRC as members of environmental organizations, community advocacy groups, tribal entities or other citizens’ groups that deal with environmental issues, or a concerned citizen who is not a member of any organization or group. Public stakeholders, such as advocacy groups, often speak for the communities that are affected by environmental issues. In this document, a differentiation is made between public stakeholders and interested parties (responsible parties, state regulators, and owners and operators of contaminated sites).

Stakeholders share greater ownership of outcomes when they can influence site characterization, remedy selection, and long-term site management. Because PFAS compounds are so abundant in consumer products, stakeholders are also concerned with the production and eventual use of these products and are seeking safer alternatives and sometimes outright bans. Environmental regulators and responsible parties also benefit from informed, constructive stakeholder involvement because it can help them make better decisions, reduce the likelihood of costly, time-consuming repeated work, and allow those in affected communities to have a voice in governing the long-term use of land, water, and other resources. Often, stakeholders such as long-time residents have unique site knowledge as well as a major stake in the remedial outcome.

Developing site-specific characterization and remediation strategies for communities and tribal organizations can be controversial, because there are many misconceptions about PFAS. The lack of scientific knowledge about many of these PFAS compounds will be an impediment for educating the public. Therefore, early and effective community engagement emphasizing timely access to test data, transparency, and responsiveness is imperative. Community engagement may be able to address many stakeholder concerns and help to communicate risks. The ITRC Risk Communication Toolkit for Environmental Issues and Concerns includes information about stakeholder engagement and is published as a separate document.

This section identifies the concerns of stakeholders who have been or may be affected by PFAS contamination. Because it is an emerging contaminant and has been detected in ecological receptors (animals and plants) and blood serum in many humans, there are many individuals who are potentially affected worldwide.

In this section, we summarize many of the concerns that have been expressed by local communities, tribes, and environmental groups. Evaluation of exposure levels and potential human health consequences are of paramount concern to stakeholders. The list of concerns below is not all inclusive, as developments in science and identification of contaminants in the environment are likely to lead to additional concerns. This list was developed from general research on PFAS, direct communication and involvement with environmental and community groups, a consultant for one of the tribes, and extensive review of news reports. It is intended to highlight the concerns that have been expressed by various groups. It is not intended to be a definitive statement of the technical merits of those concerns.

The following is a list of the concerns that have been identified. Detail of these concerns follows.

- Lack of advisories for thousands of PFAS compounds
- Desire for one standard or screening level for PFAS compounds

- Lack of advisory standards or screening levels for PFAS in environmental media other than drinking water
- Lack of advisory standards for human consumption of food
- Lack of occupational standards
- Lack of ecological risk guidelines
- Lack of comprehensive monitoring information
- Precautionary approach
- Safety of short-chain substitutes
- AFFF release sites and Unused AFFF Disposal
- Duty to warn AFFF responders
- Limitations in sampling and analysis methods
- Limited programs for health monitoring and blood testing
- PFAS in food packaging
- Potential PFAS contamination in recycling and compost
- Lack of disclosure by product manufacturers
- Lack of disclosure of information on the health effects of PFAS
- Responsibility for sampling and treatment on private property
- Lack of scientific evidence that current PFAS cleanup methods and remedies are fully protective of human and ecological health and prevent toxic emissions
- Stormwater discharges that may contain PFAS
- Psychological effects
- Economic consequences of local PFAS contamination

Stakeholders who use this document should consider that much of the information is very technical. Nevertheless, it aims to lay a framework by which to understand this set of compounds, the foundational nature of the science, and many of the uncertainties.

13.1 Stakeholder Concerns

13.1.1 Lack of Advisories for Thousands of PFAS Compounds

As of September 2019, USEPA has set health advisories for only two of the over 4,000 PFAS compounds: PFOA (perfluorooctanoic acid) and PFOS (perfluorooctane sulfonate). The lifetime health advisory has been set at 70 nanograms per liter (ng/L or parts per trillion) for the combined concentrations of PFOA and PFOS in drinking water. The health consequences of many PFAS compounds remain uncertain. Firm conclusions relating individual PFAS compounds to specific health outcomes remain elusive (Guelfo et al. 2018).

13.1.2 Desire for One Standard or Screening Level for PFAS Compounds

Many stakeholders believe that PFAS should be treated as a class of chemicals, similar to how PCBs or dioxin are currently regulated. Given the lack of toxicological information for the vast majority of PFAS, when even less is known about the potential additive and synergistic effects associated with PFAS mixtures, many stakeholders support testing for total PFAS as the preferred screening method, rather than limited compound-specific testing using target analyte lists (CSWAB 2018). For example, the Conservation Law Foundation in New England put forth a petition requesting that PFAS in drinking water be regulated as a group with a treatment technique drinking water standard. See <https://www.nhpr.org/post/activists-ask-new-england-states-regulate-pfas-chemicals-class#stream/0> and <https://www.mass.gov/lists/pfas-information-a-petition-for-rulemaking-to-establish-a-treatment-technique-drinking-water>. However, many PFAS, like certain fluoropolymers, need significantly less toxicological information because of their inability to enter cells to cause adverse effects (Henry et al. 2018).

13.1.3 Lack of Advisory Standards or Screening Levels for PFAS in Environmental Media other than Drinking Water

With the exception of regional soil screening levels for PFOS, PFOA, and PFBS, there are no federal standards or screening levels for monitoring environmental media (air, soil, and surface water and groundwater not used for drinking), and no federal requirements that compel such monitoring. USEPA is planning to develop interim recommendations regarding groundwater for PFOS and PFOA. USEPA is planning to develop interim cleanup recommendations to address groundwater contaminated with PFOA and PFOS. Section 8 includes information about regulations, guidance, and advisories for PFAS. There are few limits by the federal and most state governments on PFAS in biosolids being applied to land for food and/or

nonfood crops, nor on concentrations in surface water that may affect fish and consumers of fish. PFAS, including PFOA and PFOS, have been detected in biosolids produced at a wastewater treatment plant (WWTP), and in soil, surface waters, and leachate from landfills. WWTP sludge is commonly applied to land as a soil amendment. Botanical uptake by crops such as corn, hay, and soybeans is suspected. Section 5.6 and Section 6.5.1 discuss plant uptake of PFAS. In addition, PFAS in surface water also creates an exposure pathway that potentially affects ecological and human health.

13.1.4 Lack of Advisory Standards for Human Consumption of Food

Some states have issued new fish consumption advisories for lakes and rivers after tests confirmed the presence of PFAS in surface water. Section 15.3 includes a case study example about a recently enacted fish consumption advisory by the New Jersey Department of Environmental Protection.

In February 2018, the Environmental Protection Authority of Victoria, Australia, “assessed waterfowl from three wetlands to better understand the extent and distribution of PFAS contamination ahead of the duck hunting season. PFAS was detected in waterfowl from all three wetlands.” “In May and June 2018, the agency conducted a more extensive study into PFAS concentrations in waterfowl from 19 wetlands around the state ...Waterfowl tissue samples were found to contain variable PFAS concentrations. Perfluorooctane sulfonate (PFOS) and perfluorohexane sulphonic acid (PFHxS) concentrations in waterfowl from nine wetlands exceeded Food Standards Australia and New Zealand (FSANZ) trigger points for investigation. As a result, health risk assessments were undertaken on the samples that exceeded FSANZ trigger points for investigation, and health advisories were issued” (Environmental Protection Authority Victoria 2019)p.1.

In addition, PFOS is accumulating in the Arctic. The Alaska Community Action on Toxics (ACAT) reported that “A study on the presence of PFOS in the livers of arctic animals revealed elevated PFOS levels in almost all species studied.” Furthermore, it reported that “In a recent study of foods consumed by a Canadian Inuit population, traditional foods were more widely contaminated and contained higher concentrations of PFCs [PFAS] than nontraditional foods. Caribou had the highest concentrations of perfluorinated compounds (PFCs), including PFOS.” (A Report for the Delegates of the 4th Conference of the Parties Stockholm Convention on Persistent Organic Pollutants, see https://www.akaction.org/wp-content/uploads/2013/03/POPs_in_the_Arctic_ACAT_May_2009.pdf). At the request of the Yupik people of St. Lawrence Island, the ACAT is conducting a study to determine the safety of the traditional foods they eat for subsistence.

13.1.5 Lack of Occupational Standards

Workplace exposures seems to be poorly studied and there are no standards for occupational exposure for PFAS. Workers at paper mills and wastewater treatment plants where PFAS have been documented in indoor air, as well as developers and industrial users of PFAS, do not have specific occupational standards.

13.1.6 Lack of Ecological Risk Guidelines

There is wide concern that ecological receptors have been or will be harmed by releases of PFAS to the environment (Section 7.2). Currently, there are no federal risk-based ecological guidelines or thresholds for environmental media. Ecotoxicity studies are generally limited to a relatively small number of PFAS compounds (typically PFOA and PFOS). It is important to expand studies in this field to evaluate additional PFAS, including short-chain precursor compounds as well as “next-generation” substitute compounds. Several states have established some criteria that are intended to protect aquatic organisms in their respective surface waters. Section 8.2.3 includes more information about state regulation of PFAS. In addition, the ITRC also maintains updated tables of PFAS water values, and PFAS soil values from state, federal, and some international countries posted as an Excel file <https://pfas-1.itrcweb.org/fact-sheets/>.

13.1.7 Lack of Comprehensive Monitoring Information

Many stakeholders are concerned that most individuals and communities do not have any testing for PFAS. America’s Water Infrastructure Act of 2018 requires drinking water systems serving more than 3,300 people to test for unregulated contaminants pursuant to USEPA’s Unregulated Contaminants Monitoring Rule (UCMR). However, sampling for UCMR4 (USEPA 2016f), which occurred between 2018-2020 did not include any PFAS compounds in its analyte list. Many stakeholders are concerned that an opportunity to better understand the magnitude of PFAS contamination on public water systems (PWSs) will not be taken. Prior to this new law, only drinking water systems that served more than 10,000 people were required to monitor for unregulated contaminants. Contaminants covered by the UCMR include PFOA, PFOS, 1,2,3-TCP, hexavalent chromium, and 1,4-dioxane. Additionally, smaller PWSs and private wells were not included in the third round of USEPA’s required monitoring (Unregulated Contaminant Monitoring Rule, UCMR3). The new testing requirement, which goes

into effect in 2021, is expected to add more than 5,000 drinking water systems to the list of systems that are required to test for these unregulated contaminants. However, the UCMR4 does not cover PFAS (https://environblog.jenner.com/corporate_environmental_/2018/10/new-law-requires-widespread-testing-for-unregulated-contaminants.html). UCMR5 is going to test for some PFAS chemicals.

More information about the UCMR3 data is included in Section 8.2.2.2. It is estimated that approximately six million residents of the United States have drinking water that exceeds the health advisory for PFOA or PFOS, or both (APHA 2016). Moreover, there is no ongoing federal requirement for PFAS testing of any drinking water systems or private wells. Some states (for example, New Hampshire) have initiated testing of private wells in certain locations where there is a high potential for PFAS contamination. The Washington State Department of Health recently announced that it will be conducting additional testing for PFAS at several hundred untested water systems. The state of Michigan is also testing all public community water systems for PFAS (see <https://www.michigan.gov/pfasresponse/0,9038,7-365-88059--,00.html>).

13.1.8 Precautionary Approach

Given the lack of toxicological data for the great majority of PFAS compounds and mixtures, many stakeholders want a precautionary approach to the use, treatment, and analysis of PFAS-containing chemicals. This precautionary approach presumes compounds of similar structure may be expected to have similar modes of action and pose a similar risk to human health and the environment, lacking evidence to the contrary.

13.1.9 Safety of Short-chain Substitutes

Many stakeholders are concerned with the use of substitute short-chain PFAS. After concerns arose that PFOA and PFOS (both long-chain PFAS) have health risks at very low concentrations, industry began to develop and substitute them with shorter chain PFAS. Although some short-chain PFAS appear to be less bioaccumulative, the publicly available data are limited. Short-chain PFAS are persistent, degrade into extremely persistent forms, and tend to be more water soluble and more mobile than long-chain PFAS. Because of their greater water solubility, studies indicate short-chain substitutes are more readily taken up by plants than longer chain PFAS, including food crops (Higgins 2017). In their Interim Chemical Action Plan for PFAS, the Washington State Department of Ecology and Washington State Department of Health (2019 p. 1) states that short-chain PFAS are difficult to remove from water, noting further “Without additional health and safety data, it is impossible for us to evaluate whether short-chain replacements are safe substitutes. If environmental exposures to short-chain PFAS are found to pose health risks to people or the environment, mitigation will be difficult and expensive.” Finally, in the Helsingør Statement (Scheringer et al. 2014) and the Madrid Statement on Poly- and Perfluoroalkyl Substances (Blum et al. 2015), scientists and other professionals expressed concerns about the embrace of short-chain PFAS as preferable replacements for long-chain PFAS.

13.1.10 AFFF Release Sites

Many stakeholders believe that all potential AFFF release sites should be investigated, and where necessary, potential exposure should be mitigated. Investigations to date have identified the use of AFFF as one of the main sources of PFAS releases to the environment, and AFFF releases have been responsible for PFAS contamination of multiple drinking water sources. Although AFFF foams typically contain less than 2% total PFAS, thousands of gallons of foam mixture may be applied during a given event, and the concentrations of concern for PFAS are very low (below 100 parts per trillion (ppt)). Typical locations where AFFF is stored and used include civilian airports, military bases, chemical plants, municipal fire departments, oil refineries, bulk fuel storage facilities and terminals, and crash sites. AFFF was used abundantly for training purposes at military bases with flight operations and at civilian airports. Additional information is presented in the ITRC AFFF fact sheet (ITRC 2018a) and in Section 3.

13.1.11 AFFF Disposal

Stakeholders are concerned that the disposal method (incineration) for unused AFFF is not regulated and that there may be dangerous byproducts. The military is planning to collect and destroy unused firefighting foam that contains PFOS and PFOA (USDOD 2018a). More than 3 million gallons of the foam and related waste have been retrieved by the military. In a 2017 request for AFFF disposal research project proposals (U.S. Air Force 2017), the Air Force acknowledged that the foam, which was designed to resist extremely high temperatures, is difficult to burn and that “the high-temperature chemistry of PFOS and PFOA has not been characterized, so there is no precedent to predict products of pyrolysis or combustion, temperatures at which these will occur, or the extent of destruction that will be realized.” With unregulated chemicals, there are no protocols that require incineration to reach certain temperatures. (See <https://theintercept.com/2019/01/27/toxic-firefighting-foam-pfas-pfoa/>)

13.1.12 Duty to Warn AFFF First Responders

Aside from standard workplace safety requirements regarding hazardous materials right-to-know, there has been no legal duty to warn or to require notice of hazards to first responders who handle AFFF. Several studies have concluded that some PFAS were elevated in blood of first responders. The New Hampshire Department of Health and Human Services PFC Blood Testing Program (NH DHHS 2016) results indicate the geometric mean levels of PFOS and PFHxS in firefighters were elevated versus the geometric mean levels of those who had not worked as firefighters. Numerous other studies indicated that blood serum levels were elevated in firefighters (LeMasters et al. 2006; Jim ey al. 2006; (Dobraca et al. 2015). It is difficult to tease out whether these higher levels are related to exposures to AFFF, PFAS in firefighter gear (clothing), or consumption of water from PFAS-contaminated drinking-water wells in affected communities, especially those that may be located near training facilities that have used AFFF.

13.1.13 Limitations in Sampling and Analysis Methods

Stakeholders are concerned that current PFAS site investigations may not adequately define the types and total mass of PFAS present, due to limitations in analytical methods (see Section 11) that are still evolving. Moreover, the PFAS family of compounds contains thousands of chemicals, but standard analytical methods can identify only a few dozen.

A related concern is that the new specification for shorter chain AFFF published by the Department of Defense (USDOD 2018b; NAVSEA 2017) still allows concentrations of PFOA and PFOS up to 800 ppb in AFFF concentrate, because that is the lowest concentration of either PFOA or PFOS that can be measured in the concentrate with current analytical methods. This is because the overall high concentrations of the many chemicals in the AFFF concentrate “swamp” the lab instrument, interfering with its ability to detect any individual compound except when it is present at high concentrations. The new, short-chain AFFF formulations are fluorotelomer-based, so PFOS (and other PFASs) should not be present and PFOA may be present only as contamination from the production process (as discussed in Section 3.1), but without analytical methods to prove this users cannot know for certain if the new AFFF products are PFOS- and PFOA-free. The ITRC AFFF fact sheet (ITRC 2018a) includes more information about AFFF specifications.

13.1.14 Limited Programs for Health Monitoring and Blood Testing

Some PFAS (for example, PFOA, PFOS) bind to proteins in the blood, making blood testing a means of investigating human exposure to PFAS. Many communities where PFAS has been detected have asked that the government establish a program for blood serum testing and long-term health monitoring so that they can better understand any health risks associated with PFAS exposure. Some states have provided limited testing on people in high-impact areas. For example, New Hampshire provided blood serum testing for people who worked on, lived on, or attended childcare on an AFFF-impacted site and were exposed to contaminated drinking water (NH DHHS 2016). New Hampshire also performed blood tests in selected towns where people used private wells that tested above health advisories for PFOA and PFOS. However, many state and local governments are wary of blood testing programs because there is no correlation between the PFAS level in blood serum and any definitive health effects. People who participate in such tests are usually informed of their results and provided context about how they compare with national and location-specific averages. It does not appear that any long-term program has been established to monitor the health outcomes of exposed populations. If there is no assistance from the government, many community members cannot afford to have their blood tested.

13.1.15 PFAS in Food Packaging

Many stakeholders are concerned that food packaging containing PFAS leaches into food. Food packaging, such as bowls, plates, clamshells, trays, and pizza boxes, often includes PFAS for anti-grease resistance, and PFAS is sometimes used in the molding process to manufacture paper plates and containers. A 2008 FDA study found that “fluorochemical paper additives do migrate to food during actual package use,” and oil and grease “can significantly enhance migration of a fluorochemical from paper” (Begley et al. 2008).

There is only limited peer-reviewed information regarding PFAS transfer to food. One study documented that 6:2 FTOH moves from dishware or containers into food (Yuan et al. 2016). A Canadian analytical lab found that PFBA moves from cupcake liners into cupcakes (CEH 2018).

The FDA has approved 20 next-generation, short-chain PFAS for coating paper and paperboard used to serve food. The FDA Effective Food Contact Substance Notifications database is available online (FDA 2018). Concerns have been raised that these compounds have not been adequately tested for human impact. Because of trade secrecy laws with regard to patents, the government does not publicly disclose the identity of the specific chemicals in food packaging. However, according to

The Intercept (Lerner 2016), in documents filed with the USEPA, under TSCA section 8(e) requirements, DuPont (2010) reported that substitute PFAS, called GenX chemicals, used to produce food contact paper could pose a “substantial risk of injury,” including cancerous tumors in the pancreas and testicles, liver damage, kidney disease, and reproductive harm.

The State of Washington has enacted a law to ban PFAS use in food packaging. Not only does PFAS in food packaging pose potential risks to consumers of the food, but the used packaging may end up in compost or landfills. Compost is eventually applied to soil and potentially transferred to certain food crops. If it goes to a landfill, it potentially ends up in the landfill’s leachate.

13.1.16 Potential PFAS Contamination in Recycling, Compost, and Fertilizer

Carpeting, furniture, and numerous other items containing PFAS are often recycled. There is concern that the recycled materials are often used in products where the consumer has no way of knowing whether it has PFAS contamination. Biosolids from wastewater treatment plants are used in some composts and fertilizers and PFAS sampling is not part of the screening process for these products. Additionally, more testing and regulation is needed for land-applied paper mill waste. Paper mill waste is exempt from the Resource Conservation and Recovery Act (RCRA) as a beneficial reuse. Composting of paper mill waste to make fertilizer, which, for example, is still done in Michigan, should get more attention. It is difficult to know which mills make “waterproof” or food contact papers.

13.1.17 Lack of Disclosure by Product Manufacturers

Some stakeholders are concerned that chemical and product manufacturers are not required to disclose when they sell, make, or use PFAS in their products. For example, sturdy, waterproof and heat-resistant products are produced for the construction industry. Additionally, there is lack of disclosure and transparency concerning the composition of AFFF. AFFF suppliers claim that formulations are proprietary.

13.1.18 Lack of Disclosure of Information on the Health Effects of PFAS

Some stakeholders are concerned that politics may delay or even prevent the full disclosure of PFAS toxicity information. For example, the release of ATSDR’s Draft Toxicological Profile for PFAS was reportedly delayed because of concerns about the public response. This example, if replicated, leads to distrust and reduces the efficacy of risk communication. Additionally, collected health data may not be clearly and fully shared or explained to stakeholders.

13.1.19 Responsibility for Sampling and Treatment on Private Property

When off-site contamination is suspected or discovered, stakeholders believe that the responsible parties should be accountable for establishing an entire program to deal with the problem. This includes sampling and analysis, disclosure of PFAS content, health monitoring, and if appropriate, remediation and mitigation. Upon detection of PFAS above state or EPA limits, responsible parties should be required to provide affected residents with alternative water supplies. Additionally, stakeholders believe that the cost of the program, including long-term treatment and monitoring, should be borne by responsible parties.

13.1.20 Lack of Scientific Evidence that PFAS Cleanup Methods and Remedies Are Fully Protective of Human and Ecological Health and Prevent Toxic Emissions

Stakeholders believe that treatment systems should be monitored for effectiveness. There is also concern that disposal or regeneration of GAC canisters, resins, and byproducts will add contaminant loads of PFAS compounds to the air, land, and water. Companies that treat spent carbon filters that contain PFAS cannot document full destruction of all PFAS. Some claim all PFAS are destroyed, yet the research they cite is only on PFOS and PFOA destruction.

13.1.21 Stormwater and PFAS Manufacturing Discharges that May Contain PFAS

PFAS, including PFOA, have been detected at the storm drain outfalls at active facilities. Stakeholders are concerned that most NPDES effluent permits do not require PFAS sampling and the magnitude of PFAS concentrations in such discharge remains unknown. Older and inactive facilities’ discharge areas, many of which have not been sampled for PFAS, can also act as long-term sources of PFAS in soil.

13.1.22 Psychological Effects

It was reported at one EPA community forum that children in some communities are scared to drink water, and blood level values have become an identity. This has occurred in other communities where contaminated drinking water supplies have

the effect of deterring children from drinking clean water.

13.1.23 Economic Consequences of Local PFAS Contamination

Individuals have voiced concerns about significant economic consequences on property values and businesses. In one instance, because PFAS was detected in water used by dairy cattle, they had difficulty selling the milk products. Stakeholders are particularly concerned about facilities located in economically disadvantaged communities. These communities need the economic benefits of a facility but have few resources to demand enough testing of air emissions and of potential health impacts on the community.

13.2 Specific Tribal Stakeholder Concerns

Tribes share many concerns with other stakeholders; however, they differ from other stakeholders in several key aspects. The 573 federally recognized tribes are each culturally, governmentally, and socially unique. Some tribes view any level of contamination of their lands and natural and cultural resources as unacceptable. Many tribes have culturally significant or sacred areas, which may include springs, mountains, hunting areas, plant-gathering areas, or burial sites. When culturally significant or sacred areas are affected, traditional methodologies that nontribal environmental professionals rely on (such as the applicable exposure scenarios or factors for a risk assessment) may not be sufficient to portray the effect to a tribe. For example, some plants and animals can have tremendous cultural or religious importance to a tribe, including birds and feathers, game animals, and herbs. Additionally, many tribal cultural ceremonies include the use of water. Other areas of difference include diet (for example, some tribes consume more fish per capita) and growing crops or grazing animals on areas fertilized by biosolids from wastewater treatment facilities.

Tribes are sovereign entities that have established government-to-government relationships with federal, state, and local governments—relationships that must be recognized in the decision-making process. When a PFAS-contaminated site affects a tribe, the project timeline must include tribal approvals in addition to other typical agency approvals. Sampling, research, and services on tribal lands generally require institutional review board or tribal council approval. Each sovereign nation operates differently, ranging from tribes that have no research capacity to tribes that have a full review board with a formal application process. The initial steps in the approval process may include drafting a proposal, preparing a poster or podium presentation, and presenting to the tribal government.

Once tribal approval is granted and the project commences, the practitioner must obey tribal protocol with respect to cultural practices. The tribe may reserve the right to retain the findings in the case of exploratory research and restrict publication. Regulatory findings for water and soil concentration, level of treatment, and monitoring are first reported to the tribe's department of environmental quality or natural resources and then forwarded to state environmental organizations and USEPA.

Most of the tribal concerns are listed in Section 13.1. However, as mentioned above, there may be some distinctions that are important to tribes:

- PFAS in surface waters and lakes may have a higher level of concern when they are used for fishing, given that tribal members rely on these water bodies.
- Drinking water and irrigation water in the arid Southwest are limited, and there is heightened concern that tribes will be unduly impacted if drinking or irrigation water is contaminated.
- Tribal lands are often close to installations that used AFFF (notably DOD) or other industrial sources of PFAS (manufacturers, leather tanneries).
- Where biosolids have been applied to tribal farmlands or grazing lands, there is a need to survey these tribal lands. In some cases, cities may have paid tribal communities to spread biosolids from WWTPs that may have been contaminated with PFAS.
- Activities on and near tribal lands may have involved use of PFAS-containing chemicals that could impact tribal members working in these facilities through inhalation and dermal exposure.
- Landfills on tribal lands that accepted outside waste need to be sampled for PFAS contamination, which may be in the landfill leachate. Companies that paid a fee to the tribes to use their land managed many of these landfills. Although most required sampling, often the sampling plans did not include sampling landfill leachate for PFAS.
- A big issue facing tribes is that tribal environmental offices and budgets are typically small, and they do not have the people or money to perform appropriate site investigations to determine if they have PFAS in their community.

13.3 Stakeholder Resources

Below are a number of resources for communities. These resources are websites of major environmental organizations and projects that specifically deal with PFAS. These groups aim to help environmental and community groups to better understand the issues and science about PFAS.

<https://cswab.org/pfas/about-the-pfas-campaign/> and

<https://cswab.org/wp-content/uploads/2010/09/List-of-military-fire-and-crash-training-sites-2014.pdf>

<https://pfasproject.com> (A project of Northeastern University)

<https://earthjustice.org/features/breaking-down-toxic-pfas>

<http://www.testingforpease.com>

<https://www.civilianexposure.org/the-military-covers-up-the-extent-of-pfas-contamination-across-the-country-while-it-continues-to-poison-hundreds-of-communities/>

<https://toxicfreefuture.org/science/chemicals-of-concern/pfas-nonstick-nightmare/>

<http://gatehousenews.com/unwellwater/>

https://www.ewg.org/interactive-maps/2017_pfa/

<https://www.ewg.org/research/report-110-million-americans-could-have-pfas-contaminated-drinking-water>

<https://www.ewg.org/research/pfas-chemicals-contaminate-us-military-sites>

<https://www.ewg.org/research/many-fast-food-wrappers-still-coated-pfcs-kin-carcinogenic-teflon-chemical>

<https://greensciencepolicy.org/highly-fluorinated-chemicals/>

<https://www.sixclasses.org/videos/highly-fluorinated-chemicals>

<https://toxicsaction.org/issues/pfas-water-contamination/>

<https://www.ucsusa.org/center-science-and-democracy/preserving-science-based-safeguards/toxic-threat-pfas-contamination-military-bases>

<https://www.nrdc.org/experts/anna-reade/epa-finds-replacements-toxic-teflon-chemicals-are-also>

<https://silentspring.org/research-area/about-highly-fluorinated-chemicals-pfass>

[https://clu-in.org/contaminantfocus/default.focus/sec/Per-_and_Polyfluoroalkyl_Substances_\(PFASs\)/cat/Policy_and_Guidance/](https://clu-in.org/contaminantfocus/default.focus/sec/Per-_and_Polyfluoroalkyl_Substances_(PFASs)/cat/Policy_and_Guidance/)

USEPA conducted five community engagement events and one event with tribal representatives during the summer of 2018. Meeting materials, information, and summaries of each event are provided on USEPA's website:

<https://www.epa.gov/pfas/pfas-community-engagement> A series-specific topics of concern and associated social factors identified from presentations by public and community stakeholders during the USEPA PFAS community meetings held in 2018 are provided in the ITRC Risk Communication Toolkit for Environmental Issues and Concerns is published as a separate document.

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14 Risk Communication

The PFAS Team developed a training module video with content related to this section, it is the Risk Communication video.

The ability to communicate potential risks to human health and the environment is a vital skill to facilitate community participation and decision-making. Risk communication can be particularly challenging when dealing with science that is rapidly evolving, as in the case with PFAS. Communicators must grapple with competing interpretations of uncertain science and risk management strategies, while earning community trust and promoting meaningful engagement. This section addresses PFAS risk communication challenges and risk communication tools with PFAS-specific examples. Case studies that demonstrate successful risk communication planning and performance are included in Section 15.4.

Section Number	Topic
14.1	Role of Risk Perception
14.2	Risk Communication Challenges
14.3	Risk Communication Planning and Engagement Tools

According to USEPA's Risk Communication in Action: The Risk Communication Workbook (USEPA 2007, p.1), the overall purpose of risk communication is *to assist affected communities [to] **understand** the processes of risk assessment and management, to **form** [scientifically valid] **perceptions** of the likely hazards, and to **participate** in making decisions about how risk should be managed.* Risk is the relationship between the probability of harm associated with an activity and vulnerability of exposed elements (Slovic 1987; Slovic 2003).

The ITRC Risk Communication Toolkit for Environmental Issues and Concerns is published as a separate document. In addition, guidance on general performance of risk communication for contaminated sites is provided in *Risk Communication in Action, the Risk Communication Handbook*, (USEPA 2007); *Decision Making at Contaminated Sites: Issues and Options in Human Health Risk Assessment*, (ITRC 2015a); and *Improving Dialogue with Communities: A Risk Communication Manual for Government* (New Jersey Department of Environmental Protection; (Hance 1991).

The following subsections present risk communication challenges of PFAS and provide PFAS-specific risk communication information for components of risk communication planning.

14.1 Role of Risk Perception: Public Stakeholders and Decision Makers

It is essential for decision makers to understand stakeholders' risk perceptions of the hazard. Stakeholders include, but are not limited to, the community, public entities, potential responsible parties, regulatory agencies, and municipal and state officials. Risk perception for PFAS is challenging to address because the science is rapidly evolving, the exposure is perceived as involuntary, the risk management strategies are a moving target, and health impacts are greatest for the most sensitive populations. The risk management strategies can be a moving target because of these challenges.

The environmental management community is acting largely on the basis of growing evidence of health risks and general precaution as our understanding of PFAS exposure and associated risk is continuously redefined. In this context, risk amplification and attenuation can serve as guiding principles to better understand stakeholder context and site-specific factors contributing to stakeholders' perceived risk to proposed risk management strategies.

14.1.1 Role of Risk Perception and Public Stakeholders

In a scenario of risk amplification, stakeholders perceive their risk to a hazard as a major concern while experts assess the hazard as carrying a lesser degree of risk (for example, low or moderate) (Kasperson and Kasperson 1996). In the context of PFAS, risk perception is heightened by uncertainties and variability among policies and standards due to developing sampling methodologies and analytical procedures; new scientific information on health effects, risk assessment evaluations, and treatment technologies (NGWA 2017); and overall confidence/trust in the proponent or lead organization

that is communicating risk. Additional human health and exposure factors that heighten risk perception for PFAS are summarized in Section 14.2, Risk Communication Challenges.

This heightened sense of risk may result in opposition to proposed risk management strategies, such as source control (in which there is scientific uncertainty pertaining to the “safe” level of exposure, if any, without risk).

To address risk amplification challenges, it is important to build trust among the community by maintaining transparent communication of these uncertainties and variabilities early in the project life cycle (USEPA 2005b, 2007). New data findings and research on PFAS should be regularly shared with impacted stakeholders. Current knowledge, including uncertainties and information about variability of potential susceptibility to health effects in individuals with the same exposures, should be conveyed accurately in an understandable manner.

Uncertainties in individual causation and variability in regulatory guidance can cause the affected individuals to lack confidence in current scientific knowledge. Therefore, a risk communication project team should communicate these uncertainties to the affected individuals in collaboration with risk assessors, community involvement coordinators, and community members to develop site-specific messaging. It is important to understand that standards for the same chemical often differ depending on the entity setting them. This is not unexpected, because standard-setting guidance is not simply a mathematical formula. Risk assessment approaches used in standard-setting processes include best professional judgment in the selection of the factors involved. In addition, a collaborative effort can be made to develop performance metrics, supplemental to cleanup standards, that evaluate how the action will lead to measurable increased protection for public health and the environment, thus leading to the development of targets or objectives (Hadley, Arulanantham, and Gandhi 2015) that offer reductions in risk. These metrics are referred to as secondary risk management performance metrics and can be used to communicate and evaluate success of a proposed PFAS risk management strategy, as well as assist with alleviating stakeholder concerns associated with uncertainty. Examples of applicable secondary risk management performance metrics in the context of PFAS are reduction in contaminant bioavailability/loading, source control/removal, and mitigation of exposure pathways (NGWA 2017; Harclerode et al. 2016).

Furthermore, risk amplification can be heightened when a community perceives that they have limited control over risk. Explicit efforts to share control reduce outrage and risk amplification (Sandman 2013). Therefore, it is essential to create an atmosphere of collaboration. In situations where an open public forum is met by public outrage, it is important to be compassionate and lend a listening ear. Acknowledgment and documentation of questions that cannot be answered communicates transparency and can be a first step toward building trust. Effective participation is presented in the ITRC Risk Communication Toolkit for Environmental Issues and Concerns.

In contrast, in a risk attenuation scenario, experts judge hazards as relatively serious while stakeholders do not pay attention or pay comparatively little attention to that risk event (Kasperson and Kasperson 1996). This diminished sense of risk results in challenges in stakeholder participation in risk mitigation activities (“Why do we need to spend money/do testing, etc., for this?”). In the context of PFAS, risk mitigation and monitoring measures include participation in blood testing, installation of a water treatment system, and use of an alternate water source. To address risk attenuation challenges, site-specific risk perception factors related to inaction can be identified via stakeholder engagement and integrated into a communication plan (NGWA 2017; Harclerode et al. 2015; Harclerode et al. 2016).

14.1.2 Role of Risk Perception and Decision Makers

Due to the evolving science of PFAS, project managers, risk assessors, and risk communicators can also become caught in between those who amplify risk and those who deny risk. As noted, uncertainty in the toxicity and risk can lead to lack of consensus on how to evaluate risk and proposed risk management strategies. Due to risk amplification, there may be an elevated demand to take action to reduce potential risks beyond what is even technically and/or financially feasible. The underlying uncertainty feeding this risk amplification may also lead to opposition to proposed risk management strategies from some decision makers prior to establishment of the “right number” to dictate such action. When communicating with the public, it is essential to mitigate downplaying or embellishing risk due to lack of consensus on risk among decision makers.

Strategies should be implemented by the lead organization to navigate this rift to craft an approach and communicate a plan that is most likely to be reasonable and protective. One strategy is to incorporate the community’s needs and values to place a greater weight on how risk management is considered. A second strategy is to develop secondary risk management objectives to help evaluate how interim and long-term action will lead to measurable increased protection for public health and the environment (Hadley, Arulanantham, and Gandhi 2015; Harclerode et al. 2016). These complexities highlight the

importance of formulating a robust risk communication plan and team, including community and third-party involvement, as needed, as well as considering the dimension of perception as part of the risk communication process.

Case studies that showcase implementation of meaningful and effective community participation and inclusion of a third, neutral party to facilitate implementation of a successful risk communication strategy for PFAS-impacted communities are included in Section 15.4.

14.2 Risk Communication Challenges

There are many general challenges to risk communication about any environmental situation, including diversity of audience backgrounds, importance of establishing trust among the parties, and clearly communicating about the scientific and regulatory requirements. ITRC's Risk Communication Toolkit for Environmental Issues and Concerns includes a more detailed discussion of these challenges.

Emerging contaminants, and more specifically PFAS, pose unique challenges to achieving meaningful and effective risk communication. There is often divergent information available from different sources about the potential severity and uncertainty associated with exposure and adverse health impacts that may result from exposure, and the need for treatment or response actions. For example, people will do their own research, which may result in conflicting information. Communicators need to be prepared to explain the choices and decisions made regardless of the conflicting information. Some of the risk communication challenges for PFAS are discussed in the following sections.

14.2.1 Regulatory

There are regulatory challenges for emerging contaminants, see Section 8.

- PFAS are emerging contaminants, which means that they are the subject of intensive investigation, so new information, and thus our understanding of hazard, exposure, and risk, are emerging and evolving. This can challenge us to rethink determinations of protectiveness within very short time scales.
- Federal and state standards, guidance, and policies for PFAS are not uniform and are available for only a handful of compounds.
- Regulatory standards and health advisories are in the parts per trillion range, and it is difficult to explain to a layperson what these low levels mean in terms of risk, or how they were derived.

14.2.2 Fate and Transport

There are technical and scientific challenges and uncertainties around fate and transport of PFAS in the environment, see Section 5.

- There are many sources for PFAS and many of them have multiple release mechanisms, so simply explaining where the PFAS came from and how it got into the environment can be complicated.
- Most people have only a very basic understanding of (and lots of misconceptions about) chemistry, geology, environmental systems, and groundwater. Risk communicators often need to provide this context before even discussing site or chemical specifics.
- Fate and transport behaviors differ among individual PFAS (although broad generalizations can be made based on chain length and functional groups).
- The environmental persistence, solubility, and mobility of PFAAs can result in:
 - very large impacted areas encompassing a wide range of environmental settings and potential transport pathways
 - complex transport pathways between interconnected environmental systems (groundwater-surface water; air-soil-groundwater; etc.).
- The multiplicity of sources and pathways can create a sense that everything is equally contaminated and dangerous. Communicators need to help people understand the variability in the degree of contamination and relative risk related to each pathway.
- We are still identifying new PFAS sources (for example, PFAS from compost sites).
- Precursor transformation can affect how a PFAS site will evolve, but this is not well understood.
- Knowledge about uptake by plants and animals is increasing, but it is often difficult to answer questions about specific species.

14.2.3 Toxicological/Epidemiological Information and Risk Assessment

There are challenges and unknowns for toxicological and epidemiological information about PFAS, see Sections 7.1 and 17.2.

- One of the greatest challenges to risk communicators is having to craft messaging in the face of often intense disagreements over the interpretation of available science and the magnitude of uncertainty; we are communicating health risks when the risks are not fully known or characterized.
- While human studies may conclude that there is evidence that elevated exposure to PFAS increases the risk of certain health effects, it is not possible to relate a current health effect in a specific individual to PFAS exposure or to predict whether future health effects will occur on an individual basis.
- There is reliable toxicological information for only a small subset of PFAS.
- There is a select subset of PFAS that has been studied in sufficient detail to support risk assessment and remedial decision-making.
- Although most people have low levels of PFAS in their blood serum from consumer products and diet (anthropogenic background), certain populations may have elevated exposure due to localized sources, such as aqueous firefighting foam (AFFF) and industrial discharge, which can contaminate environmental media, particularly drinking water, leading to increased blood serum PFAS to levels that may increase the risk to human health.
- Communities often learn that they have been unknowingly exposed to PFAS for up to several decades prior to the discovery of their presence.
- Blood serum levels of certain PFAS can remain elevated for many years post-exposure, while levels of other PFAS decrease more rapidly, and currently there is no accepted method to hasten the reduction of PFAS blood levels.
- Individuals may be part of PFAS biomonitoring studies or can obtain their individual blood serum levels on their own. These individuals have access to information for comparison to regional and national reported levels, and thus may be more informed on their personal exposure than the medical practitioner.
- There is a need to provide understandable and informative public health advice to exposed individuals, including woman of childbearing age and pregnant woman who are making decisions about whether to nurse and/or use water known to be contaminated with PFAS to prepare formula (Section 7.1).

14.2.4 Technical

There are technical challenges in the areas of site characterization and treatment technologies, see Section 10 and 12.

- There may be issues in the identification of responsible parties due to the difficulty in distinguishing between low levels of PFAS from use of consumer products (anthropogenic background) and PFAS contamination resulting from discrete sources, such as industrial uses.
- Although a subset of PFAS can be effectively removed by established treatment technologies, effective methods for the remaining compounds are in development.

14.2.5 Analytical Ability

There are technical challenges in laboratory analytical methods and field sampling, see Section 11.

- There are numerous PFAS compounds in existence, yet not all can be measured. Sampling methodologies and analytical procedures to measure PFAS concentrations are still being developed and refined.
- Units used for reporting PFAS concentrations in environmental media and blood serum are not uniform, and can thereby confuse the audience.
- There are difficulties in clearly and concisely communicating unknowns and limitations of analytical technologies related to the understanding of the extent of PFAS present in the environment, exposure pathways, and magnitude of the potential risk.

14.2.6 Challenges to Risk Communication around Health Risks

When performing risk communication, it is essential to acknowledge that individuals may receive their information from a variety of sources, which may provide conflicting or inconsistent messaging. As presented in Section 7.1, there is a growing body of research pertaining the adverse health impacts of PFAS in humans and laboratory animals. The discussion potential human health risks from PFAS exposure has been taken up in multiple venues, including peer-reviewed scientific studies, news media, and public comments on draft government documents and proposed regulations. The severity and uncertainty of adverse health impacts that may be associated with PFAS and the need for subsequent action has been communicated in

an inconsistent manner. Because of the seriousness of potential health effects such as cancer, developmental delays and altered immune system response, as well as the persistence of PFAS in the human body, there is a case for prudence and precautionary mitigation practices to reduce exposures even in the absence of unequivocal human health consequences.

The risk communication challenge around health risks lends itself to a scenario in which stakeholders, including potential responsible parties and federal and state regulatory agencies, are not in consensus on the risk assessment and management strategy. Consistent messaging about uncertainties is essential for risk communication to be successful and to best help those in need. If stakeholders are in debate about the level of risk, then communicate by informing the public that all parties are striving to get the risk evaluation “right” but that there may be a delay in taking action. Communities that may be impacted may request an interim measure, such as an alternate water source, to alleviate concerns with potential exposure. Interim measures coupled with public outreach and community involvement can be a cost-effective risk management strategy in the short term. Public outreach should include measures being taken as well as associated milestones for future actions toward making a more informed risk management decision that utilizes limited resources efficiently, while integrating stakeholder values and community needs.

14.3 Risk Communication Planning and Engagement Tools

Prior to preparing risk communication materials and performing outreach, a project team should develop a risk communication plan to ensure there is a robust risk communication process in place from the outset. A risk communication plan is critical to guide decision makers to determine modes of information transfer as well as stakeholder engagement methods and tools that are appropriate and applicable for identified target stakeholders and site-specific characteristics. As stakeholder concerns and site characteristics are further defined, the communication team will need to continuously revisit the steps of communication planning. The ERIS PFAS Risk Communications Hub is a resource for risk communication information such as state FAQs, case studies and other resources.

14.3.1 Risk Communication Planning Model

The ITRC Risk Communication Toolkit for Environmental Issues and Concerns presents a risk communication planning model which has eight components or spokes on the wheel, as shown on Figure 14-1. At the center is review and evaluate. This suggests that communication is two-way, ongoing and continuous, allowing for review of where you are in your outreach efforts and where you may need to go.

This planning model, adapted from the work of NJDEP (2014), facilitates development of project-specific communication plans to be developed at each stakeholder engagement and/or outreach phase of a project. Of note, the NJDEP 2014 document relied on the work of Caron Chess, Billie Jo Hance, and Peter Sandman, Environmental Communication Research Program, Cook College, Rutgers University, as published by the New Jersey Department of Environmental Protection. The model is interactive, which allows for new information to be incorporated into the plan so that the outreach can be modified accordingly. This approach encourages establishing ongoing dialogue between the lead organization and all stakeholders so that the resulting outreach plan reflects the priorities and concerns from all of the parties. This will help you develop a robust risk communication plan. The aspects of the risk communication planning model are briefly summarized here.

- Issue identification helps you to clearly understand what the situation is in order to develop a responsive and effective risk communication plan.
- Goals are the big picture or ultimate impact that is desired for a project, issue or situation.
- Identification of communities with whom you need to establish a dialogue and those who wish to talk with your organization is important.
- Community assessment is needed to gain a deeper insight into stakeholder concerns and values that facilitate the development of a dialogue.
- Messages are the information you want/need to share with audiences about the issue or case, a question that you need them to answer, or both.
- A communication method is the means by which you communicate with your audiences.
- Once you have a clear goal, understand stakeholder concerns, know your message and have selected your method, it is time to lay out the strategy in order to implement the plan.
- Evaluation is the systematic collection of information about activities, characteristics, and outcomes of projects to make judgments about the project, improve effectiveness, or inform decisions about future programming. Many risk communication efforts require an ongoing presence or outreach to stakeholders. A debrief meeting is an opportunity for you to review the results of the evaluation and will identify what follow-up, if any is needed.



Figure 14-1. Communication plan process diagram.

Source: Modified from NJDEP 2014.

General information about risk communication planning is included in the ITRC Risk Communication Toolkit for Environmental Issues and Concerns document. This toolkit is a good resource for information about risk communication basics and tools. The toolkit can aid decision makers using this process and provide tools to assist with meeting performance metrics at each planning step. In addition, Minnesota Department of Health has developed the *Drinking Water Risk Communication Toolkit*, which can be accessed at <https://www.health.state.mn.us/communities/environment/water/toolkit/index.html>.

The following subsections are risk communication resources and tools with PFAS examples. The PFAS case studies in Section 15.4 offer examples of community and stakeholder assessment strategies.

14.3.2 PFAS Risk Communication SMART Goals and Objectives

This section includes some examples of SMART (specific, measurable, attainable, relevant, and timely) goals for PFAS. In addition, example messages are included.

Example SMART Goals

Example of Communication of Goals

Issue: The governor established an independent PFAS science advisory panel of national experts to provide guidance to the state on protectiveness of criteria and develop science-based recommendations that will guide the administration and legislature on the best regulatory policy moving forward.

Goal: The PFAS Science Advisory Panel will complete a report within 6 months that will provide a general understanding of human health risks associated with PFAS in the environment. These science-based data will be used to develop a regulatory response that the administration and legislature will take and implement by (date).

Example of Assessing Stakeholder Concerns

Issue: Due to public health concerns, the state agency will conduct a statewide study of PFAS levels in X public water supplies at X schools that operate their own (private) wells by (date.)

Goal: By (date), the environmental agency will develop an inventory and location map of sites where PFAS has been used or

disposed; prioritize sites for further investigation based upon the potential to impact drinking water supplies (based upon state groundwater maps, site history, and site ownership); incorporate data into a GIS-based data management system; and develop and implement a plan to sample private and or public water wells to assess potential impacts to drinking water supplies from prioritized sites.

For this example:

- specific: develop an inventory and location map
- measurable: testing
- achievable: implement a plan to sample private and public water supplies
- relevant: testing at prioritized sites will define impact
- timely: by X date

Example of a short-term SMART goal (from the Little Hocking Water Association case study, Section 15.4.1).

- By (date), the community is informed via the municipal website, flyers, and canvassing that bottled water is available as an alternate water source and utilized by 85% of the population.
- After (months), the extent of the impacted water supply is known via well testing and communicated to the community via a public meeting, municipal website, and newsletter.

Example of a long-term SMART goal (from the Little Hocking Water Association case study)

- By (date) and after (months), using a community-first strategy that includes the establishment of a community advisory committee and using multiple methods of communication—media, social media, internet, and meetings—determine whether the study area residents' blood PFOA levels are elevated and provide actions that 12,000 residents can take to produce a measurable reduction of PFOA blood levels.

14.3.3 Community Identification and Mapping Tools

Due to the persistent and recalcitrant nature of PFAS and its presence in the public drinking water supply, numerous and variant federal, state, private, and public stakeholders can be impacted. Actor mapping is a tool to help guide a communication team to lay out, track, and update stakeholder roles and relationships. During this exercise, practitioners learn who is the most affected by site information and decisions, as well as their level of interest and influence.

The outcome of the tool will assist in identification of unengaged/disinterested stakeholder populations, identify needs for relationship and/or capacity building, develop a site-specific communication team, and target outreach resources toward affected and unengaged/disinterested stakeholder populations. In the context of PFAS, this is of particular importance to identify and address affected groups who may not be participating in preventive and mitigation measures (such as an interim drinking water supply and a fishing ban) and/or at sites in which stakeholder groups are facing conflict resolution.

Simplified **examples** of an actor-linkage matrix and interest-influence matrix are presented, followed by resources to perform complex actor mapping, such as social network analysis. The examples provided are not representative of an existing project; stakeholder roles and relationships vary on a project-specific basis.

Example Context: A PFAS site consisting of a groundwater plume that has impacted drinking water supply wells and has identified contaminants in the local fish population.

Example 1: Actor-Linkage Matrix: A tool that assist practitioners in describing relationships among stakeholders through codes (Reed et al. 2009) (Figure 14-2).

ACTOR-LINKAGE MATRIX

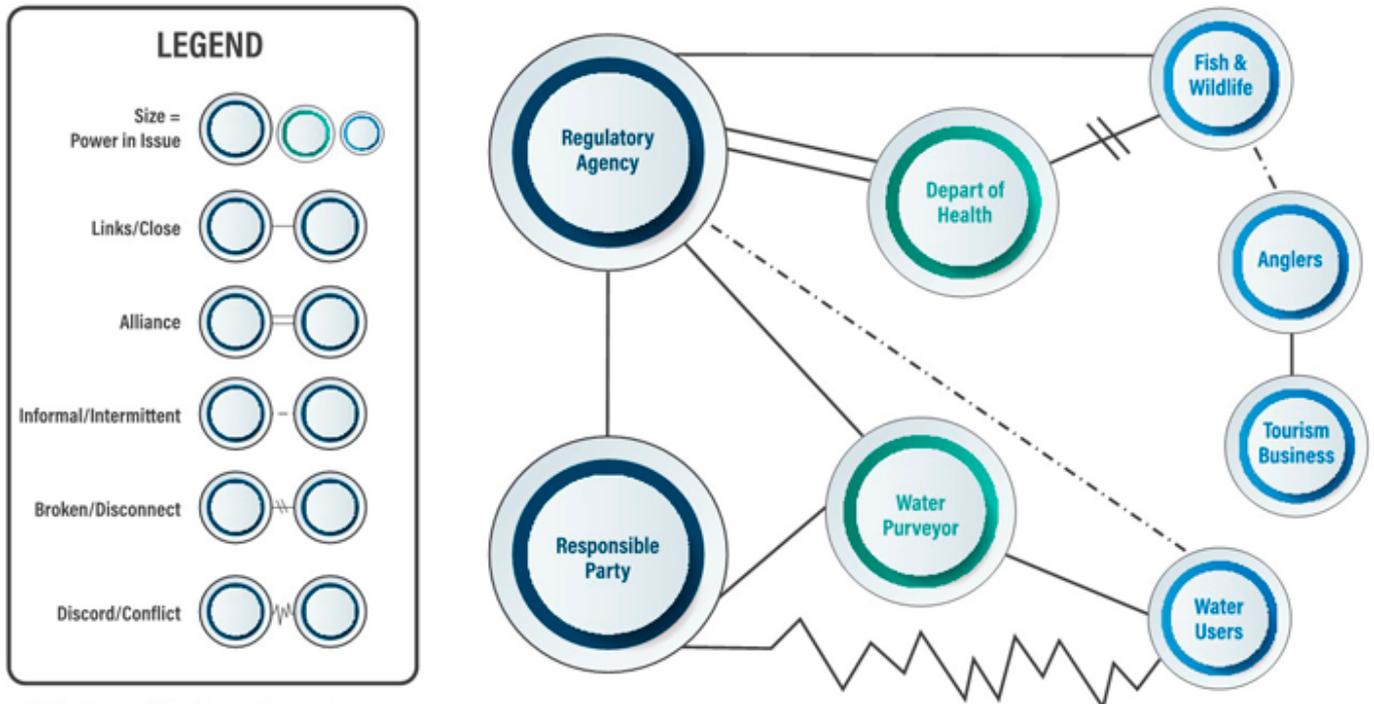


Figure 14-2. Example actor-linkage matrix.

Example 1: Actor-Linkage Matrix Evaluation

- *Identify unengaged stakeholder populations:* potentially anglers and tourism business operators
- *Facilitate relationship/capacity building:* utilize the relationship between the responsible party and water purveyor to restore relationship between the responsible party and water users
- *Identify and develop the communication team:* team consists of a representative for the lead organization and for each regulatory agency, responsible party, water purveyor, and each low-power stakeholder group
- *Target communication strategy resources:* increase information transfer to unengaged stakeholder populations and rebuild intermittent and conflicted relationships with water users in alignment with risk communication strategy SMART goals

The same example is used for the interest-influence matrix.

Example Context: A PFAS site consisting of a groundwater plume that has impacted drinking water supply wells and has identified contaminants in the local fish population.

Example 2: Interest-Influence Matrix: A tool that assist practitioners in identifying the stakes that social actors (stakeholders) have in a cleanup project. Identified stakeholders are placed in a matrix according to their relative interest and influence (Reed et al. 2009) (Figure 14-3).

INTEREST-INFLUENCE MATRIX

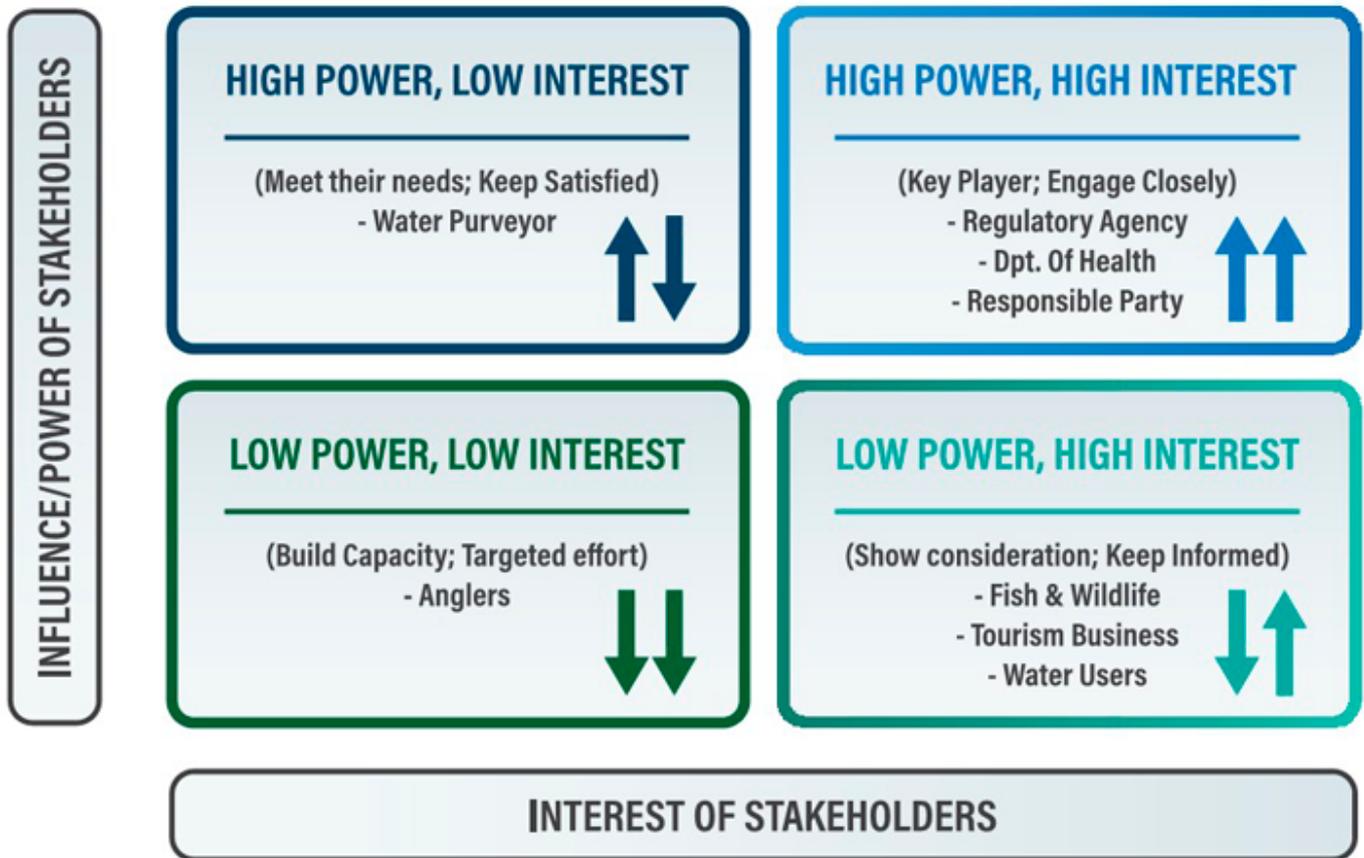


Figure 14-3. Example interest-influence matrix.

Example 2: Interest-Influence Matrix Evaluation

- Identify unengaged stakeholder populations: lead organization (for example, state agency or responsible party) (high-power) stakeholders have the role to engage lower power stakeholders who may not be currently engaged or are disengaged
- Facilitate relationship/capacity building: utilize high-interest stakeholders to build relationships with lower interest stakeholders, particularly ones with low power (such as the anglers)
- Identify and develop the communication team: team comprised of the lead organization and each regulatory agency, responsible party, water purveyor, and a representative of each low power stakeholder group
- Target communication strategy resources: increase information transfer to unengaged stakeholder populations and rebuild relationships with low-interest stakeholders in alignment with risk communication strategy SMART goals.

14.3.4 Social Factors Vision Board Tool

Stakeholder risk perception and associated social factors shape individuals’ attitudes toward management of hazards that affect personal safety and public health, and play an important role in supporting legitimacy and compliance with policies and protection measures. Due to the evolving state of the science of PFAS, including appropriate risk management strategies and relevant public policy, the present public attitude toward legitimacy and acceptance of proposed policies and strategies is hindered.

The success of public outreach in terms of exerting a positive influence on community stakeholders and in preventing and mitigating their exposure to a risk is based on site-specific physical, psychological, sociological, and demographic characteristics or “social factors.” Identification of these social factors among individual stakeholder groups can assist practitioners in refining engagement methods and outreach materials to maximize benefits to the community and meet specific needs of the targeted public sector.

A vision board can be used as a medium for stakeholders to rate their level of importance and/or interest on applicable social factors. Identified factors can then be used to further develop SMART goals and key messages, develop public outreach materials, and select engagement methods. The overall objective is to gain deeper insight into stakeholder concerns, values, and preferred communication method to facilitate a two-way street knowledge transfer and capacity building towards a successful risk management strategy. A social factors vision board tool can be used as starting materials for an engagement survey and interview. The target audience for this tool is an established community advisory group or a periodic outreach meeting, focus group, or decision maker stakeholders' group.

The vision boards (see ITRC RC Social Factors Vision Board attachment) developed for this toolkit are focused on a specific topic of concern and associated social factors identified from presentations by public and community stakeholders during the USEPA PFAS community meetings held in 2018.

Note that the vision boards for a specific project are living documents. The statements/questions and social factors should be updated to represent project-specific conditions and stakeholder concerns. Social factors presented on the toolkit vision boards are representative of affected communities' perceptions as opposed to expert opinion based on scientific studies. This toolkit was prepared as an example to provide a starting point for practitioners to understand the present needs and concerns of a PFAS-affected community. In addition, the rating system presented in each board is interchangeable to any social factor topic. More information on using the social vision board are provided in the ITRC Risk Communication Toolkit for Environmental Issues and Concerns document.

14.3.5 PFAS Key Messages

A message is information you want/need to share with communities about the issue or concern, a question that you need them to answer, or both. It is linked to the case specific goal and addresses key points about the issue that were learned through the community assessment. You start with the community and their concerns. Effective messages reflect what your target group needs are as well as what you need to communicate. In the case of emerging contaminants, elements of a message are likely to include: what is known and unknown about a contaminant, acknowledgement of uncertainty; commitment to share new information when it is learned; explanation of how decisions will be made with respect to protecting public health and remediating the problem, etc.

Message mapping is a process for developing your information so that it is concise and includes the information that is critical to convey. The objective is that the message is simple, yet comprehensive enough, and includes the most pertinent information relevant to your issue. A mapped message starts with a question, responds with three key ideas, is no more than twenty-seven words, and takes no longer than nine seconds to deliver. An example of key messages developed for a PFAS site is provided in Table 14-1. Additional resources on key messaging and mapping is provided in the the ITRC Risk Communication Toolkit for Environmental Issues and Concerns document.

Table 14-1. Message Mapping Worksheet

Source: (Covello, Minamyer, and Clayton 2007)

Stakeholder: Community member	Question/Concern/Issue: What are PFAS and why is the state concerned about them?	
Key Message/Fact 1 PFAS are a family of human-made chemicals in many products used by consumers and industry.	Key Message/Fact 2: PFAS are emerging contaminants of concern.	Key Message/Fact 3: Some PFAS may adversely impact human health.
Keywords: Supporting Facts 1.1 PFAS are a large group of thousands of manufactured compounds, produced and used for over 60 years. Some PFAS are still in use, some are not.	Keywords: Supporting Facts 2.1 PFAS are a contaminant of active scientific research. Scientific knowledge is changing rapidly.	Keywords: Supporting Facts 3.1 PFAS can build up in the body (bioaccumulate) and take a long time to leave the body.

<p>Keywords: Supporting Facts 1.2 PFAS have been used in coatings for textiles, paper products, and cookware and to formulate some firefighting foams, and have a range of applications in the aerospace, photographic imaging, semiconductor, automotive, construction, electronics, and aviation industries.</p>	<p>Keywords: Supporting Facts 2.2 Laboratory methods may or may not exist to detect all the PFAS contaminants that we know about; methods are developing and evolving with the emerging science.</p>	<p>Keywords: Supporting Facts 3.2 Some PFAS, such as PFOA, have been found to impact fetal development and are passed to babies through nursing and bottles.</p>
<p>Keywords: Supporting Facts 1.3 PFAS are found throughout the environment, in people, and in animals and fish.</p>	<p>Keywords: Supporting Facts 2.3 Federal and state regulations are changing as the scientific knowledge evolves; this leads to guidance and recommendations that may vary across the country.</p>	<p>Keywords: Supporting Facts 3.3 Studies in exposed humans suggest that some PFAS may cause high cholesterol, higher liver enzymes in blood, decreased response to vaccines, decreased birth weight, and testicular and kidney cancer.</p>

See also this website for a template of the message mapping worksheet: https://www.orau.gov/cdcynergy/erc/content/activeinformation/resources/Covello_message_mapping.pdf

14.3.6 Communication and Engagement Tools

14.3.6.1 Public Outreach

Public health and regulatory agencies have developed several public outreach materials to inform stakeholders about PFAS, from the compounds’ origins and environmental distribution to exposure pathways, associated health effects, and management strategies. Outreach tools include community education classes to inform and support high school teachers, medical professionals, journalists, and municipal water managers. The following provides a summary of available resources for accessing and developing public education materials for PFAS-impacted communities. Although printed public education materials are effective at communicating information, techniques that include face-to-face communication, such as open house meetings, focus groups, and door-to-door canvassing, are often more effective at addressing fears and building trust. Additionally, face-to-face communication provides an opportunity for practitioners to learn from the public and other impacted stakeholders.

The ITRC Risk Communication Toolkit for Environmental Issues and Concerns document includes Guidance for Writing Analytical Results Letter, Guidance for Writing Press Releases.

14.3.6.2 Fact Sheets and Frequently Asked Questions (FAQs)

To achieve effective risk communication, it is essential for public education materials to be presented in a clear and simple manner that is understandable by nonscientists and speaks to a broad audience. Common rules of thumb include writing at a sixth-grade comprehension level, using simple terminology, and providing materials in multiple languages for nonnative speakers. Over the past few years, environmental and public health agencies, nonprofit advisory groups, trade associations, and regulatory agencies have prepared numerous fact sheets and FAQ documents on PFAS-related topics to inform stakeholders, including concerned residents, agricultural and recreational entities, water purveyors, end users, public health professionals, and others. These public education materials developed specifically for PFAS-impacted communities are typically available on the organization’s website.

Fact sheets, FAQs, and other public outreach material should be distributed in multiple modes to maximize audience reach and increase opportunity for engagement. Recommended modes of distribution include mailings, websites, local municipal health departments, public health professional offices, public libraries, and information booths at community events.

The ITRC Risk Communication Toolkit for Environmental Issues and Concerns document includes additional information about FAQs.

- **Compilation of PFAS Fact Sheets, Frequently Asked Questions (FAQs)** and other resources developed by the Association of State and Territorial Health Officials (ASTHO) and the Environmental Council of the States (ECOS) are available:
 - <https://www.astho.org/PFAS/>
 - <https://www.eristates.org/projects/pfas-risk-communications-hub/>

14.3.6.3 Active Centralized Information Repository

Unlike a “passive” repository of site documentation at a central location, an “active” repository refers to a platform that remains up to date on site findings and enables two-way exchange of information among decision makers and the impacted community. A common platform for an active repository is a centralized website that contains a complete compilation of site documentation (among all agencies); frequent updates on site activities, health information and regulatory policy; and a depiction of the CSM (such as a source-exposure pathway graphic and geologic maps). The website should also contain a platform to facilitate stakeholder involvement by providing an opportunity for them to ask questions, submit information, and join a listserv (an application that distributes messages to subscribers on an electronic mailing list).

Examples of centralized websites can be found at the following web links:

- Michigan Department of Environmental Quality, *Michigan PFAS Action Response Team (MPART)*:
<https://www.michigan.gov/pfasresponse/>

Michigan agencies representing health, environment, and other branches of state government have joined together to investigate sources and locations of PFAS contamination, to take action to protect people’s drinking water, and to keep the public informed as we learn more about this emerging contaminant.

- New Hampshire Department of Environmental Services (NHDES), *NH PFAS Investigation*:
<https://www4.des.state.nh.us/nh-pfas-investigation/>

NHDES maintains a website to update interested parties on NHDES’s investigation into the presence of PFAS in New Hampshire. The website includes a map that shows PFOA and PFOS data from water samples collected around the state.

- Vermont Department of Environmental Conservation (VDEC), *Vermont PFOA Contamination Response*:
<https://dec.vermont.gov/pfas/pfoa>

Numerous Vermont agencies, including VDEC, Department of Health (VDH), Emergency Management, Agency of Agriculture, and Agency of Education have joined together to investigate and address PFAS contamination in Vermont. VDEC and VDH have created and maintained web pages to push information out to the public as it becomes available to keep the public informed of the PFAS issue.

Not all stakeholders have access to the internet, and depending upon the seriousness of the site’s situation, it may be appropriate to hold regular meetings and/or office hours to provide more than one mode for stakeholders to obtain information and engage with decision makers.

14.3.6.4 Community Education

Individual stakeholder groups and individuals themselves process information in a variety of modes and media. An effective risk communication strategy takes this factor into consideration and encompasses multiple forms of outreach. In addition to informative materials, such as fact sheets, stakeholder meetings and interactive sessions (such as poster presentations, question and answer sessions) can be held to involve individuals in the learning and understanding process. Prior to selection of a method, an audience assessment should be conducted to determine how a community communicates and to learn what tool is the most effective to use.

Community Education Example—Bennington College Community Education Strategy, Vermont

In 2016, PFAS were discovered in the public water system of Hoosick Falls, New York, and in hundreds of private residential wells in Petersburg, NY, and North Bennington, Vermont. In response to this nearby problem, Bennington College asked how the scientific resources of a college or university might become a civic resource in times of environmental uncertainty. After some discussion about how to maintain the scientific and educational integrity of the college while also being a good neighbor to impacted communities, Bennington College decided to open the doors of its science classrooms to the problem

of PFAS contamination. This was done primarily in two ways: (1) a new introductory class on PFOA was offered to local communities free of charge, and (2) students in more advanced science classes in chemistry and geology worked to produce independent data on PFAS contamination in the region. More information about both of these strategies is below.

Many residents impacted by PFAS voiced a desire to learn about the science of the problem even as there was a recognition that much of that science was currently quite difficult for residents to grasp. Indeed, many of the risks and ramifications of PFAS contamination are currently published in daunting regulatory reports and peer-reviewed research articles (often behind paywalls). Addressing these concerns, Bennington College designed a new class to review the chemical properties, environmental pathways, and policy concerns of PFOA, entitled "Understanding PFOA." This class also taught residents how to collect water samples for PFAS analysis at a commercial lab and how to interpret laboratory results from PFAS analysis. Bennington College has offered this class every spring to local residents since 2016, free of charge. A number of local teachers, journalists, nurses, elected officials, parents, and students enrolled, and the class has become a vehicle for the community to get up to speed on the science of PFAS so they can engage the issue more productively.

Bennington College also put together faculty-led research teams to produce independent data on PFAS contamination in conversation with community questions. Bennington College realized that impacted communities often had interesting questions about PFAS that fell outside of the urgent protocols of state agencies, which rightfully focused on safeguarding public health. These community questions, however, provided useful pathways to educate residents about the problem and to encourage local participation in research into PFAS contamination. Working with residents of Hoosick Falls, Petersburg, and North Bennington, the college helped investigate a number of community concerns, such as:

- "Is there any PFOA in my maple syrup?"
 - Bennington College tapped two maple trees in the spring and analyzed the sap, finding 8.8 parts per trillion (ppt) of PFOA in the sap of a maple tree about 1,000 feet from a plastics plant and 2.3 ppt of PFOA in the sap a maple tree about a mile from the plant.
- "My well had high levels of PFOA but now I have a filtration system in my basement. If my well was contaminated for years, I wonder if there might be any residual PFOA in my water pipes. Could any built-up PFOA still be contaminating the water coming out of my kitchen faucet?"
 - Bennington College analyzed water from the kitchen faucet from three homes with high levels of PFOA in their well and a point of entry treatment filtration system (Hoosick Falls house, 2,100 ppt of PFOA in well; Petersburg house, 1,800 ppt of PFOA in well; North Bennington house, 3,000 ppt of PFOA in well). In all three homes, PFAS were nondetectable in water from the kitchen sink.
- "When the state tested my well, they found PFOA levels just below the health guidance level and thus we did not get a filtration system. How stable are detected levels of PFOA in the groundwater?"
 - Bennington College reviewed data from over 200 residential wells that had been sampled and analyzed for PFOA at least twice in one year. They found an average variation of 24% in individual wells. PFOA levels increased in about half of the wells and decreased in about half the wells. This increase and decrease did not have an obvious spatial pattern (for example, a plume moving in one direction) but appeared to be fairly randomly scattered across the sampling area.

More information about Bennington College's ongoing engagement with PFAS can be found at www.bennington.edu/pfoa.

Updated September 2020.

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15 Case Studies

Currently the PFAS team has identified case studies supporting the following sections:

- Section 10 Site Characterization
- Section 12 Treatment Technologies
- Section 9 Risk Assessment
- Section 14 Risk Communication

15.1 Site Characterization Case Studies

15.1.1 Case Study—Data Visualization at an AFFF Release Site

McGuire et al. (2014) and McGuire (2013) presented a detailed characterization of a subset of PFAS soil and groundwater concentrations, focused on PFAAs in the vicinity of a former unlined burn pit where fire training activities were conducted up to 1990. Data presented in McGuire et al. (2014) were used for this visualization example. For brevity, this example shows relative concentration trends between shallow and deep soil samples collected at six borings where total PFAA concentrations exceeded 5,000 ug/Kg in shallow soil. The inset map in the top left of Figure 15-1 shows the former burn pit location, as well as the locations of these six borings (S-2, S-4, S-5, S-6, S-7, and S-10). Shallow soil samples were collected at a depth of approximately 2 ft below ground surface (ft bgs) (0.61 m), and the deep soil samples were collected at the water table, which is approximately 15–20 ft bgs (4.6–6.1 m) on average.

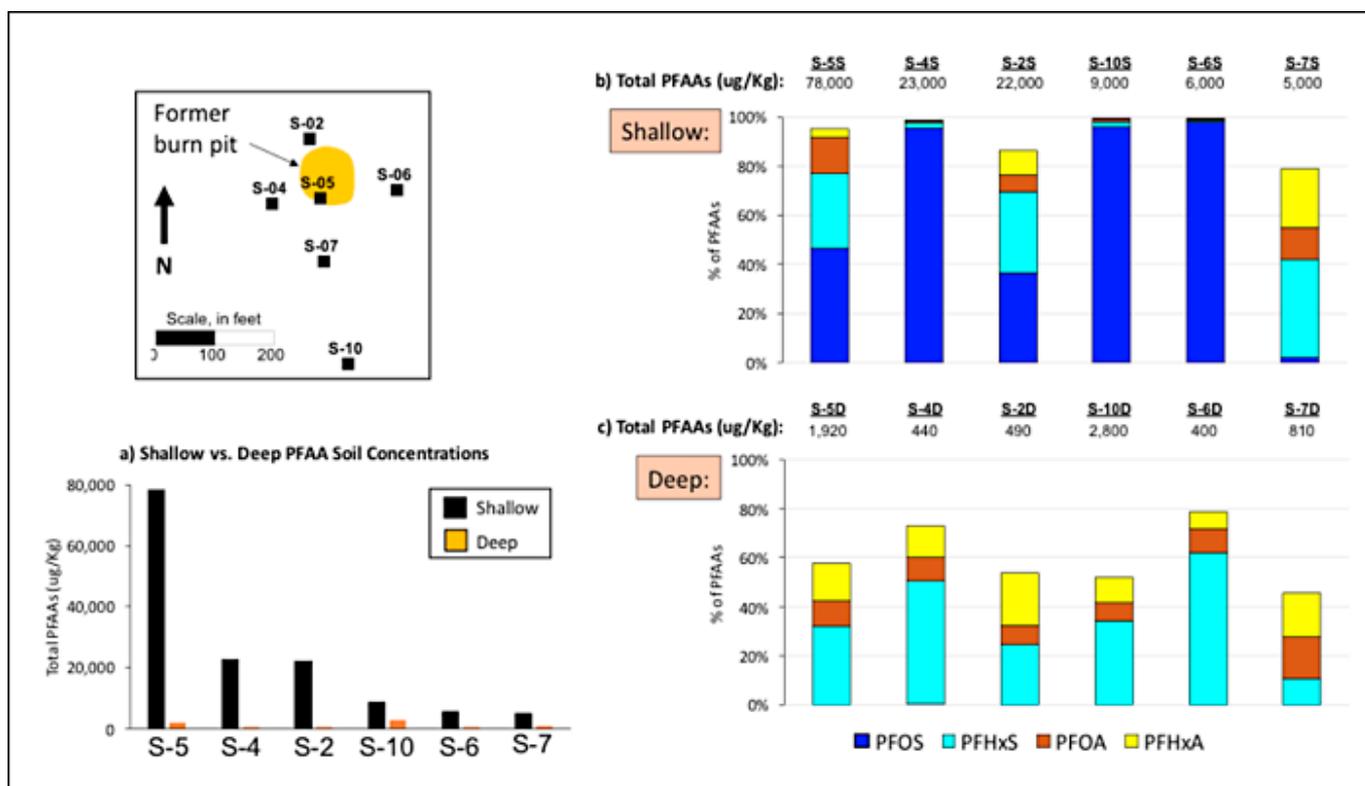


Figure 15-1. Comparison of shallow and deep soil samples at an AFFF release site.

Source: G. Carey, Porewater Solutions. Used with permission.

The bar chart in Figure 15-1a compares concentrations of shallow and deep soil concentrations for total PFAAs at these six boreholes and clearly demonstrates that shallow PFAA soil concentrations are much higher than deeper soil concentrations at the water table. This figure indicates that there is likely attenuation that limits vertical migration of PFAAs. McGuire (2013)

attributed this to the high clay content of vadose zone soils, and high VOCs and TOC in this area, which may enhance retardation.

A different type of bar chart is shown in Figure 15-1b to illustrate the composition of the main PFAA constituents in shallow soil samples (PFHxS, PFOS, PFHxA, PFOA). Review of Figure 15-1b reveals the following trends:

- In three of the six boring locations, PFOS is greater than 95% of total PFAA concentrations in shallow soil.
- In the other three borings, PFOS is less than 50% of total PFAAs. These borings have higher relative concentrations of PFHxS, PFHxA, and PFOA.
- PFHxS, PFOS, PFHxA, and PFOA combined represent at least 80% of total PFAA concentrations in shallow soil.

The difference in PFOS composition shown in Figure 15-1b suggests that some borings were drilled in an area that was influenced by a mixture of different AFFF products, whereas other borings with a high proportion of PFOS may be influenced primarily by AFFF produced using electrochemical fluorination.

Figure 15-1c shows the same type of bar chart with relative percent of total PFAA concentrations for the deeper soil samples collected at the water table. Comparison of Figures 15-1b and 15-1c indicates that there is a clear difference in PFAA composition between the shallow and deep soil samples. PFOS is very low in terms of relative concentrations in deep soil samples, compared to the shallow soil samples where PFOS makes up a higher proportion of the total PFAA concentration. This may be due to enhanced retardation of PFOS in the vadose zone relative to the other compounds (PFHxS, PFHxA, and PFOA), which is consistent with the relative site-specific K_{oc} values determined by McGuire et al. (2014). In addition, Figure 15-1c shows that these four compounds typically represent only around 50% of total PFAA concentrations in the deep samples, which suggests that shorter chain compounds are more prevalent at the water table and in underlying groundwater, most likely due to precursor transformations.

Radial diagrams may also be used as visual aids to illustrate spatial and/or temporal trends for individual PFAS constituents or total concentrations for various PFAS groups. As an example, Figure 15-2 presents a radial diagram map showing trends for various PFASs (PFOS, PFHxS, PFBS) as well as perfluorohexane sulfonamide FHxSA, which is a precursor to PFHxS. The radial diagram legend in the top right portion of Figure 15-2 shows that the four axes are arranged in order of FHxSA, PFOS, PFHxS, and PFBS. There are two data series shown on the radial diagram legend: (1) the blue-filled data series, which represents PFAS constituent concentrations at monitoring well location; and (2) a darker blue outline that represents maximum source concentrations at well GW13, which is situated directly adjacent to the former burn pit area. This latter data series is a reference and is the same at all monitoring well radial diagrams. Including this reference data series makes it easier to visualize changes in concentrations throughout the plume. The radial diagram legend also shows how symbols may be plotted to represent where constituents were not detected in a groundwater sample. Another option for radial diagram symbols is to indicate where concentrations are above groundwater cleanup criteria at each well location (not shown). The compound axes are logarithmic in this example, to allow for visualization of order of magnitude concentrations between wells, or between compounds at any one well location.

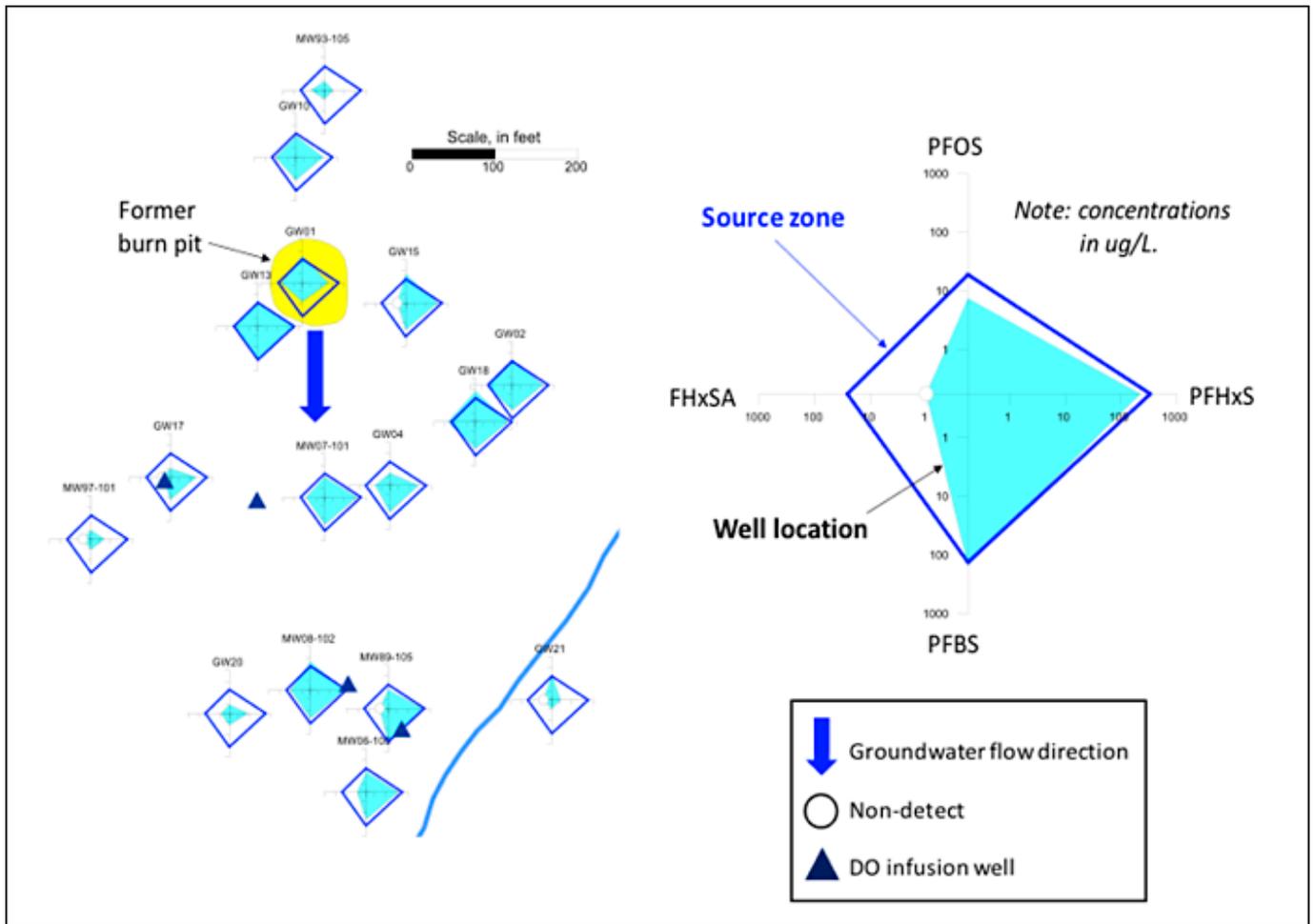


Figure 15-2. Radial diagrams illustrating PFSA trends at an AFFF release site.

Source: G. Carey, Porewater Solutions. Used with permission.

Groundwater flow in this area is generally to the south/southeast. The main radial diagram map shown in Figure 15-2 facilitates an analysis of how concentrations for these four constituents vary along the groundwater flow path downgradient from the former burn pit area, and how concentrations vary across the width of the plume. For example, the radial diagram shown at GW01, which is located inside the footprint of the former burn pit, indicates that concentrations of the longer chain compounds (FHxSA and PFOS) are similar to those in the nearby well at GW13, whereas PFHxS and PFBS are about an order of magnitude lower at GW01 than GW13. The radial diagrams also clearly show that groundwater downgradient of the DO infusion wells (triangle symbols) has low to non-detect FHxSA, indicating that aerobic transformation of this precursor has occurred downgradient of these infusion wells (Section 10.4.4).

Although not shown with this case study, radial diagrams are also helpful for visualizing redox indicator trends, to confirm whether redox conditions are favorable for the transformation of precursors to PFAAs. Examples of a modified radial diagram method used for redox zone delineation are presented in Carey et al. (1999) and Carey et al. (2003).

15.1.2 Case Study—Application of Radial Diagrams

Figure 15-3 presents another type of application of radial diagrams for visualizing certain PFAS trends, in this case for an aquifer contaminated with PFAS from several fire training areas in the vicinity of Uppsala, Sweden. The blue outlines shown in Figure 15-3 represent the boundaries of eskers (deposits formed by streams flowing beneath a glacier), which essentially act to channel groundwater flow in the aquifer. The legend shown on Figure 15-3 indicates that the four axes of the radial diagram now represent concentrations of 6:2 FTS (which dominates the other FTSS), total PFCAs, total PFASAs, and total concentrations of other chemical-specific precursors. Symbols are shown to represent non-detects at each well location. Groundwater flow in the main aquifer channel is from northwest to southeast (parallel to the river channel) and is to the west in the inset box shown in the bottom center of Figure 15-3.

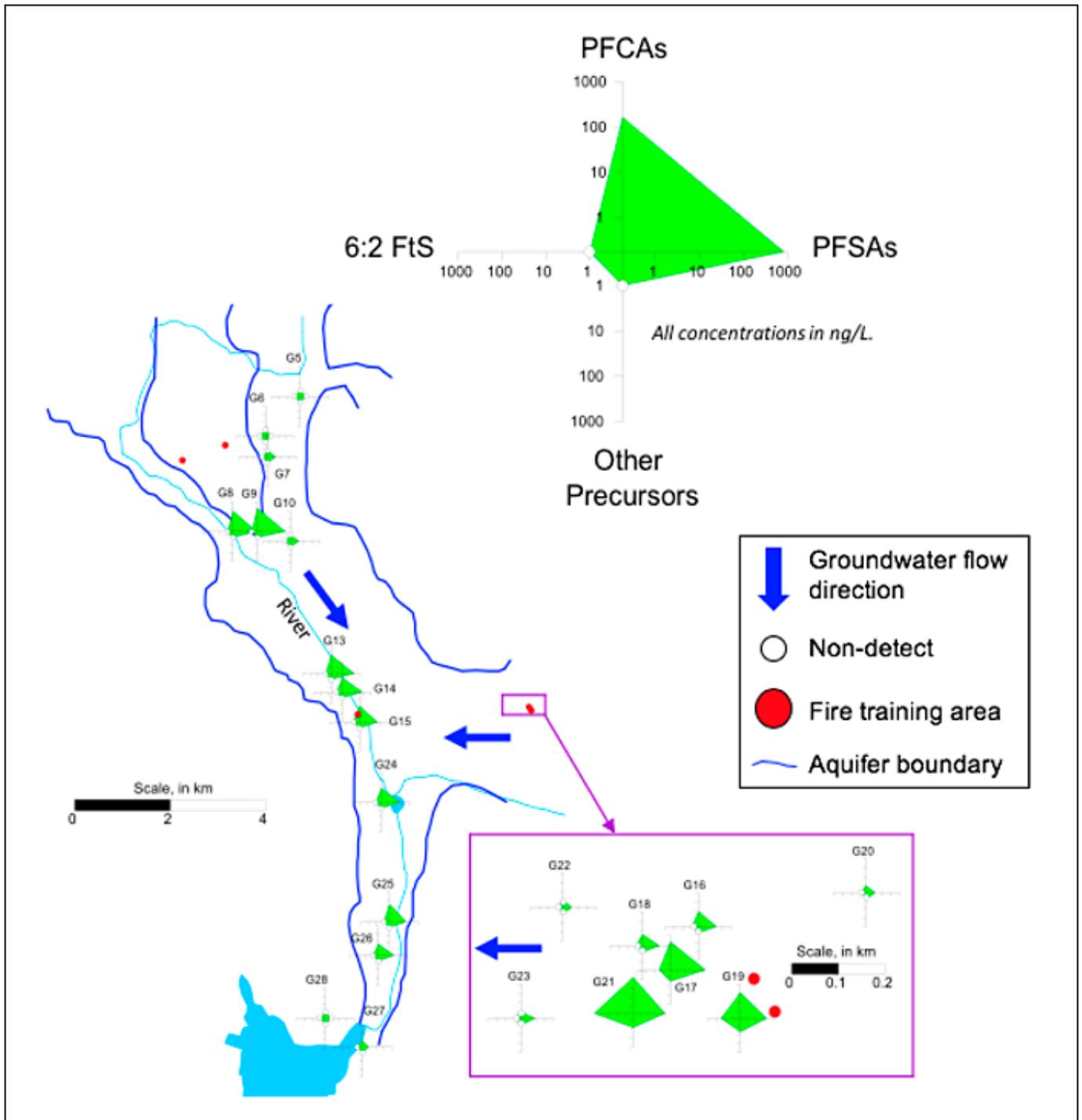


Figure 15-3. PFAS composition in groundwater.

Source: G. Carey, *Porewater Solutions*. Used with permission.

Examples of trends that are evident based on the radial diagram map (Figure 15-3) include:

- All chemical-specific precursors are nondetect in the main aquifer channel, indicating that precursors were effectively attenuated closer to the fire training areas.
- PFSAs and PFCA concentrations appear to be declining along the main flow channel (for example, downgradient of G8 and G9).
- Concentrations of precursors in the vicinity of the fire training areas shown in the inset map are much higher than in the main groundwater flow channel. This indicates that precursors may be attenuating prior to reaching the main flow channel in this area, due to sorption, biotransformation, and/or possibly discharge to the nearby creek.
- The combination of elevated PFCAs and PFSAs, as well as high 6:2 FtS near at least two of the fire training areas, indicates that AFFFs produced using telomerization were used at one point at some of these fire training areas.

15.2 Treatment Case Studies

Several well-developed technology case studies are presented in the following sections. Additional information on other water treatment case studies is summarized in Table 15-1 provided as a separate Excel file.

15.2.1 Granular Activated Carbon (GAC)

Case Study: Granular Activated Carbon System—Oakdale, Minnesota (Contributed by Virginia Yingling, Minnesota Department of Health, used with permission)

Background

Oakdale is a suburban community located east of St. Paul, Minnesota, with a population of approximately 28,000. Prior to state or federal laws regulating such waste disposal, industrial wastes from a PFAS manufacturer were disposed of in a privately operated 55-acre unlined dumpsite (Oakdale Disposal Site, 1940s–1960s) and in the Washington County Landfill, a permitted 40-acre unlined municipal landfill in Lake Elmo, Minnesota (1969–1975). In 2005, PFAS were detected in six of the eight operating Oakdale city drinking water supply wells.

Eight PFAS have been detected in groundwater associated with these sites, with PFBA, PFHxS, PFOA, and PFOS being present at the highest concentrations. PFAS have also contaminated a stream that drains the wetlands that comprise part of the Oakdale Disposal Site and PFAS re-infiltration has contributed to groundwater contamination in areas not immediately downgradient of the waste disposal sites. Both sites underwent remedial activities in the 1980s to address industrial solvents and in 2009–2011 to address PFAS. These actions included soil and waste excavation with on- and off-site encapsulation, and groundwater pump and treat (GAC) for hydraulic containment.

The regional groundwater flow direction at both sites is to the south-southwest toward the Mississippi River, approximately 8 miles away. The primary source for PFAS impacts to groundwater appears to be the Oakdale Disposal Site, but the Washington County Landfill may have contributed to the contamination in the easternmost city wells.

Water Characteristics

The maximum concentrations detected to date in the city wells are shown in Table 15-2 along with the relevant Minnesota health-based guidance values for PFAS in drinking water.

Table 15-2. Maximum concentrations of PFAS in drinking water from Oakdale city wells.

Chemical	Maximum Concentration Detected in Any Oakdale City Well (µg/L)	Minnesota Department of Health’s Health-Based Guidance Value (µg/L)
PFBA	2.15	7
PFBS	0.136	3 (acute), 2 (chronic, subchronic)
PFPeA	0.176	None established
PFHxA	0.382	None established
PFHxS	0.142	0.047
PFOA	0.871	0.035
PFOS	1.38	0.015

NOTE: All concentrations reported as of August 2019 and guidance values reported are as of December 2019.

The Minnesota Pollution Control Agency (MPCA), Minnesota Department of Health (MDH), City of Oakdale, and the chemical manufacturer agreed to address the situation by constructing a GAC treatment plant to treat the water from the two most highly contaminated wells. In addition, the city shut off one well and drilled a replacement well north of the contaminated area. Other wells with PFAS detections are used seasonally and to maintain pressure throughout the distribution system, but the pumping schedule is managed to ensure PFAS remain below MDH guidance values in the water delivered to the community. This includes meeting the MDH’s Health Risk Index, which is a toxic equivalency quotient (TEQ)-like assessment of the additive toxicity of multiple PFAS.

Treatment Technology Design Details

The GAC treatment facility (Figure 15-4) began operations in October 2006. It consists of ten filter vessels (each containing 20,000 lbs. of GAC) set up in five parallel lead-lag pairs (shown below) housed in a 7,000 ft² facility. The system treats 2,500 gallons per minute with a minimum empty bed contact time (EBCT) of 10 minutes per vessel. The water is combined back into one stream, chlorinated and fluoridated to meet state and federal standards, and then piped to the distribution system.



Figure 15-4. GAC treatment system, Oakdale, MN.

Source: Courtesy of the Minnesota Department of Health.

System Performance

The city and MDH monitor the PFAS concentrations in the influent, lead vessel effluent (that is, between vessels), and post-treatment facility effluent (Figures 15-5 and 15-6). Monitoring currently occurs quarterly for the first three quarters following GAC change-out and monthly in the final quarter prior to change-out.

The GAC is changed out approximately every 12 months to prevent breakthrough of any PFAS above MDH guidance values. GAC change-out may involve a complete replacement of all GAC or just the lead vessel GAC and change of flow to make the former lag vessel the new lead vessel. This will depend on the effluent concentrations at the time of change-out. Initial removal rates are 100% (below analytical limit of detection) for all seven PFAS analyzed (PFBA, PFPeA, PFHxA, PFOA, PFBS, PFHxS, PFOS).

Breakthrough order follows the expected sequence of shorter chain and PFCAs preceding longer chain and PFSAs. PFBA breakthrough of the full system typically occurs within 2 months after a complete GAC replacement, but because the influent PFBA does not exceed its health-based guidance value of 7 µg/L, this does not pose a health risk and does not trigger any response actions. Interestingly, PFBA effluent concentrations eventually exceed influent concentrations, presumably due to PFBA desorbing in the presence of more readily sorbed, longer chain PFAS. As shown in the graphs below, PFOS has broken

through the full system only once (2012; max effluent concentration = 0.019 µg/L) and PFOA has broken through only four times (2010, 2012, 2015, 2018; max effluent concentration = 0.086 µg/L). At no time did any PFAS exceed the then-current health-based guidance values.

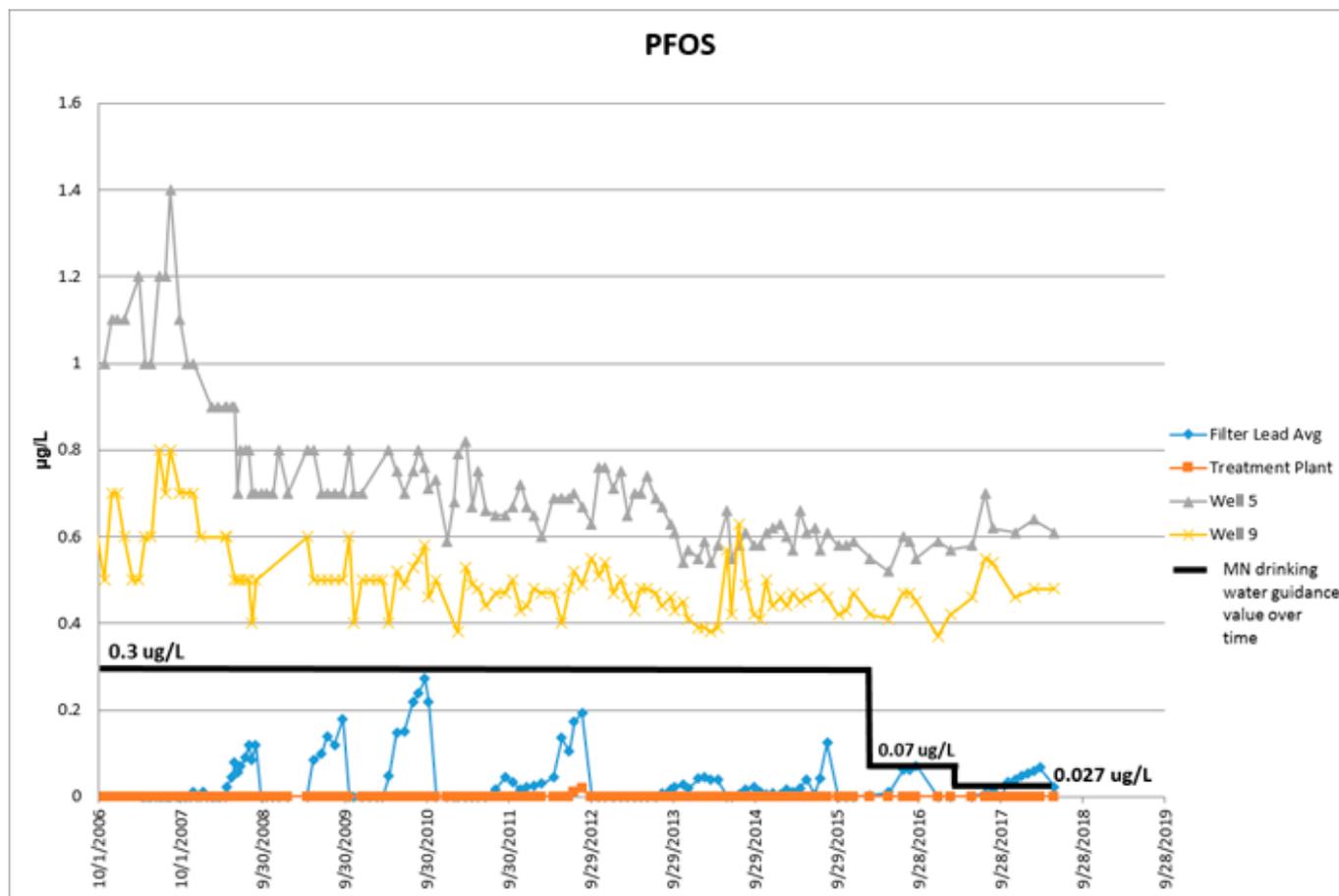


Figure 15-5. Influent and effluent concentrations for PFOS.

Source: Courtesy of the Minnesota Department of Health.

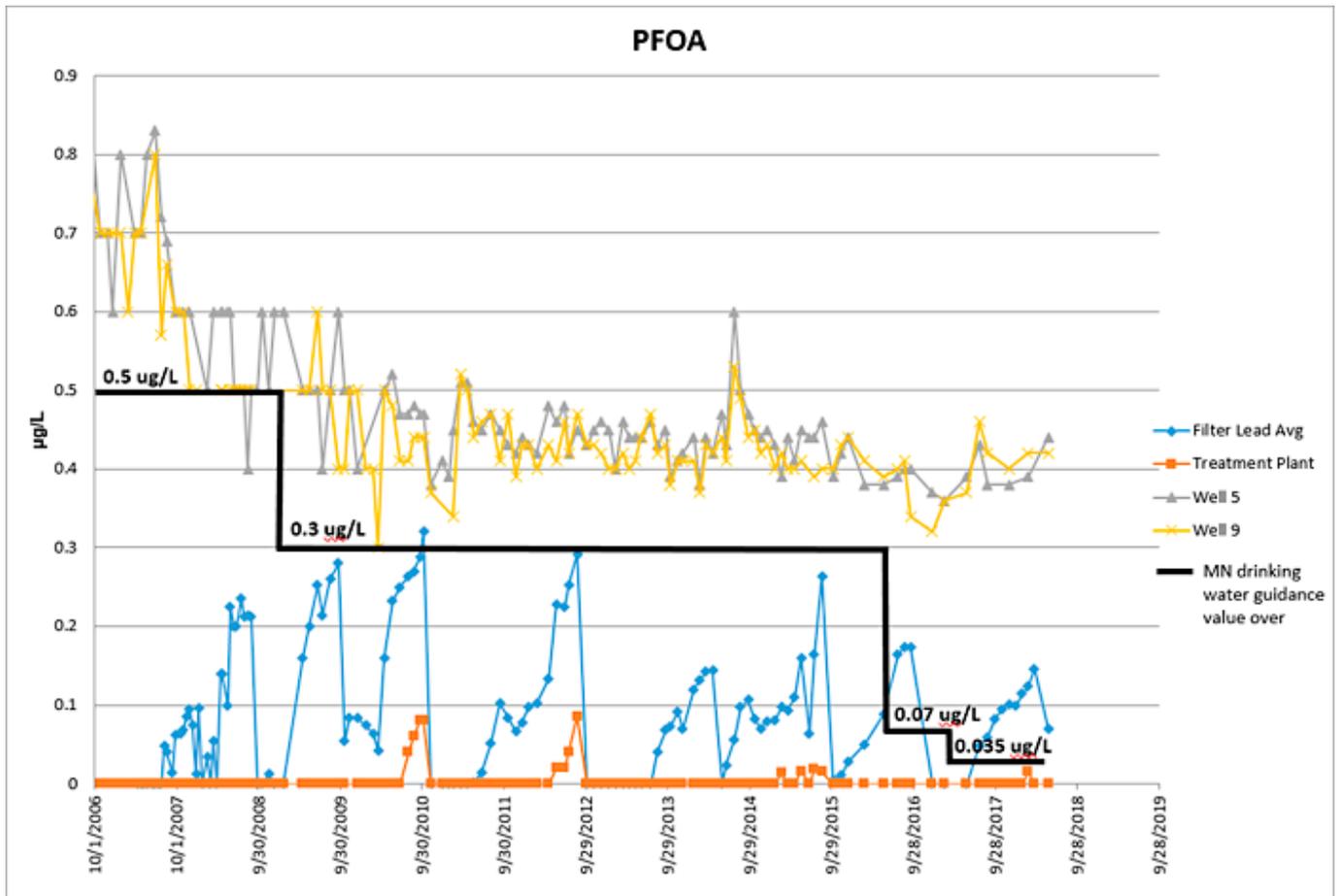


Figure 15-6. Influent and effluent concentrations for PFOA.

Source: Courtesy of the Minnesota Department of Health.

Costs

Capital costs for the GAC treatment facility were approximately \$2.5 million. Annual operation and maintenance (O&M) costs, including sampling and GAC change-out, are approximately \$250,000.

15.2.2 Ion Exchange (IX) Resins

Ion exchange resins can be utilized as single-use, where the media is disposed when it has reached the limit of its sorptive capacity, or regenerable, where the resin is regenerated and reused indefinitely (theoretically). The following two case studies outline field applications for these two related technologies.

15.2.2.1 Single-Use IX

Case Study: Horsham Township, Pennsylvania (Contributed by Francis Boodoo, Purolite Corporation, used with permission)

Background

The township of Horsham, Pennsylvania, located close to an AFFF release site, supplies drinking water to 7,800 residential, commercial, and industrial customers using 15 deep water wells. In 2014, five of the wells were confirmed to be impacted with PFAS. PFOS and PFOA were found in two wells at concentrations approaching the USEPA 2009 provisional health advisories (HAs) of 200 ppt and 400 ppt, respectively. These wells were immediately taken out of service. In June 2016, one month after EPA issued final HAs of 70 ppt for the combined concentrations of PFOS and PFOA, three more wells were removed from service due to elevated concentrations. The township began purchasing supplemental water from a nearby water supplier and began installing GAC filters to remediate and return the five impacted wells to service. Responding to consumer concerns, the township adopted an aggressive removal plan to reduce average PFOS/PFOA concentrations to less than 1 ppt (essentially to nondetect levels) in its entire water system by the end of 2016.

In addition to GAC filtration, the township started up a 50-gallon-per-minute selective ion exchange (IX) resin pilot in November 2016 on Well 10 to evaluate the performance of the resin in consistently reducing PFOS/PFOA to nondetect levels. A temporary 1-year permit was obtained from Pennsylvania Department of Environmental Protection (PA DEP) to install the resin pilot downstream of an existing GAC pilot that had been started up 20 days earlier. This was the first permit issued by the state of Pennsylvania for treating PFAS in drinking water using ion exchange resin.

Influent Water Characteristics

Influent concentration of a total of seven PFAS during the test period from November 2016 to August 2018 was an average of 103 ppt, a minimum of 78 ppt, and a maximum of 147 ppt. Individual PFAS concentrations are shown in Table 15-3. Average influent values for PFOS and PFOA were 34.1 and 20 ppt, respectively, somewhat lower than EPA's 70 ppt combined HA. Other influent geochemical parameters included sulfate at 8-23 ppm, nitrate at 10-11 ppm, alkalinity at 148-232 ppm, chloride at 35-50 ppm, pH at approximately 7.5, TDS at 296-358 ppm, suspended solids at 0.5-0.6 ppm, TOC at 0.2 ppm, and one sample detection for 1,1-dichloroethane at 37 ppt.

Table 15-3. Influent PFAS Characteristics of Well 10 *

	nanograms per liter (ng/L) (or parts per trillion (ppt))							
	PFBS	PFHpA	PFHxS	PFHxA	PFNA	PFOS	PFOA	Total PFAS
Lab Detection Level	1	1	2	1	2	2	1	
Minimum	6	4	17	6		27	13	78
Average	9	5	28	9		34	20	103
Maximum	14	8	41	13	2	48	40	147
* PFBS =perfluorobutanesulfonate; PFHpA = perfluoroheptanoate; PFHxA = perfluorohexanesulfonate; PFHxA = perfluorohexanoate; PFNA = perfluorononanoate, PFOS = perfluorooctanesulfonate, PFOA = perfluorooctanoate, PFAS = total poly- and perfluoroalkyl substances								

Treatment Technology Design Details: GAC and Ion Exchange System

Well 10, with a peak design flow rate of 100 gpm, was used for large-scale piloting at a reduced flow rate of 50 gpm under the terms of the permit from PA DEP. The water was first passed through a 20-micron suspended solids filter, then in series through two 2.5-ft diameter stainless steel vessels, each vessel containing 20 cubic feet of bituminous GAC. EBCT for each charge of GAC amounted to 2.8 minutes or a total of 5.6 minutes for the two GAC vessels; linear velocity was approximately 10 gpm/ft². The township recognized that EBCT was lower than the 10-20 minutes specified in the PA Public Water Supply design manual and that linear velocity, even though it complied with the PWS, was higher than the typical 4 gpm/ft² used for GAC; however, the township and PA DEP considered the design acceptable for the low levels of PFAS measured and for the temporary nature of the pilot. After initial treatment by the GAC pilot, the water was passed through a 2.5-ft diameter vessel containing 20 cubic feet of Purolite Purofine PFA694E selective resin. Bed depths for both the GAC and resin media were approximately 34 inches. Sampling points were installed on the outlet of each vessel. An extra sampling point was installed in the resin polishing vessel at two-thirds of the resin bed depth. This allowed monitoring corresponding to EBCT of 1.8 minutes at the two-thirds sampling point and 2.8 minutes EBCT for the entire resin bed. The two-thirds sampling point would provide advanced notice of PFAS breakthrough.

System Performance

The entire system became operational on November 29, 2016. PFOS and PFOA sampled at the two-thirds point of the resin bed remained consistently at nondetect levels until rising to 2.6 ppt on day 394 and 4 ppt on day 472 (see Figure 15-7). For reporting purposes, the township decided to use a minimum reporting level of 2.5 ppt for each of PFOS and PFOA; values below the minimum reporting level would be considered nondetect. Once the PFOA concentration reached 2.6 ppt at the two-thirds sampling point for the resin, the treated water was diverted to the local sanitary sewer in keeping with the PA DEP permit. PA DEP has since granted permission to bypass the GAC system to enable performance evaluation of just the resin.

On day 514, with permission from PA DEP, the two GAC vessels were taken out of service while the raw water was routed

directly to the resin vessel, which continued to operate. In this way, the performance of the resin could be evaluated without pretreating with the GAC. The resin operated for 639 days before PFOA was detected at a concentration of 2 ng/L of PFOA in an effluent sample from the resin bed. At that point the concentrations of PFBS, PFHxS, and PFOS were still at nondetect levels. Operating capacity of the resin at that point was equivalent to treating 511,000 bed volumes (BVs) of water based on two-thirds of the resin volume, or 329,000 BV based on the entire volume of resin.

Following successful and consistent performance of the resin-only system, PA DEP has issued an operating permit for use of resin only in a pair of lead-lag ion exchange vessels. Similar permits have also been issued at neighboring townships.

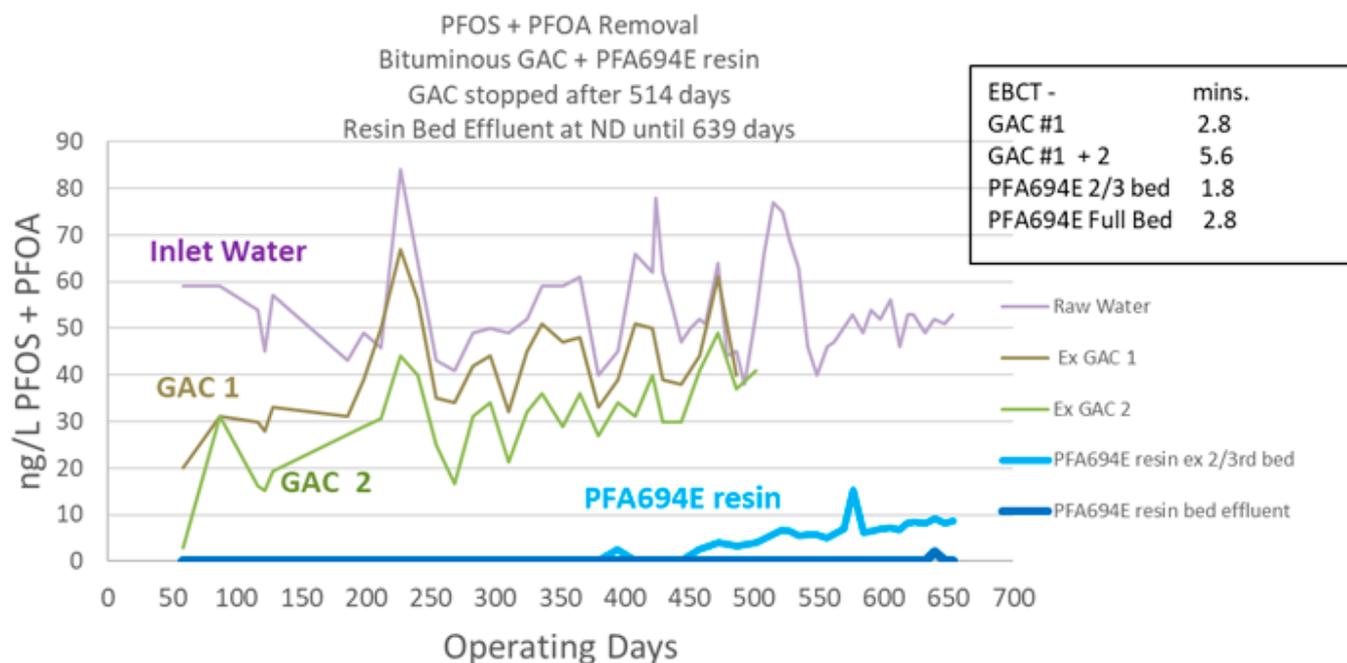


Figure 15-7. Combined PFOS/PFOA breakthrough.

Source: F. Boodoo, Purolite Corporation. Used with permission.

Even though PFOS and PFOA were the initial targets for reduction, consistent reduction of other short- and long-chain PFAS to nondetect levels was also achieved after passage through the resin. For conciseness, only total PFAS breakthrough graphs are shown in Figure 15-8, but the order of breakthrough observed was PFHxA < PFHpA < PFOA < PFNA < PFBS < PFHxS < PFOS.

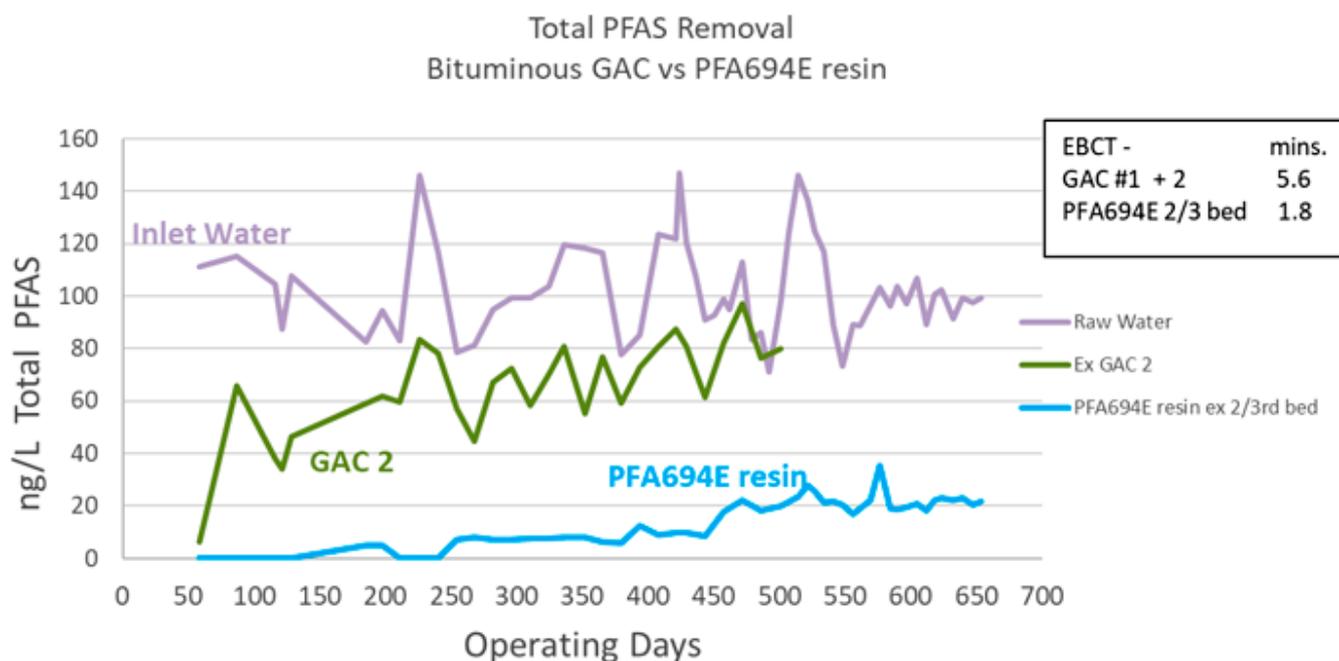


Figure 15-8. Combined breakthrough of total PFAS.
Source: F. Boodoo, Purolite Corporation. Used with permission.

Costs

The proposed permanent full-scale system is designed for a peak flow rate of 100 gpm with a pair of lead-lag vessels for the media. Design for ion exchange will include one 20-micron cartridge filter followed by two 4-ft diameter vessels with resin bed depth of 36 inches and EBCT of 2.8 minutes. Design for GAC will be one 20-micron cartridge filter followed by two 6-ft diameter vessels with GAC bed depth of 60 inches and EBCT of 10.6 minutes.

Annual operating cost, including replacement media, labor, trucking, spent media profiling, and incineration, is estimated at approximately \$8,000 and \$15,000, respectively, for ion exchange and GAC. These estimates are based on a very conservative operating capacity estimate of 350,000 BVs for a lead-lag pair of resin vessels; a generous capacity of 34,000 BVs is assumed for the GAC system. Operating costs are estimated at \$0.16 and \$0.29 per 1,000 gallons of water treated by the resin and GAC systems, respectively. Larger vessels needed for the GAC system will further add to the cost of using GAC versus the PFAS-selective resin.

15.2.2.2 Regenerable IX

Case Study: Regenerable Ion Exchange Resin Pilot Test and Full-Scale Application (Contributed by Steve Woodard, ECT2, and Nathan Hagelin, Wood Group, used with permission)

Background

The Air Force Civil Engineering Center (AFCEC) is conducting ongoing response activities to remove and remediate groundwater impacted by poly- and perfluoroalkyl substances (PFAS) at the former air force base in New Hampshire. The two primary PFAS compounds found at the site are perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), at combined concentrations (PFOA+PFOS) above the USEPA lifetime health advisory (LHA) of 0.07 micrograms per liter ($\mu\text{g}/\text{l}$). In 2015, the USEPA issued an administrative order to establish maximum hydraulic containment of PFAS compounds to reduce source zone mass and mitigate migration of PFAS compounds to off-site receptors.

AFCEC responded by contracting with Wood Group, PLC, to conduct a side-by-side pilot test in 2016, comparing the performance of Emerging Compound Treatment Technologies' (ECT2) regenerable ion exchange (IX) resin and bituminous GAC. The resin outperformed GAC and was selected for full-scale implementation, mainly on its life cycle cost advantages, as determined by the results of the pilot study.

To evaluate the resin's ability to be regenerated, regeneration trials were conducted throughout the pilot test using a

proprietary regeneration procedure with a solution of organic solvent and brine. Overall, PFAS removal results for the regenerated resin were consistent with new resin, as shown in Figure 15-9. Extended follow-on pilot testing utilized multicycling to confirm the effectiveness of the regeneration procedure to restore the resin’s PFAS removal capacity. The regenerable resin system was selected for full-scale application, based on system performance and a favorable life cycle cost comparison.

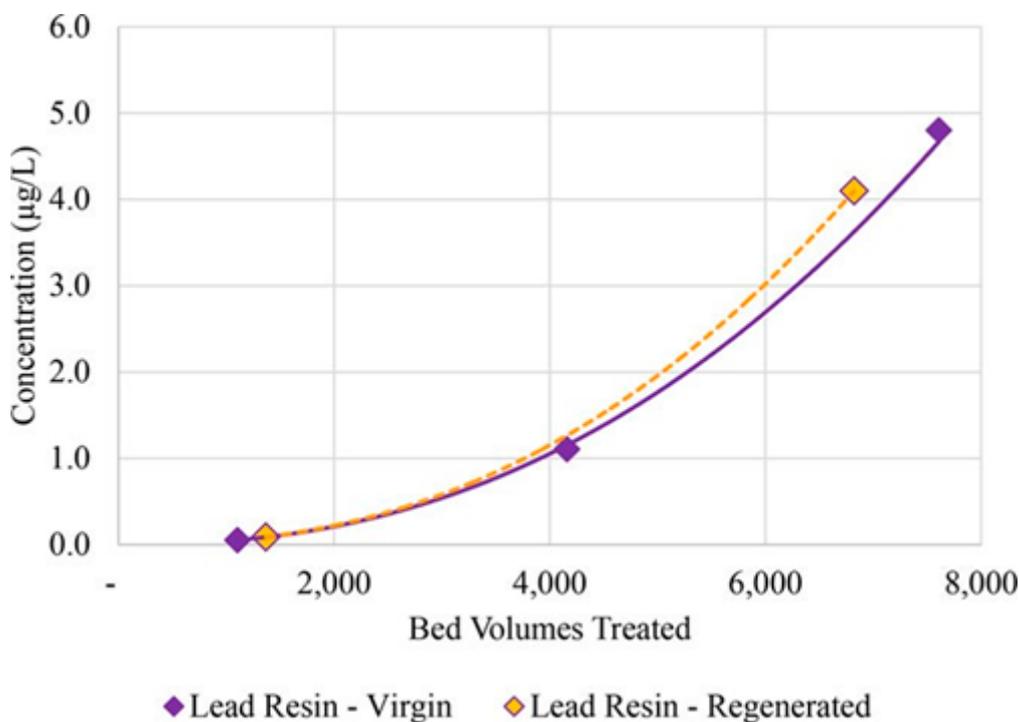


Figure 15-9. Postregeneration breakthrough curve (total PFAS).

Source: Steve Woodard, ECT2, and Nathan Hagelin, Wood Group, PLC. Used with permission.

Influent Water Characteristics

Table 15-4 provides a summary of influent PFAS concentrations observed throughout the pilot test. Total PFAS concentrations ranged from 65 to 112 µg/l, with an average of 94 µg/l. Average influent concentrations for PFOS and PFOA were 26 and 12 µg/l, respectively. Influent general chemistry parameters included pH of 6.8, alkalinity of 115 milligrams per liter (mg/l), TDS of 230 mg/l, total suspended solids of less than 2 to 5.6 mg/l, sulfate of 17 mg/l, TOC of 4.5 mg/l, and chloride ranging from 30 to 250 mg/l.

Table 15-4. Influent PFAS Concentrations

Analyte	Analyte Acronym	Influent Concentration Observed During Pilot Test (µg/L)		
		Low	High	Average
6:2 Fluorotelemer sulfonate	6:2 FTS	15	22	18
8:2 Fluorotelemer sulfonate	8:2 FTS	0.055	0.3	0.23
Perfluorobutane sulfonate	PFBS	0.81	1.3	1.1
Perfluorobutanoic acid	PFBA	0.89	2.1	1.3
Perfluoroheptane sulfonate	PFHpS	0.85	1.4	1.1
Perfluoroheptanoic acid	PFHpA	1.6	2.2	1.9
Perfluorohexane sulfonate	PFHxS	18	25	22
Perfluorohexanoic acid	PFHxA	5.9	8.9	7.7
Perfluorooctanoic acid	PFOA	9.1	13	12
Perfluoronananoic acid	PFNA	0.046	0.082	0.054

		Influent Concentration Observed During Pilot Test (µg/L)		
Perfluorooctane sulfonate	PFOS	4.2	32	26
Perfluoropentanoic acid	PFPeA	3.1	5.1	4.2
Sum of PFAS	-	65	112	94

Treatment Technology Design Details for Full-Scale System

The permanent full-scale resin system was designed for a maximum flow rate of 200 gpm (0.76 m³/min), with influent total PFAS concentrations of approximately 90 µg/l. The primary project objective was to consistently produce treated water with combined PFOS plus PFOA concentrations below the USEPA lifetime health advisory (LHA) of 0.07 micrograms per liter (µg/l). The full-scale IX resin system was installed between fall 2017 and spring 2018, and the system officially commenced operation in April 2018.

Figure 15-10 shows a process flow diagram of the treatment system. The pretreatment portion includes bag filters to remove suspended solids and 6000-lb backwashable liquid GAC pretreatment filter to remove iron. The PFAS removal system consists of two parallel trains of lead-lag regenerable IX resin vessels, each 86" tall x 36" diameter, packed with 49 cubic feet of ECT's SORBIX A3F regenerable resin. These vessels are designed to operate up-flow during normal operation, and down-flow during regeneration. Two parallel, 86" tall x 36" diameter polish vessels are filled with IX resin for PFAS polishing, including short chains. The polish vessels operate in the down-flow mode and contain a blend of IX resins tailored to the general water chemistry and PFAS species and their relative concentrations.

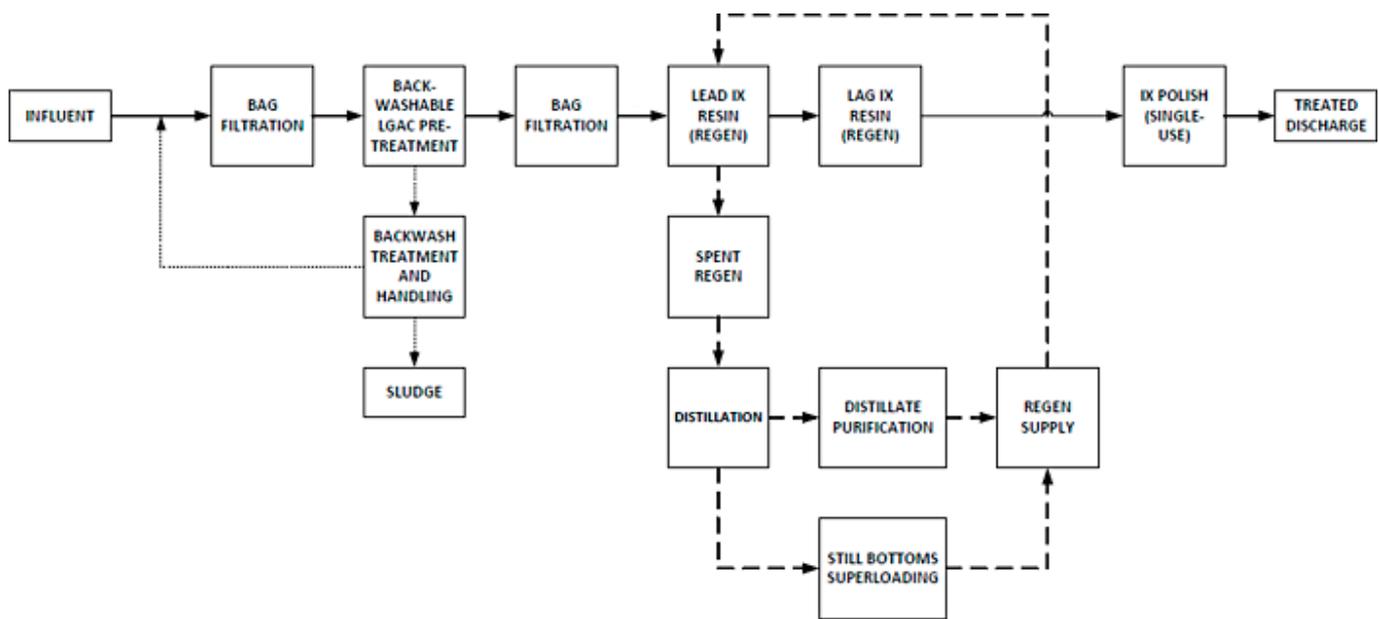


Figure 15-10. Block flow diagram of full-scale treatment system.

Source: Steve Woodard, ECT2, and Nathan Hagelin, Wood Group, PLC. Used with permission.

The in-vessel regeneration system (Figures 15-11 and 15-12) consists of a regenerant solution holding tank and pump skid. The regenerant solution is a mixture of organic solvent and brine, which effectively strips PFAS from the IX resin and then flows into a spent regenerant holding tank. The spent regenerant is recycled for reuse in the next regeneration cycle by using a distillation and super-loading process. First, the spent regenerant is transferred to a solvent recovery unit. Solvent makes up the majority of the regenerant solution and is recovered through distillation, given its low boiling point relative to water, and transferred to the regenerant supply tank for reuse in the next regeneration cycle. The remaining distillate residue, known as the "still bottoms," is a low-volume, high PFAS concentration brine solution. The still bottoms are pumped through super-loader vessels that contain a proprietary resin blend, transferring the PFAS mass onto the super-loaded media. Super-loading is the process by which a relatively small volume of highly concentrated PFAS solution is passed very slowly through a small volume of media. The long EBCT approaches equilibrium (isotherm) conditions, thereby maximizing PFAS mass transfer onto the media and minimizing the amount of solid waste requiring disposal or incineration.



Figure 15-11. Regenerable and polish IX resin vessel skids.

Source: Steve Woodard, ECT2, and Nathan Hagelin, Wood Group, PLC. Used with permission.



Figure 15-12. Resin regeneration system.

Source: Steve Woodard, ECT2, and Nathan Hagelin, Wood Group, PLC. Used with permission

System Performance

The PFAS remediation system has been successfully treating the groundwater since system start-up in April (Figure 15-13). Through December 2018, the effluent water quality from the IX resin system has been consistently nondetect for the monitored PFAS compounds, including the short-chain species, readily achieving compliance with the treatment objective of 0.70 µg/l LHA target for PFOS and PFOA. Although 6:2 FTS has not been detected in samples collected from the IX vessel effluent, it has been detected in the system effluent and is believed to be the result of transformation processes that are not yet understood.

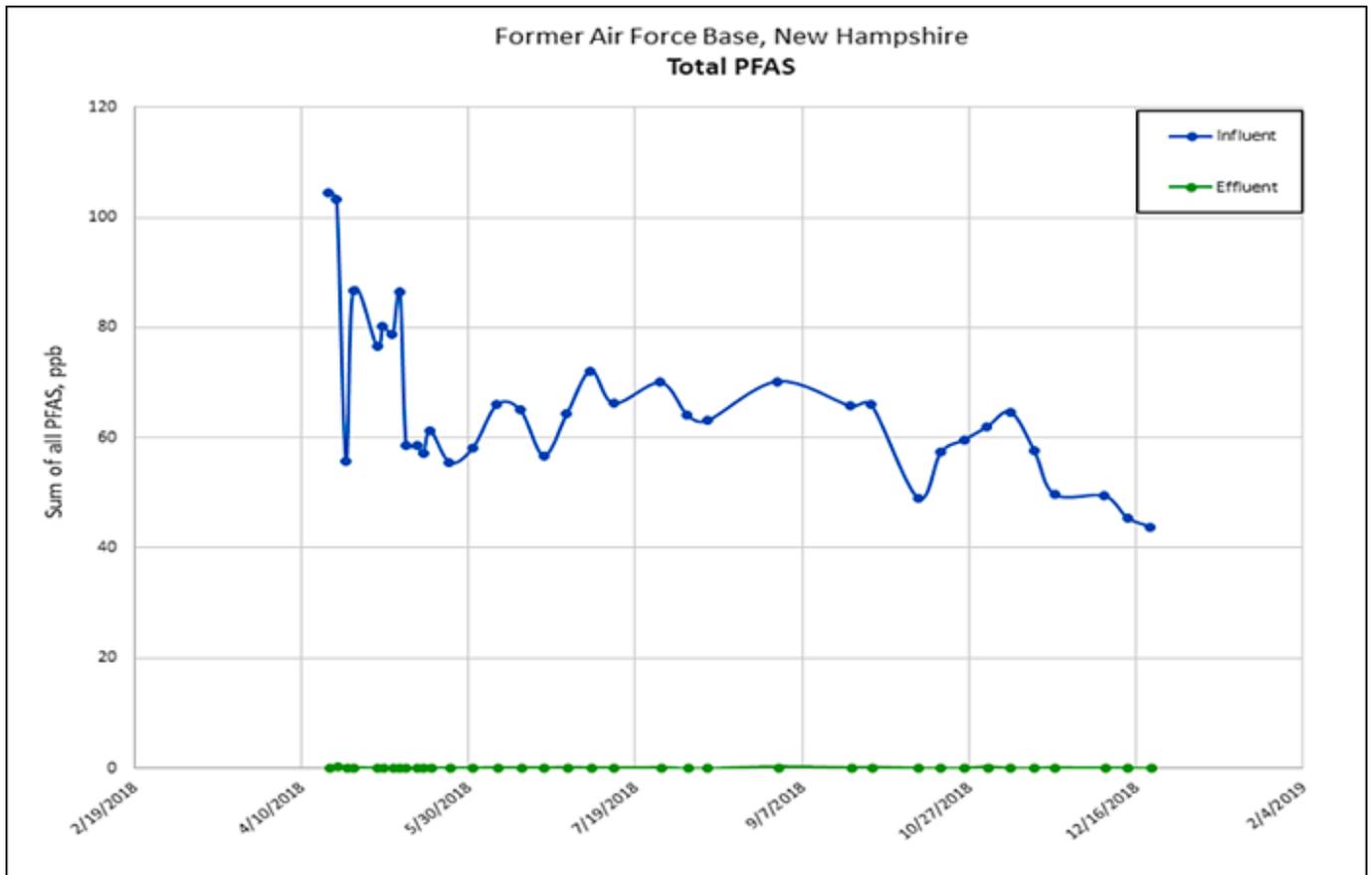


Figure 15-13. Influent and treated effluent total PFAS concentrations.

Source: Steve Woodard, ECT2, and Nathan Hagelin, Wood Group, used with permission

The system has been operated in the 35- to 70-gpm range since start-up, somewhat less than the design flow rate. This has been done to accommodate higher than anticipated influent iron concentrations that have resulted in the requirement for frequent bag filter change-outs. The resulting extended EBCTs in both the backwashable GAC pretreatment vessel and the IX resin vessels have resulted in better than projected PFAS removals. Also, the resin regeneration schedule has been modified to accommodate the lower flow rate by removing one of the two parallel trains from service. This has allowed the resin vessels to be loaded closer to design values. Four resin regenerations have been performed successfully through December 2018; however, the IX media regenerated through December 2018 was not loaded to the full design capacity due to the reduced flow during early operation. Operational modifications have been made to address and correct minor challenges with the distillation system, and regenerant recovery and super-loading processes have proven successful. The original super-loading media is still operational, having removed and concentrated greater than 99.99% of the recovered PFAS mass; therefore, no PFAS waste has needed to be hauled off site to date.

Costs

The capital cost for the regenerable IX was \$2.9M for all treatment equipment, process piping, pumps, instrumentation, and system electrical. It does not include project management, construction management, the extraction network and field piping, or the building and building mechanical or electrical systems.

15.3 Risk Assessment Case Study

The New Jersey Department of Environmental Protection (NJDEP) Division of Science, Research, and Environmental Health conducted an initial assessment of PFAS impacts at a select group of surface water bodies in New Jersey (NJDEP 2018) (Figure 15-14). The results of fish tissue sampling from each site were used in a risk assessment methodology to determine the need for fish consumption advisories for PFAS in each of those water bodies.

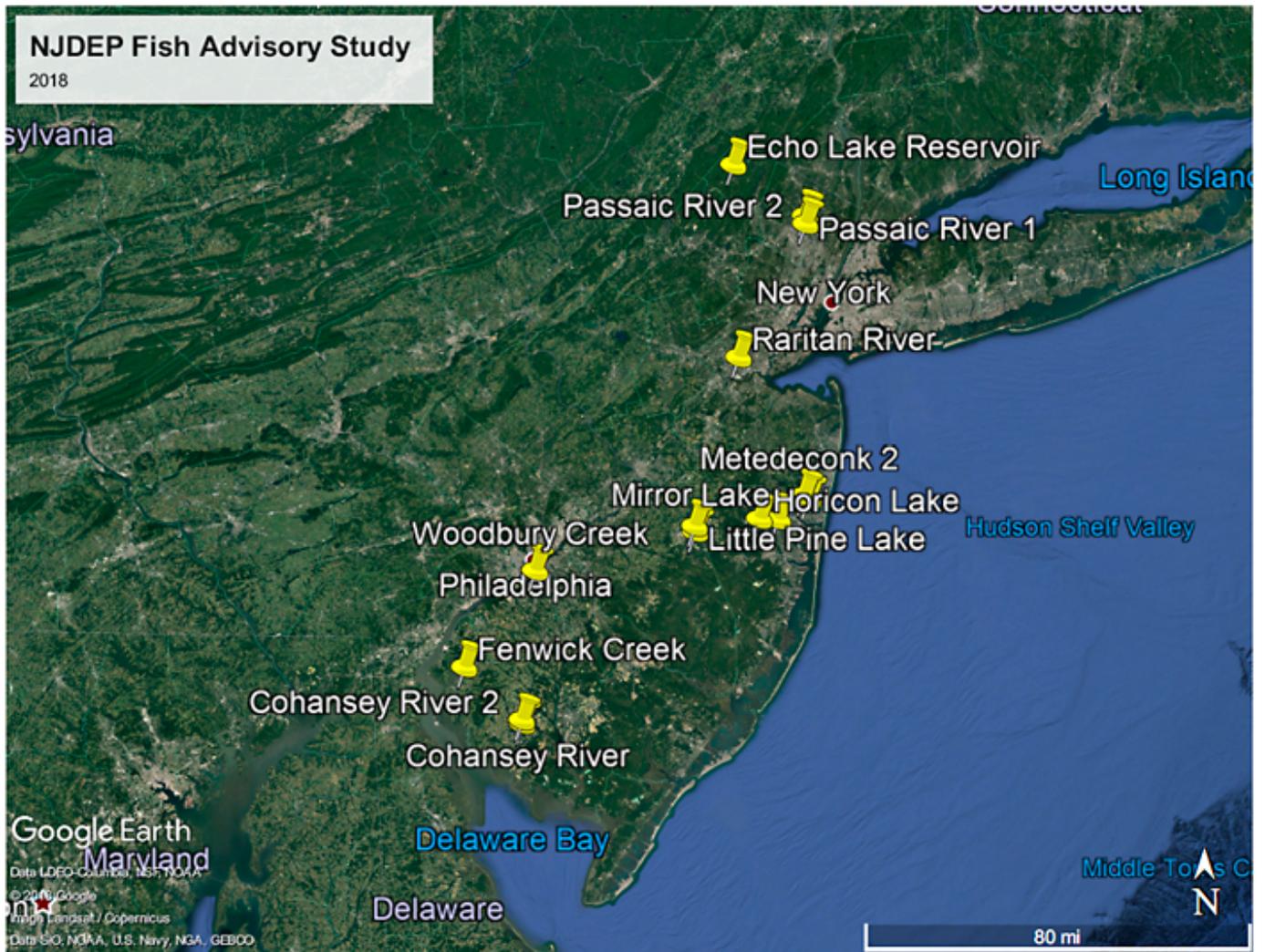


Figure 15-14. Map of water bodies included in NJDEP fish tissue study.

Overall, fish tissue samples from up to 12 different species were collected from 11 specific water bodies throughout the state. The water bodies were selected for sampling based upon their location relative to possible PFAS sources and the likelihood that they could be used for recreational fishing. Samples were analyzed for 13 PFAS (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFBS, PFHxS, PFOS, and PFOSA), and as presented in Figure 15-15, the results indicated that the predominant PFAS detected in the fish tissues was PFOS.

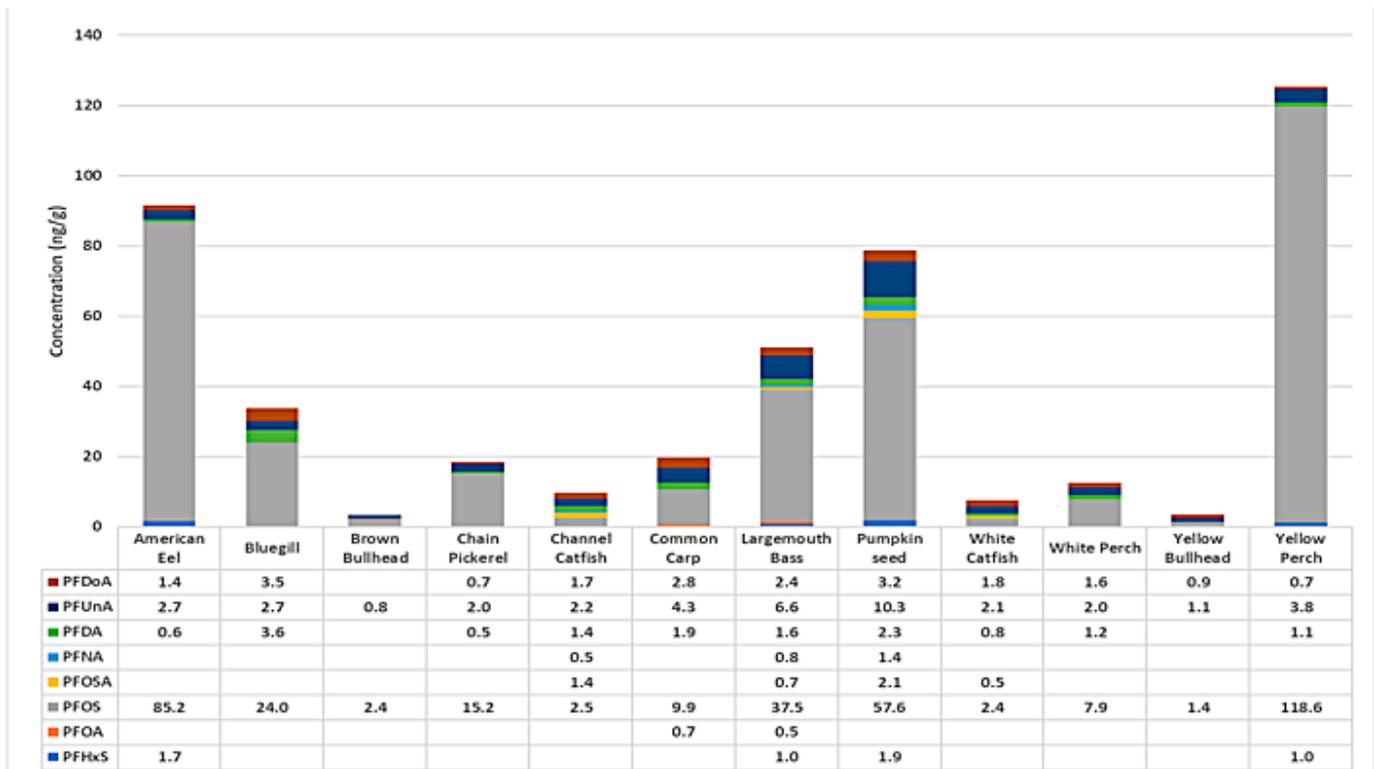


Figure 15-15. Fish tissue sampling results. Average concentration detected per species.

Data from NJDEP (2018).

Using the noncancer oral reference doses (RfDs) New Jersey Department of Environmental Protection derived for PFOA (2 ng/kg-day; (NJDWQI 2017a)), PFOS (1.8 ng/kg-day; NJDWQI, 2018a}), and PFNA (0.74 ng/kg-day; (NJDWQI 2015)) and generic conservative assumptions regarding fish consumption exposure, NJDEP derived risk-based advisory triggers for each of these compounds based upon different fish consumption frequencies specifically, once/day, once/week, once/month, once/3 months, once/year.

The following equation was used to derive their risk-based triggers (which are presented in Figure 15-16):

where

- C_{fish} is the risk-based fish concentration (ng/g)
- HQ is the target hazard quotient = 1 (unitless)
- M is the number of meals during the exposure period
- CR is the fish consumption rate (g/meal) = 8 oz/meal (227 gram/meal)
- BW is the body weight (kg) = 70 kg
- RfD is the chemical-specific oral reference dose (ng/kg-day)
- AT_{nc} is the noncancer averaging time (days)

	General Population			High Risk Population*		
	PFOA (ng/g; ppb)	PFNA (ng/g; ppb)	PFOS (ng/g; ppb)	PFOA (ng/g; ppb)	PFNA (ng/g; ppb)	PFOS (ng/g; ppb)
Unlimited	0.62	0.23	0.56	0.62	0.23	0.56
Once/Week	4.3	1.6	3.9	4.3	1.6	3.9
Once/Month	18.6	6.9	17	18.6	6.9	17
Once/3 months	57	21	51	N/A	N/A	N/A
Once/Year	226	84	204	N/A	N/A	N/A
Do Not Eat	>226	>84	>204	>18.6	>6.9	>17

*High risk individuals are considered to be at higher risk from contaminants in fish than members of the general public. This group includes infants, children, pregnant women, nursing mothers and women of childbearing age.

Figure 15-16. Risk-based fish advisory triggers.

Data from NJDEP (2018).

Because of concerns associated with the potential developmental health effects associated with these chemicals and given a lack of acute toxicity values for these compounds, NJDEP did not recommend advisory levels for the once/3 months and once/year exposure frequencies for high risk populations (young children, pregnant and lactating women, women of childbearing age), and the once/month value is the least frequent consumption category recommended for these high risk populations.

A comparison of the derived risk-based advisory levels with the measured concentrations in fish tissue samples from each of these waterways resulted in NJDEP recommending the following fish consumption advisories for the general population (Figure 15-17).

Site	Advisory (Driven By)
Echo Lake Reservoir	No more than once/month (PFOS, Largemouth Bass)
Passaic River 1&2	No more than once/3 months (PFOS, Largemouth Bass-Bluegill Sunfish)
Raritan River	No more than once/month (PFOS, Common Carp-White Perch)
Metedeconk 1&2	No more than once/3 months (PFOS, Largemouth Bass)
Pine Lake	No more than once/year (PFOS, American Eel-Largemouth Bass-Pumpkinseed Sunfish)
Horicon Lake	No more than once/month (PFOS, Chain Pickerel)
Little Pine Lake	No more than once/year (PFOS, Largemouth Bass-Yellow Perch)
Mirror Lake	No more than once/3 months (PFOS, American Eel-Bluegill Sunfish-Largemouth Bass)
Woodbury Creek	No more than once/3 months (PFOS, Largemouth Bass-Pumpkinseed Sunfish)
Fenwick Creek	No more than once/month (PFOS, Common Carp)
Cohansey River 1&2	No more than once/week (PFOS, White Perch)

Figure 15-17. NJDEP fish advisories for general population.

Data from NJDEP (2018).

15.4 Risk Communication Case Studies

15.4.1 Little Hocking Water Association (LHWA), Ohio

The communication and community participation strategy used for residents served by the Little Hocking Water Association (LHWA) in southwest Ohio produced effective results in motivating actions by individuals, government, and industry which led to a significant, measurable reduction in residents' blood PFOA levels.

A community-first strategy was implemented at the Little Hocking, Ohio, site to effectively communicate scientific results and findings in a manner that embodies the principles of community-based participatory research (CBPR). This type of strategy combines scientific methodology with community capacity-building strategies to address the disparities and power

imbalances among stakeholder groups (business owners, residents, regulatory, and responsible party). If properly implemented, CBPR can result in trust rebuilding, management of environmental justice matters, empowerment to those affected by providing information for informed action, and improved research and data collection (Viswanathan (Viswanathan et al. 2004; Hartwig, Calleson, and Williams 2006; O'Fallon, Tyson, and Deary 2000; Executive Order 12898 1994). The following is a case study summary of the Little Hocking, Ohio, site (Emmett et al. 2006; Emmett et al. 2009; Emmett and Desai 2010).

15.4.1.1 Site Description

The LHWA is a rural water authority that serves several small communities with a total population of approximately 12,000 residents in 4,000 households. The reticulation system extends around 25 miles into Ohio from Little Hocking, a small rural community along the Ohio River in Washington County, Appalachian Ohio. Based on the 2010 U.S. Census, the total population of Little Hocking was 263, predominately Caucasian, majority between the ages of 18-64 years, and 21.5% of individuals live below the poverty level. The water intake wells for the LHWA are located directly across the Ohio River from a Teflon production plant that used ammonium perfluorooctanoate (APFO, the ammonium salt of PFOA). This plant was physically located in West Virginia; therefore, the enforcement and regulation of the plant and its emissions fell to the West Virginia agencies.

Since the 1950s, the plant was known to historically release APFO into the air and water and to dispose of byproducts containing APFO in local landfills (WV DEP 2002). APFO readily converts to its anionic form, PFOA, in the environment. When tested in 2001 and 2002, the LHWA source wells had levels ranging from 0.855 ppb to 7.69 ppb. Community concerns were raised because PFOA detections in the water supply were considerably higher than any reported PWS in the United States at the time. Prior to the study summarized here, there was no information about the sources of PFOA that was being detected in human blood in widespread locations. In the absence of this information, the West Virginia Department of Environmental Protection convened the C-8 Assessment of Toxicity Team, and developed a health protective screening level for water at 150 ppb. In addition, an interim action level of 14 ppb was established by a USEPA Consent Order with the responsible party. In August 2002, groundwater borings advanced in the LHWA well field contained PFOA concentrations up to 78 ppb. A class action suit was initiated, and distrust increased among the affected community and both the government and responsible party.

To investigate community concerns about potential PFOA contamination of residents in the LHWA district, a partnership was formed between the University of Pennsylvania School of Medicine, a local health provider, and the Decatur Community Association, made up of residents living within the LHWA district. The partnership obtained an environmental justice research grant from the National Institute of Environmental Health Sciences. The research was designed to engage the affected community on all aspects of the study to determine (1) whether blood PFOA levels were elevated in the community, compared with Philadelphia residents and with published population values; (2) if blood PFOA levels were elevated, was the source air, water, or some other combination of exposures; and (3) if levels were elevated, were there changes in certain biomarkers of potential toxic effects.

A community advisory committee (CAC) was formed with local residents served by the water supply, local physicians, state and federal government representatives, a health researcher, and a school system representative. A community project coordinator was employed as a communication enabler. The CAC met quarterly and all meetings were open to the public with the only participation restrictions being that the attorneys and plant representatives were not permitted to take part in the discussions. Community advice was particularly sought as to which scientific questions to address, development and wording of questionnaires, communications with residents, and citizen concerns. The CAC utilized newsletters to keep local residents and other stakeholders informed. These newsletters and CAC meeting minutes were posted on a CAC study website.

The study team collected blood serum PFOA, hematologic and biochemical biomarkers, a questionnaire to obtain information on demographic and occupational information, and health conditions from a stratified random sample of residents in the LHWA reticulation area. The median blood PFOA levels for residents were approximately 80 times those of the general population and similar to levels reported for production workers at the fluoropolymer facility. PFOA levels were higher in children and the elderly. Residents using LHWA water who worked in production areas of the plant had PFOA levels that reflected additive effects from both exposure pathways. Residents who primarily used well water for domestic purposes had PFOA levels that correlated with the PFOA concentration in well water. No impact was seen from living in areas with higher estimated air levels.

15.4.1.2 Community-First Communication Strategy

After data had been collected from participants, but before any results were available, the CAC discussed and developed a communication strategy. For this purpose, the CAC developed a set of general principles for communication and a list of priority targets representing the community's preferred order for communication of results:

LHWA Residents' General Principles for Communications, from Emmett and Desai (2010) and Emmett et al. (2009).

- Results should be released promptly, but not before the investigators are comfortable in doing so.
- Individual participants should receive their results first to avoid participants first learning study results from the press, neighbors, or friends.
- The press should be informed in a manner that is both timely and allows the investigators to control the message as much as possible.
- The study must remain a credible source of information.
- Communications should maximize constructive responses to the findings.
- Communications should minimize pointless concern.
- Questions from individuals should be answered promptly.

LHWA District Residents' List of Priority Targets for Communication of Results, from Emmett et al. (2009).

- study participants and community (residents of the water district)
- community advisory committee
- relevant authorities and representatives (county and state health departments, state Department of Environmental Protection, local water authorities, state and federal elected government representatives for the area, local townships, sheriffs' departments, USEPA)
- local medical providers
- local media
- national media, as necessary.

Once the general principles of engagement were established, the CAC developed a communication strategy and plan. The CAC determined that the strategy required multiple modes of engagement that enforced consistent simple messages and consideration of careful timing to mitigate development of inaccurate perception of risk and management strategies. The communication plan was a "living document" to facilitate continued integration of stakeholder input, regulatory development, and scientific advancement. The sequence of communications commenced with mailings to participants at the end of July 2005 and culminated in a community meeting on August 15, 2005, where full results were presented.

15.4.1.3 Results and Use of Risk Communication Tools

1. *Notifications to Participants and Authorities*—Biomonitoring results were sent via next-day-delivery mailings to individual study participants. These results included the individual's blood PFOA and biomarker levels as well as comparative information on PFOA levels (including blood levels for national and site facility workers, general US population, and community neighborhoods) and a toll-free telephone number to contact a study physician with any questions. Letters containing aggregated, not individual, results were sent simultaneously to identified authorities and CAC members, to ensure that recipients would be able to respond appropriately to inquiries from the public.
 - *Lessons and Takeaways:* Calls often needed to be returned after business hours. Most concerns focused on higher levels in children and the elderly, and possible interactions of elevated PFOA levels and particular medical conditions.
2. *Initial Press Release and Briefing*—Key local and regional media were identified and informed of the communication plan around the date the participant letters were sent. An initial press release and briefing were made the second day after the results were mailed to ensure that participants did not first learn of the issue through the press, while still providing investigators an opportunity to be the primary source of information to the press. Identified media representatives and national news outlets were invited to the news briefing. The release simply identified that levels in LHWA residents were much higher than those in the general US population, and that water had been identified as the major source of exposure. Interested stakeholders were urged to attend a community meeting where comprehensive results would be released and discussed.
 - *Lessons and Takeaways:* The reporting by local and national media did not misconstrue information and local media participated as per the communication plan. The CAC perceived the media coverage

as constructive. The community expressed great satisfaction that participants had received their results first.

3. *Closed Rehearsal of Community Presentation*—A full closed-door rehearsal presentation (summarized in the subsequent bullet) was presented by the study team to the CAC prior to the community meeting. The closed rehearsal ensured that the community meeting presentation was as inclusive and useful as possible.
 - *Lessons and Take-Away:* The CAC requested a presentation that was careful and simple to understand, incorporating a clear visual map so that residents could locate their residences with respect to the study results. During rehearsal, the CAC members provided feedback on the order of the agenda, comprehensibility of slides, choice of wordings to accord with terminology and usage in the area, structure of the presentation, and dealing with likely questions.
4. *Community Meeting*—The meeting commenced with “ground rules,” such as lawyers were not to solicit clients and questions were to follow the presentation. It was also communicated that continual stakeholder feedback is a success factor of the communication plan. In addition, representatives from the facility were invited to attend but were not permitted to present. The 45-minute presentation given by the study team detailed partnership objectives and study methods, results, and recommendations. A two-hour question and answer period followed the presentation. A summary of the study, recommendations (including the use of bottled water), sources of information, and how to access a study physician were distributed to all attendees on exit. The meeting summary and information on accessing free bottled water were mailed to households in the LHWA district and local authorities and representatives.
 - *Lessons and Takeaways:* The meeting proceeded in a constructive manner as CAC community members had predicted and not in the angry manner outside public relations experts had predicted. Any anger was directed at the responsible party and not at the investigators.
5. *Publication of Results and Information*—Following the community meeting, a newsletter with test result summaries was issued. A website with meeting presentation slides, test results, and FAQs was also developed. A summary of results was sent to all LHWA district residents.
 - *Lessons and Takeaways:* The website received many hits. The study and recommendations did not prove controversial. The practitioners did not encounter antagonistic relationships between the different parties.
6. *Availability to Answer Questions*—Physicians from the study team made themselves available to the public to answer questions from individuals and also from treating health care professionals.
 - *Lessons and Takeaways:* This service was appreciated. Questions mostly focused on the impact on residents with particular conditions such as liver and kidney disease. The many uncertainties surrounding the risk to humans were openly acknowledged.

15.4.1.4 Effectiveness of Communications

On the day results were presented and approximately 2 weeks after the initial press release, the responsible party announced that it would make free bottled water available to LHWA district residents (3 liters per day per person). Seventy-eight percent of eligible households accepted the offer.

Sixteen months after dissemination of the study results, a follow-up study of participants was made, which included repeat blood PFOA levels and questions about any changes in water usage. Sixty-five percent of those in the initial study participated in the follow-up, of whom 95 percent had made some change in their residential water usage in a way that would be expected to reduce PFOA intake. Eighty-eight percent had followed study recommendations to switch to using bottled water. The group median blood PFOA had declined 26%, consistent with a large effect for a pollutant with a half-life of approximately 4 years in humans.

USEPA used the results to enter into a consent agreement with DuPont to provide bottled water for the other impacted communities near the plant with >0.5 ppb of PFOA in water, and the states of Minnesota and New Jersey set provisional standards for PFOA levels in drinking water.

Lessons and Takeaways: The results and communications strategy resulted in 95% of participants had made a change to their water source. This response greatly exceeds the usual level of response seen with public health interventions. All parties, individuals, corporations, and governments acted in a prudent way with the disseminated information. Not all residents reacted by adopting the specific recommendations from the study; the alternate actions some individuals took are consistent with the information being incorporated into individuals' own risk perceptions and with the development of a free market of solutions (individual decision making based on available information).

15.4.1.5 Case Study Summary

The Little Hocking Community-First Communication Strategy resulted in a great increase in alternate water source use by impacted community members and subsequently, a reduction in community PFOA blood levels. The success of the communication plan at the Little Hocking site was underlain by the four dimensions of risk communication:

- **Understanding:** Investigators worked with the community through the CAC to establish the communities' preferences and priorities in the form of a communication strategy and plan to maintain simplified and consistent messaging among stakeholder groups and interested parties, such as the media.
- **Perception:** Risk perception factors were incorporated into the outreach strategy, including residents' knowledge of PFOA biomonitoring results and associated illnesses, ability to access a physician, presence of vulnerable subpopulations (higher PFOA levels in children and the elderly), proximity of individual residences to elevated concentrations within the study area (sense of a safe place), and possible interactions of elevated PFOA levels and particular medical conditions.
- **Participation:** The affected community actively participated in all components of the communications.
- **Evaluation:** Success and effectiveness of the communication process were assessed based on feedback from the CAC, surveys of residents, and review of newspaper articles and other media content. In addition, a follow-up study was performed that addressed the effectiveness in terms of lowered blood levels of PFOA and a questionnaire about whether and how community members had changed their drinking water source as a result of the risk communication strategy.

15.4.2 State-Led Community Involvement Case Studies

The Environmental Council of the States (ECOS), in collaboration with the USEPA Office of Research and Development and the Association of State and Territorial Health Professionals, has developed a series of case studies presenting how state regulatory agencies are performing risk communication to PFAS-impacted stakeholders:

<https://www.ecos.org/documents/state-level-risk-communication-of-pfas-and-habs/>

15.4.3 Washington County, MN: A State's Approach to Risk Communication

Washington County is home to 3M's Cottage Grove manufacturing facility as well as several disposal facilities where PFAS had been routinely disposed. Beginning in 2002, the State of Minnesota pursued drinking water investigations at the 3M facility and later near 3M's waste disposal sites in Washington County. According to the 2010 US Census, the population of Washington County, Minnesota was about 238,136, with the majority being Caucasian and between the ages of 18 and 64. Over 1,800 private wells, four major aquifers, eight municipal water supply systems, and over 150 square miles of groundwater were affected by the contamination. This impacted the drinking water supply of over 140,000 residents. After they were determined as the responsible party, 3M remained involved in the remediation efforts and paid for the majority of sampling throughout the county in coordination with MPCA.

This case study is discussed in the context of the risk communication plan.

15.4.3.1 Identify the Issue

The most widespread PFAS compound found in the region is PFBA. Additional prominent compounds include PFOS, PFOA, PFHxS, PFPeA, PFHxA, and PFBS which were always present as a mixture. When investigations began in 2002, there were many challenges to determining the impact for people as the science was in the very beginning stages of development. Therefore, MDH developed health-based guidance for PFOA and PFOS and the MDH lab developed the method to analyze water sample for PFOA and PFOS. As the science has progressed, MDH continues to update methods and health-based guidance.

Site communications are organized and performed in collaboration primarily between the Minnesota Department of Health and the Minnesota Pollution Control agencies. However, as with other PFAS sites, the site covers multiple local, county and state entities. Communications frequently entail only one or a few cities rather than the entire site. They may also need to be coordinated through all the cities and the county. This leads to multiple plans with multiple partners that are specific to an issue or communications plans developed for a specific project. The fundamental traits of successful risk communication over time and with all stakeholders for MDH include: empathy, care, competence, expertise, honesty, dedication, and commitment.

15.4.3.2 Set Goals

General communication goals and objectives for the site:

- Goal: Inform people about potential hazards to their person, property, or community and help them to make informed decisions about risks to their health.
 - Objective: Develop approved message blocks for PFAS topics and house in accessible format to encourage consistent information is used for all materials developed.
 - Objective: Provide regular updates about remediation activities at stakeholder group meetings including agency PFAS training meetings, county workgroup meetings, city council meetings and public meetings
 - Objective: Provide regular updates about health risks as scientific information changes/evolves at stakeholder group meetings including agency PFAS training meetings, county workgroup meetings, city council meetings and public meetings
- Goal: Encourage people to take precautions to reduce exposure to PFAS
 - Objective: Homes with contaminated drinking water are issued drinking water advisories and either connected to the city water or supplied with GAC filters that are maintained by the state.
 - Objective: Keep updated information about actions people can take to lower their exposure to PFAS on MDH website and MPCA website.
 - Objective: Mobilize stakeholder groups in the county or local communities to encourage people in their area to participate in remediation activities and processes offered by MPCA and contractors.
- Goal: Provide background information and present risks in an understandable way, using plain-language messaging.
 - Objective: Provide opportunities for people impacted by contamination to connect with appropriate staff to find information and to ask questions if concerned.
 - Objective: User test materials using MDH Plain Language Workgroup
- Goal: Bring new information as soon as available to build trust

Objective: Provide public meetings with open house sessions before and after a main presentation to bring new information to community

Objective: Provide availability sessions to encourage concerned people impacted by changes to learn more about their individual situations.

Project specific communications goals example:

Since 2002, there have been multiple changes in PFAS health based values provided by MDH, analytical advances which have impacted lab results, an investigation that looked at PFAS in garden produce and dust, multiple biomonitoring studies, fish monitoring and consumption guidance, drinking water and source water investigations, and a study to test point-of-use water treatment devices. All of these projects and scientific advances have resulted in specific communications to affected communities with goals and objectives tailored to the issue or project.

15.4.3.3 Identify Communities and Constraints

MDH catered their risk communication strategy to the following:

- Residents of affected communities
- Local governments: cities, townships, and their staff of varying sizes
- Washington County public health and environmental staff
- Legislators
- Other state agencies including MPCA

Constraints include the size of the area and the multiple local governments. The character of each township and city vary widely with different capacities to manage local information dissemination to affected residents. This requires communicators to develop relationships with each stakeholder group. The risks and impacts of PFAS contamination are managed differently for those on public water and private wells. Therefore, the correct information needs to be available in many different forms for different stakeholders.

15.4.3.4 Community and Stakeholder Assessment

Minnesota's risk communication strategy in response to the Washington County PFAS drinking water contamination has been centered around community engagement and forging strong relationships with community members. Building these relationships enabled them to build trust with the community and develop new communication channels.

The Minnesota Department of Health (MDH), in conjunction with the Minnesota Pollution Control Agency (MPCA), maintains a hands-on risk communication approach. Information about community needs for information is gathered through regular update meetings with stakeholder groups and local government leaders. Public meetings, availability sessions and face to face interactions with community members during remediation activities provides a base of information for the ongoing communication efforts. MDH also maintains a 24/7 email and phone line for people to access with concerns or for information about site activities.

Minnesota had been engaging directly with affected communities since 2002. Having had a long-standing relationship with affected communities, MDH has a history of responding to the specific needs of the affected communities and has tailored its messaging to their knowledge level. Although basic information about PFAS is always available, the general level of knowledge amongst key stakeholders is high. For this reason and with these communities, MDH representatives lead with high-level information, as the attendees to the public meetings typically are interested in specific updates as opposed to rudimentary background information.

15.4.3.5 Identify Messages

MDH maintains a message block document with approved message blocks about a variety of topics for internal staff use. This document serves as the basis for specific information sheets developed for different stakeholder activities. It is also a resource to answer questions from concerned community members. Topics include health risk of PFAS, MDH guidance value information, current site activities, exposure information, fish consumption guidance, swimming, cumulative health risk, breastfeeding and health risks, PFAS and links to health problems, testing blood for PFAS, biomonitoring information, gardening and PFAS, and results of MN Cancer Surveillance System reports.

MDH notes the importance of discussing the scientific method with stakeholders to remain transparent about their course of action. They also share new knowledge as it becomes available and do not wait until they have a perfect message or until they know all of the facts to engage with the community. In an effort to uphold their principle of transparency, MDH acknowledges points of uncertainty and are clear about what they do not know when communicating with the public.

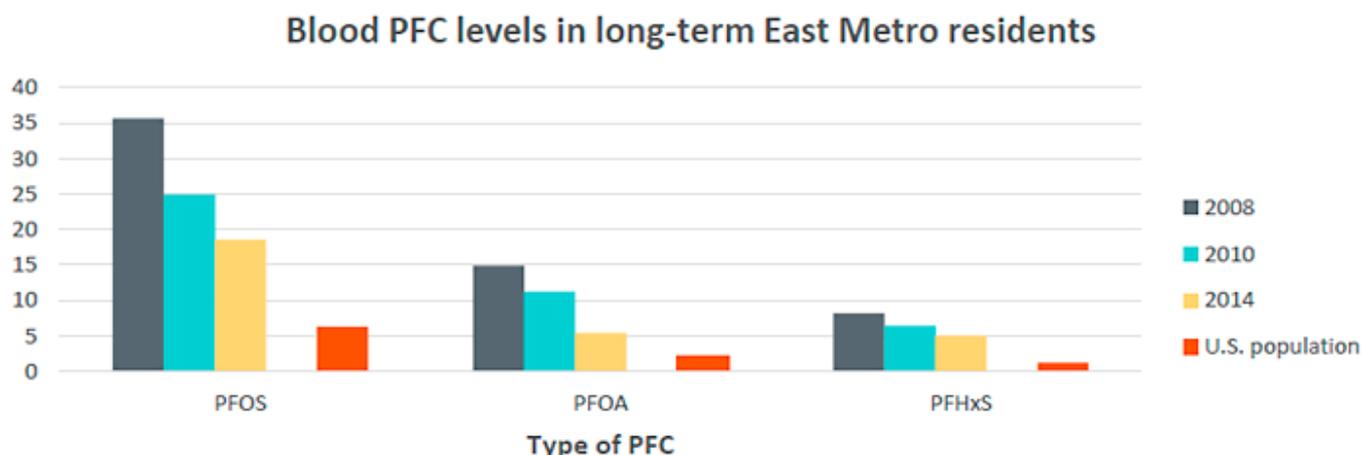
The messages are presented in different ways to different communities depending on the level of understanding that a community has about PFAS. For example, we had several meetings in 2018 for communities. One meeting was to a community which had not had PFAS contamination issues until 2018. The information for this community was presented in more of an elementary, broad overview style and level. Another presentation in the same month was to a neighboring community that had been involved with PFAS contamination since 2002. The presentation focused more on what the new information was rather than PFAS basics as the community had a more developed understanding of PFAS.

Examples of specific messages:

- Testing is available for households on private wells that would like their drinking water tested for PFAS. If test results show elevated levels, options are available from the MPCA for treating the water and reducing exposures.
- Currently, PFAS levels found in the drinking water supply in impacted communities have been within the margin of safety for the current drinking water guidance values, and outright negative health effects from these exposures are not expected with what is currently known about PFAS exposures and health effects.
- Affected water supplies are safe to use to water produce in home gardens.
- Biomonitoring Data Shows Interventions are working

Figure 15-18 includes biomonitoring data for three PFAS compounds over the time period from 2008 to 2012. This study shows that although we can't answer questions about health effects, we can demonstrate the work we are doing to reduce exposures has paid off.

PFC levels continue to go down in long-term residents



The averages are geometric means in microgram of PFC per liter of blood. U.S. population levels are from the 2011-12 National Health and Nutrition Examination Survey, which measures chemicals in a group of people 12 and older that represents the U.S. population.

Figure 15-18. Biomonitoring Data

Source: Courtesy of the Minnesota Department of Health

- Because of the extreme persistence and mobility of these compounds, a PFAS megaplume developed which is much larger than early modeling predicted. One of the primary factors in this was the unanticipated transport of PFAS via surface water and then re-infiltration to groundwater far away from the source areas – a transport pathway not typically seen in persistent environmental contaminants, which tend to adsorb to organic carbon in soils and sediments.

15.4.3.6 Select Communication and Engagement Tools

MDH's risk communication strategy facilitates community engagement and open dialogue.

- Engaging with stakeholders and communities as soon as possible when there is any change in risk management of PFAS. Builds trust over time that MDH will be there to support and help communities.
- MDH sends the right people/experts/staff to deliver messages. Over time, staff have built relationships with stakeholders.
- When interacting with people impacted by the site, staff stays until all questions are answered – whether it is a phone call, a public meeting or availability session
- MDH has a service-oriented approach to community engagement. They recognize that educating the community members will carry a ripple effect. Attendees from the meetings who learn through the presentations and the open house format will then take the information and share it with other members of the community.

MDH used the following strategies to connect with and inform the affected communities:

- Hosting Public Meetings: Public meetings have been a significant part of community engagement in Washington County. MDH has held public meetings in an open house, presentation, and Q&A format. An open house is followed by a presentation given to the attendees, after which they provide a time for questions and answers, followed by additional open house time. Participants are able to ask questions about their particular situations in an open forum setting or in one-to-one conversations. For example, in Spring 2017, MDH in collaboration with MPCA held two presentations in different areas of Washington County. The city of Cottage Grove meeting attracted 130 people. In Lake Elmo, a region where the majority of residents have private wells, approximately 120 people attended the public meeting.
- Hosting Availability Sessions/Office Hours: MDH organized opportunities to provide people with time to interact with staff one on one and ask questions. Typically, MDH held these events after major sampling events happened or when new or updated information was released. MDH extended these opportunities upon request of the community. The events were widely used. In an event held in Fall 2017, the office hours held in Lake Elmo where the majority of residents have private wells attracted 45 people. With the affected area being so large,

personal communication was helpful in establishing relationships with members of the community.

- Providing Online Resources: The MDH website outlined the history of PFAS in Minnesota as well as actions they have taken and health-based guidance information. An electronic online sampling request form was available on the MDH website. An electronic map on the website shows where MDH is sampling and community members could see and check their property's location in relation to the PFAS contaminated sites. MDH also had a widely used email address for residents to ask questions directly to the department. They could also subscribe to the government's delivery email list to get new information directly to their inbox.
- Communicating with Local Government: MDH prioritized communication with local government because it was a useful tool in keeping the communities informed. They visited city councils to provide updates on the PFAS investigations. They also provided technical support to local governments and their staff that were responsible for protecting public drinking water.
- Using the Media: MDH used press releases and interviews to disseminate information. Social media became a useful tool as well.

15.4.3.7 Implement Strategy

Strategies implemented included:

- Drinking Water Advisories: Over 2700 private wells have been sampled in the East Metro and over 1, 100 drinking water advisories have been issued. Homes that have been issued drinking water advisories are either connected to city water or provided bottled water and/or GAC filters maintained by the state. MDH and MPCA collaborated to communicate and coordinate action for this work.
- Public Water Systems: There are five community public water supplies in the East Metro that have individual wells above the MDH health-based guidance values. All of these cities put in place interim measures to manage their public water supply systems to provide drinking water at or below the MDH health-based guidance values. MDH collaborated with these communities to provide information to residents.
- Messages to Community: After developing health-based guidance values for PFAS compounds, MDH sought to explain to the community what these values mean and what concerns they address. They also explained the next steps in their action plan.
- Reiterating Commitment: MDH drives home the message that they are committed to bringing updated information to the communities to inform them of the status of their efforts. This assures the community that MDH is determined to support them and address their concerns.
- Collaboration with Other Stakeholders: MDH collaborated with MPCA on a response to the PFAS contamination. Any message that were released to the public by MDH was in conjunction with MPCA. ATSDR also developed a community engagement book which has guided MDH's risk communication strategy. Additionally, MDH worked closely with city administrators and community leaders to keep them informed prior to the public meetings.
- Concessions: When drinking water levels were found to be above guidance values in private wells, bottled water was provided by MPCA until a GAC system can be installed.

15.4.3.8 Evaluate, Debrief and Follow Up

Continuous improvement of risk communications and activities through evaluation and through providing feedback loops with stakeholders supports the ongoing implementation strategies described above. The sampling and remediation activities have been widely successful in part due to the community engagement and communications efforts that have built trust in the community for the state agencies.

Evaluation methods used to understand effectiveness of communications content and process include one on one surveys at events, hot washes with partner agencies after communications efforts, and feedback from community leaders at regular update meetings.

Continuously improving, refining, and developing materials to meet community concerns and needs that are identified by inquiries or contacts staff have with community members. Contacts are primarily through 24/7 email and phone line as well as in person while in the field or at public events.

Materials have been developed in many formats over the years and have changed due to capacity for communities to use various methods and MDH capacity to produce them - video, face to face meetings, print, social media in coordination with partners. Investigations and other information have also resulted from community concerns. These include Cancer Incidence Reports, home and garden study, site-specific meal advice for fish consumption, point-of-use filter testing, clinician

information sheet, and an information sheet about testing blood for PFAS.

15.4.3.9 Successful Outcomes

The Minnesota Department of Health has been very successful in community engagement:

- They have earned the trust of the community, and residents are assured that MDH is working hard to solve the issue at hand. The number of people participating in sampling and remediation speaks to the efforts made to connect with affected people. Exit surveys from public events have shown that people feel staff are working hard and are good at the work they do.
- MDH also has invested their resources in research and has made strides in understanding the health impacts of the PFAS contamination their state is facing. Many of the investigations and projects were in response to concerns collected through contacts with community members and leaders. These include Cancer Incidence Reports, home and garden study, site specific meal advice for fish consumption, point-of-use filter testing, clinician information sheet, and an information sheet about testing blood for PFAS.
- They have used biomonitoring to demonstrate that their efforts have reduced the PFAS levels in people's bodies. This has provided the community with tangible evidence that the work they are doing is making a difference.

15.4.3.10 Lessons Learned

- It is vital to be on the ground and engage with the community face-to-face. This helps build trusting relationships with the community which has facilitated the remediation efforts and supported reducing exposures to PFAS for community members.
- The cross-agency effort to address the PFAS concerns in Minnesota is a challenge and takes effort to coordinate, but over time has been an effective strategy to address exposures to PFAS in a timely manner.
- Dealing with residential homes and homeowners can be complex. Because PFAS is a complex emerging contaminant for which research and information is constantly evolving, it can be a challenging to return to residents with new guidance values based on new health risks. The information has to fit for those who are familiar with PFAS and those who are new homeowners or residents in affected communities.
- It is important to learn what information residents are looking for and relay it in an articulate manner and in a way that is useful to them. Another concern Minnesota residents have had is a potential decline in property value, but this concern has faded with time.
- Additionally, it is important to be understanding and sympathetic toward the affected residents when they are upset. They are concerned for the well-being of their families.

15.4.3.11 Better Practices Moving Forward

Moving forward, MDH notes that sites across the state have similar circumstances and similar concerns. The lessons learned from sites they have already worked with have been beneficial in refining their approach with other affected communities and contaminants. They have had success with duplicating their strategies and methods at other sites. Although the general principles have been effective, every community is slightly different. MDH takes the time to understand the dynamics of each particular community and tailor their risk communication methods accordingly.

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17 Additional Information

The following sections will be included in the Additional Information menu item for the web-based document.

17.1 Additional Information for Media-Specific Occurrence

This section includes the tables of information that are summarized in Section 6 and included in the figures that section.

Table 17-1A and Figure 6-1A, Observed PFAS concentrations in outdoor air

Table 17-1B and Figure 6-1B, Observed PFAS concentrations in indoor air

Table 17-2 and Figure 6-2, Observed PFAS concentrations in soil and sediment

Table 17-3 and Figure 6-3, Observed PFAS concentrations in groundwater

Table 17-4 and Figure 6-4, Observed PFAS concentrations in surface water

Table 17-5 and Figure 6-5, Observed PFOS concentrations in fish

Table 17-1A. Observed PFAS concentrations in outdoor air

Location	Information	Concentrations (pg/m ³)
Japan (Kanazawa and Okinawa), Hong Kong, and Chennai, India (Ge et al. 2017)	Included sampling and analysis of ambient particles at four sites for 24 PFAS (9 PFASs and 15 PFCAs). 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.	The yearly average PFAS mass concentration, between summer and fall samples, in Chennai was Σ PFAS = 21.5, in Okinawa Σ PFAS = 7, in Kanazawa Σ PFAS = 13. In Hong Kong, the concentration varied from Σ PFAS = 11.5 in the summer to 53 in the winter.
North Greenland (Bossi R. 2016)	Measured a range of neutral PFAS and other persistent organic pollutants (POPs) at a research station in North Greenland from 2008 to 2013.	Reported concentrations of PFAS (sum of particle and gaseous phase) [mean (range)]: <ul style="list-style-type: none"> • 6:2 FTOH: 2.82 (<0.45-16.5) • 8:2 FTOH: 4.93 (<0.45-22.4) • 10:2 FTOH: 1.59 (<0.20-9.68) • N-MeFOSA: 0.44 (<0.20-3.41) • N-EtFOSA: 0.33 (<0.22-1.93) • N-MeFOSE: 0.61 (<0.15-7.46) • N-EtFOSE: 0.50 (<0.11-5.96) Average Σ PFAS ranged from 1.82 to 32.1.
Northern South China Sea (Lai et al. 2016)	Air samples collected and analyzed for neutral PFAS onboard ship during a cruise campaign over the northern South China Sea in 2013.	Reported concentrations of PFAS [mean (range)]: <ul style="list-style-type: none"> • ΣFTOHs: 53 (17.8-105.8) • ΣFTCAs: mean not reported (0.1-0.4) • ΣFASAs: 1.2 (0.1-3.6) • Overall ΣPFAS: 54.5 (18.0-109.9)

Location	Information	Concentrations (pg/m ³)
Shenzhen China (Liu et al. 2015)	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 \pm standard deviation (SD) (range): <ul style="list-style-type: none"> • PFHxS: 0.31 \pm 0.39 (ND-1.2) • PFOS: 3.1 \pm 1.2 (ND-4.3) • PFBA: 1.9 \pm 1.8 (ND-5.0) • PFPeA: 1.9 \pm 1.4 (ND-4.0) • PFHxA: 1.5 \pm 1.5 (ND-3.6) • PFHpA: 0.042 \pm 0.10 (ND-0.30) • PFOA: 5.4 \pm 3.8 (1.5-15) • PFNA: 0.49 \pm 0.33 (ND-1.0) • PFDA: 0.48 \pm 0.38 (ND-1.2) • PFUDA: 0.018 \pm 0.064 (ND-0.22) • PFDoA: 0.20 \pm 0.19 (ND-0.54) • Overall ΣPFAS: 15 \pm 8.8 (3.4-34) Highest PFAS concentrations found within an industrial district downwind of other industrial cities.
Atlantic Ocean from North Atlantic to Antarctic (Wang, Xie, et al. 2015)	Measured 12 neutral PFAS (4 FTOHs, 3 FOSAs, 3 FOSEs, and 2 FTCAs) in the atmosphere across the Atlantic from the North Atlantic to the Antarctic, as well as snow from the Antarctic Peninsula.	Total Σ PFAS in air in the gas-phase mean (range): 23.5 (2.8 to 68.8). FTOHs were found to be the dominant compound representing 93% of the total Σ PFAS.
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.	Reported concentration range of gas-phase PFAS: <ul style="list-style-type: none"> • ΣFTOHs (most abundant PFAS in the gas phase): 39-153 • ΣFOSAs: 0.02-1.1 • ΣFOSEs: 0.33-0.79 • ΣFTCAs: 0.87-5.9 • PFBA (dominant PFCA): 4.0-22
Japan Sea to Arctic (Cai, Xie, et al. 2012)	Neutral PFAS were measured on board ship during an expedition from the Japan Sea to the Arctic Ocean in 2010.	Reported concentrations of PFAS in the gas phase(g)/particle-phase (p) [mean (range)]: <ul style="list-style-type: none"> • ΣFTOHs: 174 (61-358)(g)/3.6 (1-9.9)(p) • ΣFTCAs: 18 (5.2-47.9)(g)/0.3 (0.1-0.5)(p) • ΣFASAs: 1.4 (0.5-2.1)(g)/0.2 (0.1-0.24)(p) • ΣFASEs: 5.8 (1.9-15.0)(g)/1.8 (0.4-4.9)(p)
Birmingham and Harwell, United Kingdom (Goosey and Harrad 2012)	Measured atmospheric concentrations of a range of PFAS in homes, offices, and outdoor locations in Birmingham and Harwell, UK during 2008 and 2009. Outdoor sampling included two urban and one semirural locations. (PFAS reported as MeFOSA, EtFOSA, MeFOSE and EtFOSE).	Reported concentrations of PFAS in outdoor air [mean (range)]: <ul style="list-style-type: none"> • PFOS: 2.3 (<1.0-6.1) • PFOA: 3.5 (<1.9-20) • PFHxS: 7.0 (<1.1-30) • MeFOSA: 6.3 (<2.4-41) • EtFOSA: 89 (<5-170) • FOSA: 13 (1.8-27) • MeFOSE: 58 (3.4-130) • EtFOSE: 73 (20-120)

Location	Information	Concentrations (pg/m ³)
Vancouver, Canada (Shoeib et al. 2011)	Measured a range of ionic and neutral PFAS in indoor air, indoor dust, and clothes dryer lint in 152 homes in Vancouver, Canada in 2007-2008. The study included six outdoor air samples.	Reported concentrations of PFAS in outdoor air were [mean (range)]: <ul style="list-style-type: none"> • Σ FTOHs: 305 (161-906) • Σ FOSA/Es: 18 (8.1-108) • Σ PFCAs: below detection to 35
Atlantic Ocean: Gulf of Mexico to northeast coast of USA; Bermuda, and Nova Scotia (Shoeib et al. 2010)	Air sampling was performed in 2007 in Bermuda and Nova Scotia, and along a cruise track from the Gulf of Mexico to the northeast coast of the USA to assess air concentrations, particle-gas partitioning, and transport of a range of neutral PFAS.	Reported mean concentrations of dominant PFAS (gas + particle-phase): <ul style="list-style-type: none"> • Σ FTOHs: 11-165 • MeFOSE: 1.6-73
Atlantic Ocean, Antarctic Ocean, and Baltic Sea; and Hamburg, Germany (Dreyer et al. 2009)	Air samples were taken onboard several research vessels in the Atlantic Ocean, Antarctic Ocean, and the Baltic Sea as well as at one land-based site close to Hamburg, Germany, in 2007 and 2008 and were analyzed for a range of neutral and ionic PFAS.	Total gas-phase concentrations of ship-based samples (ΣPFAS) ranged from 4.5 in the Antarctic to 335 near source regions. Concentrations of 8:2 FTOH (typically the most dominant PFAS) were between 1.8 and 130. Concentrations of individual particle-bound precursors were usually below 1. Reported overall mean PFAS concentrations for all samples: <ul style="list-style-type: none"> • Σ FTOHs: 47 • Σ FTCAEs: 3.6 • Σ FASAs: 7.6 • Σ FASEs: 3.8
Canadian Rocky and Purcell Mountains, Western Canada (Loewen et al. 2008)	Air and lake water samples were collected along an altitudinal transect across Western Canada during the spring and summer of 2004 and analyzed for a range of PFAS.	The reported ranges of vapor phase PFAS concentrations were estimated as: <ul style="list-style-type: none"> • Σ FTOHs: 0.8-27 • Σ FOSAs: 3.7-19 • Σ FOSEs: <25-88 The concentrations of FTOHs and FOSEs were found to increase with altitude.
Parkersburg, West Virginia. USA (F)	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.
Atlantic Ocean from Germany to South Africa (Jahnke et al. 2007)	Air samples were collected on board a research vessel during cruise in the Atlantic Ocean from Germany to South Africa in 2005 and analyzed for a range of neutral and ionic PFAS.	Reported concentration ranges of PFAS: <ul style="list-style-type: none"> • 6:2 FTOH: ND-174 • 8:2 FTOH: 2-190 • 10:2 FTOH: 0.8-48 • N-EtFOSA: ND-2.2 • N-MeFOSA: 0.4-4.2 • N-MeFOSE: ND-22 • N-EtFOSE: ND-11.8
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.	Overall range of PFAS concentrations in air: <ul style="list-style-type: none"> • ΣPFAS (gas phase): 5.10-11.6 • ΣPFAS (particle-phase): 2.05-6.04

Location	Information	Concentrations (pg/m ³)
Okinawa, Japan, and Central Oregon, USA (Piekarz et al. 2007)	Air samples were collected and analyzed for a range of neutral PFAS from locations in Okinawa, Japan, and central Oregon, USA, between 2004 and 2006. (PFAS reported as MeFOSE and EtFOSE).	Reported PFAS concentration in the gas phase (g)/particle-phase (p): <ul style="list-style-type: none"> • ΣFTOHs: <0.4-32 • MeFOSE: <1-25 (g)/<1-21 (p) • EtFOSE: <1-8.7 (g)/<1-6.9 (p) • N-EtFOSE: <0.4-12 (g)/<0.4-12 (p)
Parkersburg, West Virginia USA (Barton, Kaiser and Russell 2007)	This study included six sampling events over a 10-week period during 2003-2004. Air samples were collected along the fence line of a fluoropolymer manufacturer and analyzed for PFOA.	The measured concentration of PFOA ranged from 120,000-900,000.
Canada (Shoeib et al. 2004)	Indoor and outdoor air was collected from laboratories and homes in Canada from 2001-2003 and analyzed for several PFAS. The study included two outdoor sample locations.	Reported range of PFAS concentrations in outdoor air (gas + particle-phase): <ul style="list-style-type: none"> • MeFOSE: 16.0-31.7 • EtFOSE: 8.47-9.79
North American cities (Stock et al. 2004)	Air samples were collected in six North American cities (Reno, NV; Griffin, GA; Cleves, OH; Winnipeg, MB; Long Point, ON; and Toronto, ON) and analyzed for three FTOHs (6:2, 8:2, and 10:2) and three polyfluorinated sulfonamides (NEtFOSE, NEtFOSE, and NMeFOSE).	Reported PFAS concentration range: <ul style="list-style-type: none"> • ΣFTOHs: 11-165 • Σ(N-EtFOSE, N-EtFOSE, and N-MeFOSE): 22-403
ND = Nondetect		

Table 17-1B. Observed PFAS concentrations in indoor air

Location	Information	Concentrations (µg/kg)
Global Distribution		
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.	<ul style="list-style-type: none"> • ΣPFCAs: 0.029-14.3 • ΣPFASs: ND-3.27 (only one sample was ND) Remote area (Lake Bonney, Antarctica): <ul style="list-style-type: none"> • PFOA = 0.048 • PFOS = 0.007

Location	Information	Concentrations (µg/kg)
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: <ul style="list-style-type: none"> • PFOA: 0.124 • PFOS: 0.472
Point Sources		
Location near industrial PFAS source (Davis et al. 2007)	Concentrations of ammonium perfluorooctanoate (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: <ul style="list-style-type: none"> • 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: <ul style="list-style-type: none"> • Median: 53 • Max: 9,700
Industrial Areas (Zareitalabad, Siemens, Hamer, et al. 2013)	PFOA and PFOS concentrations in soil were compiled.	Max: <ul style="list-style-type: none"> • PFOS: 48 • PFOA: 10
Sludge-Biosolids Application		

Location	Information	Concentrations (µg/kg)
Soil, groundwater, and tile water sampled after a single high-rate application of municipal biosolids (Gottschall et al. 2017)	Soil cores collected from 0–0.3 meters, entire interval homogenized; (values picked from concentrations plots).	PFOA: 0.4–0.8 PFOS: 0.2–0.4 PFNA: 0.1–0.22 PFDA: 0.05–0.33 PFUDA: 0.07–0.12
Municipal Biosolids (Sepulvado et al. 2011)	Six municipal biosolids and biosolids-amended surface soils. Soil concentrations decreased with depth. Values approximated from plots in supplemental information.	Biosolids: • PFOS: 80–219 • N-MeFOSAA: 63–143 • N-EtFOSAA: 42–72 • PFOA: 8–68 Biosolid amended soil <10 cm depth: • PFOS: 2,438 • PFOA: ~8–38 • PFNA: ~2–7 • PFHpA: ~2–8 • PFHxS: ~3–12
Sediment		
Lake Ontario, Yangtze & Mississippi Rivers (Qi et al. 2016; Yeung et al. 2013; Oliaei et al. 2013; Pan, Ying, Zhao, et al. 2014)	Maximum sediment concentrations of PFOA, PFOS, and other PFAAs.	10s–100s
Estuarine sediments–South Carolina (White et al. 2015)	Analysis of 11 PFAS.	Average of 3.79 (ΣPFAS)
Surface sediments–China (Qi et al. 2016)	Analysis of 17 PFAS. Dominant PFAS: PFOA, PFOS, and PFUDA.	0.086–5.79 dry weight and an average of 1.15 (ΣPFAS)
Surface sediments and cores–Great Lakes (Codling et al. 2018)	22 PFAS analyzed, surface sediment averaged for 3 different lakes, and dated cores used to approximate depositional trends over time.	1.5, 3.1, and 4.6 (surface sediment average for ΣPFAS 3 lakes)
ND = Nondetect LOQ = Limit of quantitation		

Table 17-2. Observed PFAS concentrations in soil and sediment

Location	Information	Concentrations (µg/kg)
Global Distribution		
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; PFOA the most frequently detected.	<ul style="list-style-type: none"> • ΣPFCAs: 0.029-14.3 • ΣPFASs: ND-3.27 (only one sample was ND) Remote area (Lake Bonney, Antarctica): <ul style="list-style-type: none"> • 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: <ul style="list-style-type: none"> • PFOA: 0.124 • PFOS: 0.472
Point Sources		
Location near industrial PFAS source (Davis et al. 2007)	Concentrations of ammonium perfluorooctanoate (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: <ul style="list-style-type: none"> • PFOS: 2,400 • PFOA: 21

Location	Information	Concentrations (µg/kg)
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: <ul style="list-style-type: none"> • Median: 53 • Max: 9,700
Industrial Areas (Zareitalabad, Siemens, Hamer, et al. 2013)	PFOA and PFOS concentrations in soil were compiled.	Max: <ul style="list-style-type: none"> • PFOS: 48 • PFOA: 10
Sludge-Biosolids Application		
Soil, groundwater, and tile water sampled after a single high-rate application of municipal biosolids (Gottschall et al. 2017)	Soil cores collected from 0-0.3 meters, entire interval homogenized; (values picked from concentrations plots).	PFOA: 0.4-0.8 PFOS: 0.2-0.4 PFNA: 0.1-0.22 PFDA: 0.05-0.33 PFUDA: 0.07-0.12
Municipal Biosolids (Sepulvado et al. 2011)	Six municipal biosolids and biosolids-amended surface soils. Soil concentrations decreased with depth. Values approximated from plots in supplemental information.	Biosolids: <ul style="list-style-type: none"> • PFOS: 80-219 • N-MeFOSAA: 63-143 • N-EtFOSAA: 42-72 • PFOA: 8-68 Biosolid amended soil <10 cm depth: <ul style="list-style-type: none"> • PFOS: 2,438 • PFOA: ~8-38 • PFNA: ~2-7 • PFHpA: ~2-8 • PFHxS: ~3-12
Sediment		
Lake Ontario, Yangtze & Mississippi Rivers (Qi et al. 2016; Yeung et al. 2013; Oliaei et al. 2013; Pan, Ying, Zhao, et al. 2014)	Maximum sediment concentrations of PFOA, PFOS, and other PFAAs.	10s-100s
Estuarine sediments-South Carolina (White et al. 2015)	Analysis of 11 PFAS.	Average of 3.79 (ΣPFAS)

Location	Information	Concentrations (µg/kg)
Surface sediments-China (Qi et al. 2016)	Analysis of 17 PFAS. Dominant PFAS: PFOA, PFOS, and PFUDA.	0.086-5.79 dry weight and an average of 1.15 (ΣPFAS)
Surface sediments and cores-Great Lakes (Codling et al. 2018)	22 PFAS analyzed, surface sediment averaged for 3 different lakes, and dated cores used to approximate depositional trends over time.	1.5, 3.1, and 4.6 (surface sediment average for ΣPFAS 3 lakes)

ND = Nondetect
LOQ = Limit of quantitation

Table 17-3. Observed PFAS concentrations in groundwater

Location	Information	Concentrations (ng/L)
Firefighting Foam Sites		
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): <ul style="list-style-type: none"> • PFHxS: 870 (290,000) • PFHxA: 820 (120,000) • PFOS: 4,220 (4,300,000) • PFOA: 405 (250,000) • PFPeA: 530 (66,000) • PFBA: 180 (64,000) • PFHpA: 235 (75,000)
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: <ul style="list-style-type: none"> • PFOA: 6,570,000 • PFOS: 2,300,000
Landfill Impacts		
Raw and Treated Landfill Leachates (Yan et al. 2015)	5 municipal landfill sites in China were included in a study of 14 PFAAs concentrations in raw and treated leachate. Total PFAAs ranged from 7.28 to 292 µg/L in raw and 0.1 to 282 µg/L in treated. Dominant compounds included PFOA (28.8% of raw and 36.8% of treated) and PFBS (26.1% of raw and 40.8% of treated).	Raw leachate Range (mean contribution %): <ul style="list-style-type: none"> • PFOA: 281-217,000 (28.8) • PFBS: 1,600-41,600 (26.1) • PFPeA: 640-10,000 (15.9) • PFOS: 1,200-6,00 Treated leachate Range (mean contribution %): <ul style="list-style-type: none"> • PFOA: 30-206,000 (36.8) • PFBS: 20-55,300 (40.8)

Location	Information	Concentrations (ng/L)
Firefighting Foam Sites		
Landfill Leachates (Eggen, Moeder, and Arukwe 2010)	Leachates from two landfills were analyzed for different emerging pollutants, including PFAS. Landfills had clay liners and tubing system to collect the leachate. Data presented include PFAS concentrations in water and particle phases.	<p>Water maximum:</p> <ul style="list-style-type: none"> • PFHxS: 281 • PFOS: 2,920 • PFHxA: 757 • PFHpA: 277 • PFOA: 767 • PFNA: 539 <p>Particle maximum:</p> <ul style="list-style-type: none"> • PFHxS: 0.15 • PFOS: 339 • PFOA: 4.05 • PFOSA: 0.44
Landfill Leachate and Groundwater (NY DEC 2017b)	PFOA was detected in public and private drinking water in Petersburg, NY. In the site investigation groundwater and leachate from the Petersburg/Berlin landfill was tested.	<p>PFOA groundwater range:</p> <ul style="list-style-type: none"> • 1.4–1,600 <p>PFOA leachate:</p> <ul style="list-style-type: none"> • 4,200
Landfill Groundwater (NY DEC 2016)	The City of Newburgh, NY, identified PFAS in their water in 2016. Included in their investigation was the Town of New Windsor landfill, which had its monitoring wells tested for PFAS compounds.	<p>Range:</p> <ul style="list-style-type: none"> • PFOS: 2.59–50.3 • PFOA: 4.0–40.4 • PFHxS: 3.72–86.6 • PFHpA: 2.36–5.93 • PFBS: 8.08–23.9
Landfill Groundwater (VT DEC 2018b)	Analysis of groundwater monitoring wells around landfills in Bennington, VT, for PFOS and PFOA. Nine locations were tested in 2016.	<p>Median (maximum):</p> <ul style="list-style-type: none"> • PFOA: 18 (900) • PFOS: 4.98 (140)
Biosolids/Sludge		
Soil, Groundwater, and Tile Water Sampled after a Single High-Rate Application of Municipal Biosolids (Gottschall et al. 2017)	Shallow groundwater (2-meter depth) sampled at 2, 7, and 10 months after application. Values picked from concentrations plots. Tile water was similar except PFOA range nondetect to 23.	<p>PFOA: 1.5–3</p> <p>PFOS: nondetect–0.8</p> <p>PFNA: nondetect–1.1</p> <p>PFHpA: nondetect–6</p>
Contaminated Biosolid Application Effects on Groundwater in Decatur, Alabama (Lindstrom et al. 2011)	Fluorochemical industry contaminated biosolids were applied on local agricultural fields for as much as 12 years in Decatur, Alabama. Sampling of well water near the fields showed elevated PFAS concentrations.	<p>Range:</p> <ul style="list-style-type: none"> • PFNA: 25.7 • PFOA: 149–6,410 • PFHpA: 77.2–5,220 • PFHxA: 9.7–3,970 • PFPeA: 12.2–2,330 • PFBA: 10.4–1,260 • PFOS: 12–151 • PFHxS: 12.7–087.5 • PFBS: 10.1–76.6
Industrial Sites		

Location	Information	Concentrations (ng/L)
Firefighting Foam Sites		
Industrial Use Contamination (Procopio et al. 2017)	Study by NJDEP and the NJ Brick Township Municipalities Authority on concentrations of PFAS compounds in various water sources. A plume of contamination was detected and attributed to a small manufacturer using materials containing PFOA.	Maximum: <ul style="list-style-type: none"> • PFOA: 70,000 • PFBA: 2,000 • PFPA: 560 • PFHxA: 3,800 • PFHpA: 4,300 • PFNA: 63 • PFDA: 560 • PFHxS: 6 • PFOS: 50
Fluorochemical Industrial Facility (Davis et al. 2007)	Environmental media (soil and water) were investigated in a PWS well field near a fluoropolymer manufacturing facility for the presence of PFOA.	Maximum: <ul style="list-style-type: none"> • PFOA: 78,000
Teflon Fabric Coating Facility (VT DEC 2018b)	2016 investigation of PFAS contamination in relation to a former Teflon coating factory in North Bennington, VT. Over 600 drinking water wells tested and more than 300 wells exceeded the state's PFOA/PFOS standard of 20 ppt.	Maximum: <ul style="list-style-type: none"> • PFOA: 4,600
Fluorochemical Industrial Facility (3M Company 2007)	Study completed at the 3M Company's Cottage Grove, Minnesota, plant. 8 groundwater monitoring wells were installed and sampled throughout the site for the presence of FCs.	Maximum: <ul style="list-style-type: none"> • PFOA: 619,000 • PFBA: 318,000 • PFBuS: 26,100 • PFHxS: 40,000 • PFOS: 26,000
Water Supplies-Nonsite-Related		
Domestic Drinking Water Wells on Cape Cod, Massachusetts (Schaidler, Ackerman, and Rudel 2016)	20 domestic drinking water wells in Cape Cod, MA, were investigated for the presence of organic wastewater compounds, including PFAS. All wells were located in areas served exclusively by onsite wastewater treatment systems.	Maximum: <ul style="list-style-type: none"> • PFBS: 23 • PFHxA: 2 • PFHpA: 1 • PFHxS: 41 • PFOS: 7
Survey across European Countries (Loos et al. 2010)	164 groundwater samples tested from 23 European countries. Sampling sites were not chosen to be "representative" or "contaminated," but most were from official monitoring stations also used for drinking water monitoring.	Median (maximum) [freq. %]: <ul style="list-style-type: none"> • PFOA: 1 (39) [65.9] • PFOS: 0 (135) [48.2] • PFHxS: 0 (19) [34.8] • PFHpA: 0 (21) [29.9] • PFDA: 0 (11) [23.8] • PFBS: 0 (25) [15.2] • PFNA: 0 (1) [15.2]
Public Drinking Water Sources across the U.S. (USEPA 2017g)	Results from finished groundwater testing by the EPA under UCMR3.	Range (freq. %): <ul style="list-style-type: none"> • PFBS: 90–220 (0.05) • PFHpA: 10–410 (0.64) • PFHxS: 30–1,600 (0.56) • PFNA: 22–56 (0.05) • PFOA: 20–350 (1.03) • PFOS: 40–7,000 (0.79)

Table 17-4. Observed PFAS concentrations in surface water

Location	Information	Concentrations (ng/L)
Freshwater		
Remote Areas (Filipovic (Filipovic et al. 2015) (Eriksson et al. 2013) (Stock et al. 2007) (Lescord et al. 2015))	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 up to single nanogram per liter range.	Range: PFOS/PFOA ND to <10
Industrial Areas, Japan, and Tennessee River, USA (Saito et al. 2004; Hansen et al. 2002)	Concentrations of PFOS and PFOA as high as 144 ng/L and 67,000 ng/L, respectively, have been measured.	Maximums: PFOS: 144 PFOA: 67,000
Fire Training/Fire Response (Saito (Saito et al. 2004; Anderson et al. 2016))	Concentrations of PFOS and PFOA as high as 8,970 ng/L and 3,750 ng/L, respectively, have been measured in AFFF-impacted surface water.	Maximums: PFOS: 8,970 PFOA: 3,750
Municipal Wastewater Treatment Facilities (Becker, Gerstmann, and Frank 2008; Boulanger 2005; Wilkinson et al. 2017; MDH 2008))	Data presented typically for upstream, downstream, and effluent wastewater. Generally low frequency of detection upstream. Some treatment facilities show evidence for precursors with greater PFAS in effluent than influent.	PFOA: ND-220 PFOS: ND-814 PFHxS: ND-26 PFBS: ND-115 PFNA: ND-209
Public Drinking Water Sources across the US (USEPA 2017g)	Results from finished water testing with surface water source by the EPA under UCMR3.	Range: PFBS: 90-370 PFHpA: 10-60 PFHxS: 30-190 PFNA: 20-54 PFOA: 20-100 PFOS: 40-400
Marine Water		
Open Water (Benskin, Muir, et al. 2012; Cai, Yang, et al. 2012; Zhao et al. 2012)	The sum of PFAA concentrations in the mid-Northwest Atlantic ranged from 0.077 to 0.19 ng/L, while PFAAs in the Northeast Atlantic ranged from 0.28 to 0.98 ng/L. The sum of PFAS in the North Atlantic ranged from 0.13 to 0.65 ng/L, and in the Greenland Sea from 0.045 to 0.28 ng/L.	Range: Σ PFAA 0.077-0.98 Σ PFAS 0.045-0.65
Coastal Areas (Benskin, Muir, et al. 2012; Cai, Yang, et al. 2012; Zhao et al. 2012)	Along the Rhode Island coast the sum of PFAAs ranged up to 5.8 ng/L. Along the coast of Antarctica the sum of PFAS ranged from 0.59 to 15.3 ng/L, and along the southern Atlantic coast of South America the sum of PFAA ranged from <0.21 to 0.54 ng/L.	Range: Σ PFAA <0.21 to 5.8 Σ PFAS 0.59-15.3
Stormwater		
Residential/Undeveloped (Xiao, Simcik, and Gulliver 2012), (Wilkinson et al. 2016) (Zhao, Zhou, et al. 2013)	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

Location	Information	Concentrations (ng/L)
Commercial/Heavy Traffic–Minneapolis/St. Paul, MN; Eastern and Central China cities; and England (Xiao, Simcik, and Gulliver 2012; Zhao, Zhou, et al. 2013; Wilkinson et al. 2016)	PFOS and PFOA measured in stormwater runoff from streets in areas not related to specific releases, but unidentified local or consumer sources may be responsible for higher concentrations detected.	Range: <ul style="list-style-type: none"> • 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, Simcik, and Gulliver 2012)	PFOS measured in stormwater in an industrial area with suspected PFAS.	Range: <ul style="list-style-type: none"> • 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

Table 17-5. Observed PFOS concentrations in fish (µg/kg)

Location	Information	Mean (max)
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.	PFOS: <ul style="list-style-type: none"> • Liver: (6,350) • Blood: (29,600) • Muscle: <3–100 (2,000)
AFFF Release (Moody et al. 2002) (Gewurtz et al. 2014) (Lanza et al. 2017)	PFOS in fish liver, muscle, and whole fish samples were detected following a release of AFFF during emergency or fire training activities.	PFOS: <ul style="list-style-type: none"> • Liver: (100) 72,900 • Muscle: (6,160) • Whole fish: ~200–2,000 (15,000)
Wastewater Treatment Plant (Becker, Gerstmann, and Frank 2010; Li et al. 2008) Schuetze (Schuetze et al. 2010)	PFOS concentrations have been detected in fish collected near the outfall of wastewater treatment plants.	PFOS: <ul style="list-style-type: none"> Liver: (400) Serum: (64) Muscle tissue: 7–250 (400)
Freshwater fish from New Jersey (NJDEP 2018)	PFOS concentrations in 12 species of freshwater fish from New Jersey.	PFOS: 1.4–119 (162.5)
Freshwater fish from U.S. urban rivers and the Great Lakes (Stahl et al. 2014)	PFOS concentrations in freshwater fish from U.S. urban rivers (25 species) and the Great Lakes (18 species).	PFOS: 10.7 (127)

17.2 Additional Information for Human Health Effects

This section supplements information provided in Section 7.1 on biomonitoring, exposure, toxicokinetic, toxicology, and epidemiology data for long-chain and short-chain PFAAs. The PFAS discussed here include perfluorocarboxylic acids (PFCAs) with four to fourteen carbons and perfluorosulfonic acids (PFSAs) with four or more carbons. Also covered are two fluorinated ether carboxylates (FECAs)—ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoate (also known as perfluoro-2-propoxypropanoic acid (PFPrOPrA); hexafluoropropylene oxide [HFPO] dimer acid), commonly known as GenX (Section 2.2.3.5); and 4,8-dioxa-3H-perfluorononanoate, commonly known as ADONA. These FECAs are replacements for PFOA as processing aids in certain fluoropolymer production. They are included because they are of current interest and health effects data are available. There is little or no publicly available health effects information for most of the many other PFAS used in commerce (Section 2.3), including precursors that can be converted to PFAAs in the environment and in the human body.

For further detail of scientific names and carbon chain length of PFAAs see Section 2.2.

17.2.1 Overview

Based on the number of studies located through searches of the National Library of Medicine's PubMed, a database containing relevant peer-reviewed publications, much of the information summarized here is recent. Additional studies may be available, particularly for those compounds with large health effects data sets, and additional information on the topics in this section can be found in databases such as PubMed and references listed in Section 7.1.

The publicly available toxicological data set is currently largest for PFOA and PFOS, with considerable data also available for PFBA, PFBS, PFHxA, PFNA, PFDA, and GenX, a few studies for PFHxS, PFUnA, PFDoA, and ADONA, and little or no data for PFPeA, PFHpA, PFTrA, PFTA, PFPeS, PFHpS, PFNS, or PFDS. Most of the mammalian studies were conducted in rodents, with a few in nonhuman primates (monkeys). The most notable toxicological effects from the mammalian studies of these PFAS, with relevant citations, are discussed in Section 17.2.5 and are summarized in Table 17-8 (provided as a separate Excel file). However, due to the large size of the toxicological data set, it is beyond the scope of this section to identify no observed adverse effect levels (NOAELs) and lowest observed adverse effect levels (LOAELs) for these effects. The numerous reviews of potential epidemiological associations of health endpoints with PFAAs are discussed in Section 17.2.4. Many of the epidemiology studies evaluate associations of health endpoints with multiple PFAAs detected in the blood serum of the subjects. Finally, data gaps and research needs are discussed.

17.2.2 Human Biomonitoring and Sources of Exposure

Several long-chain PFAAs (from highest to lowest geometric mean [GM] serum levels, as follows: PFOS, PFOA, PFHxS, PFNA) are present in the low parts per billion (ng/ml) range in the blood serum of almost all adult residents of the United States, while other PFAS are detected in a smaller percentage of the population (CDC 2018; Olsen et al. 2017)). In contrast, short-chain PFAAs such as PFBS and PFHxA are more rapidly excreted and were infrequently detected in the blood serum of the U.S. general population (CDC 2018; Olsen et al. 2017). For example, PFBS was detected in less than 5% of serum samples in all National Health and Nutrition Examination Survey (NHANES) years except 2005-'06 (CDC 2018). Both NHANES and the blood donor studies show generally higher levels of long-chain PFAAs in males than females, with generally decreasing serum levels of long-chain PFAAs over time. NHANES 2013-'14 evaluated PFAS in children 3-11 years old (CDC 2018) and found serum levels of PFOS, PFOA, PFHxS, and PFNA generally similar to those in older adolescents and adults in the same time period. It was noted that most of the children studied were born after PFOS manufacturing was phased out in the United States in 2002 (Ye et al. 2018). Long-chain PFAA human serum levels in other industrialized countries are generally similar to the United States (Kato 2015) and may be lower in less developed nations (for example, Afghanistan) where they are less likely to be used industrially and consumer products containing them are less frequently used (Hemat et al. 2010). Testing in 2017 by the North Carolina Department of Health and Human Services (NC DHHS) did not detect HFPO-DA ("GenX") in the blood serum or urine of North Carolina residents with previous or current exposure from private wells, but did detect other PFAS (NC DHHS 2018). A North Carolina State University study of a public water system and its users included a larger list of PFAS analytes and, although no GenX was detected, they identified four newly identified PFAS in the drinking water and blood serum of most participants (Hogue 2019; Hopkins et al. 2018). A recent study of a potentially exposed population detected ADONA in only a few subjects (Fromme et al. 2017).

Human exposures can result from consumption of fish from waters contaminated with bioaccumulative PFAAs (for example, MDCH (2014)). PFASs with more than eight fluorinated carbons (that is, PFOS and longer chain for PFASs; PFNA and longer chain for PFCAs) are substantially more bioaccumulative than shorter chain PFAAs, with PFASs generally more bioaccumulative than PFCAs with the same number of fluorinated carbons (Conder et al. 2008; Martin et al. 2003). When drinking water is contaminated with even relatively low levels of long-chain PFAAs, exposure from drinking water may dominate contributions from exposure sources such as food and consumer products that are prevalent in the general population. For example, (USEPA 2011a) predicted that ongoing exposure to 20 ng/L PFOA in drinking water will increase serum PFOA levels more than two-fold from the U.S. median of 2 ng/L. Elevated serum levels of long-chain PFAAs have been observed in communities with contaminated drinking water in several U.S. states, including Ohio and West Virginia (WV University 2008; Emmett et al. 2006; Steenland et al. 2009) (Hoffman et al. 2011), New Hampshire (NH DHHS 2015), Alabama (ATSDR 2013), Minnesota (MDH 2009; Landsteiner et al. 2014), New York (NYS DOH 2016a), and in other nations, including Germany (Hölzer et al. 2008) and Sweden (Li et al. 2018) (Table 17-6). ATSDR (2019b) plans to conduct exposure assessments that will include biomonitoring in eight U.S. locations impacted by PFAS in drinking water.

Understanding exposures to PFAS at different developmental phases (for example, fetus, infant) is important to ensure protection of the most sensitive subpopulations. Evidence for developmental effects from early life exposures to long-chain

PFAAs in humans is discussed in Section 17.2.4 and in animals in Section 17.2.5. PFAAs (primarily PFHpA and longer chain PFCAs; PFHxS and longer chain PFSAs) have been detected in human amniotic fluid (Stein et al. 2012; Zhang, Sun, et al. 2013), umbilical cord blood (Kato 2015; Kudo 2015), and breast milk (Liu, Li, et al. 2010; White et al. 2011; Post, Cohn, and Cooper 2012; Kato 2015) (Kudo 2015). Although the specific compounds analyzed for and/or detected vary among studies, other PFAAs that have been analyzed for in breast milk rarely exceeded the limit of quantitation (Tao, Kannan, et al. 2008; Tao, Ma, et al. 2008). Serum levels of several long-chain PFAAs were higher in breast-fed infants than in their mothers and declined slowly following weaning (Mogensen et al. 2015), and serum levels of infants who drank formula prepared with PFAS-contaminated water were higher than in older individuals using the same water source. Infants and toddlers may also receive higher exposures because of age-specific behaviors such as hand-to-mouth activity that results in greater ingestion of house dust, and more time spent on floors with treated carpets relative to older children or adults (Trudel et al. 2008; Shoeib et al. 2011).

Elevated serum levels of PFAAs, in some cases >100,000 ng/ml, have been found in industrially exposed workers (Olsen 2015). Serum concentrations of PFCAs (PFHpA and longer) were also increased in professional ski waxing technicians due to exposures to fluorinated ski waxes (Freberg et al. 2010; Nilsson et al. 2010). Higher serum levels of PFDA (Dobraca et al. 2015), PFOS, and PFHxS (Rotander et al. 2015) have been reported in firefighters relative to those in the general population.

17.2.3 Toxicokinetics

PFAAs for which data are available (PFOA, PFHpA, PFHxA, PFOS) were well absorbed orally ($\geq 90\%$) in rodents (Kudo 2015). PFOA and PFNA were absorbed via inhalation as dusts or aerosols (Kinney, Chromey, and Kennedy 1989; Hinderliter, DeLorme, and Kennedy 2006). PFOA was absorbed to a limited extent from dermal exposure in studies of isolated human and rodent skin (Fasano et al. 2005) (Franko et al. 2012).

PFAAs, particularly long-chain PFCAs and PFSAs, have unique toxicokinetic properties as compared to other types of POPs. Unlike most other bioaccumulative organic compounds (for example, dioxins, PCBs), PFAAs do not have a high affinity for adipose tissue. In contrast, PFAAs are water soluble, have an affinity for proteins (which varies among compounds), and generally distribute primarily to the liver, blood serum (where they are bound to albumin and other proteins), and kidney (Bischel et al. 2011; Lau 2012, 2015; Kato 2015).

PFAAs are highly resistant to chemical reactions. As such, they are not metabolized, and this is also true for HFPO-DA (Gannon et al. 2016) and ADONA (Gordon 2011). However, PFAA precursors can be metabolized to PFAAs within the body, and reactive intermediates may be formed in these metabolic pathways (Rand and A. Mabury 2016). Some examples are the metabolism of 6:2 fluorotelomer alcohol (6:2 FTOH) to PFBA, PFPeA, PFHxA, and PFHpA (Buck 2015); 8:2 FTOH to PFOA and PFNA (Kudo 2015; Kabadi et al. 2018); and perfluorooctane sulfonamidoethanols (FOSEs), perfluorooctane sulfonamides (FOSAs), and perfluorooctane sulfonamidoacetic acids (FOSAAs) to PFOS (Gebbink, Berger, and Cousins 2015). Additionally, larger PFAS molecules such as polyfluoroalkyl phosphoric acid diesters (diPAPs) have been found in human blood serum and can be metabolized to FTOHs, which are further metabolized to PFCAs (D'Eon and Mabury 2011) (Lee and Mabury 2011).

Table 17-6. Long-chain PFAA serum levels in populations exposed through drinking water (ng/ml = $\mu\text{g/L}$ = ppb)

(Means, medians, and maximums available from the cited studies are shown. AM—arithmetic mean; GM—geometric mean;

95th–95th percentile; — indicates that data are not available)

Location	Study Population	Attributed Source	Year	PFOA			PFOS			PFHxS		
				Mean	Median	Max.	Mean	Median	Max.	Mean	Median	Max.
C8 Study Population: WV/Ohio (WV University 2008) Includes occupationally exposed subject	n = ~69,000 <1 - >90 yrs. M-48%, F-52%	Industrial-PFOA	2005-06	83 (AM)	28	22,412	23 (AM)	20	759	—	—	—

Location	Study Population	Attributed Source	Year	PFOA			PFOS			PFHxS		
				Mean	Median	Max.	Mean	Median	Max.	Mean	Median	Max.
Arnsberg, Germany (Hölzer et al. 2008)	n=90 Children 5-6 yrs.	Industrial waste applied to agricultural land-mainly PFOA	2006	25 (AM)	—	97	5 (AM)	—	21	1 (AM)	—	13
	n=164 Mothers 23-49 yrs.			27 (AM)	—	100	6 (AM)	—	17	1 (AM)	—	6
	n=101 Men 18-69 yrs.			29 (AM)	—	78	12 (AM)	—	36	3 (AM)	—	9
East Metro, MN (MDH 2009)	n = 196 20-86 yrs. M-45%, F-55%	Industrial-multiple PFAS	2008-09	23 (AM)	16	177	48 (AM)	41	448	15 (AM)	9	316
Decatur, AL (ATSDR 2013)	n=153 "child" - >60 yrs. M-41%, F-59%	Industrial-multiple PFAS	2010	16 (GM)	—	144	40 (GM)	—	472	6 (GM)	—	59
Ronneby, Sweden (Li et al. 2018)	n = 3418 4-83 yrs. M-47%, F-53%	AFFF	2014	14 (AM)	10	92	245 (AM)	176	1,870	228 (AM)	152	1790
Portsmouth, NH (NH DHHS 2015)	n = 108 < 12 yrs.	AFFF	2015	4 (GM)	5	12	9 (GM)	9	31	6 (GM)	7	26
	n= 363 >12 yrs.			3 (GM)	—	16	8 (GM)	—	75	8 (GM)	—	75
Hoosick Falls, NY (NYS DOH 2016a)	n = 2,081 <17 - >60 yrs. M-45%, F-55%	Industrial-PFOA	Feb.-April 2016	24 (GM)	28	—	—	—	—	—	—	—
Merrimack, NH (NH DHHS 2017)	Public water system n = 217	Industrial-PFOA	2016	3.9 (AM)	—	10.1 (95 th)	5.5 (AM)	—	15.2 (95 th)	1.3 (AM)	—	3.2 (95 th)
	Private wells N=219			4.4 (AM)	—	26.6 (95 th)	5.4 (AM)	—	16.4 (95 th)	1.3 (AM)	—	3.4 (95 th)

Excretion of PFAAs and HFPO-DA is primarily through the urine, with a much smaller percentage, if any, eliminated in the feces. In women of childbearing age, excretion also occurs through menstruation and lactation (Harada and Koizumi 2009; Thomsen et al. 2010). Serum PFAS levels were lower in adult males undergoing venesection (ongoing blood withdrawal) for medical reasons (Lorber et al. 2015) and in firefighters who had donated blood, as compared to other firefighters (Rotander et al. 2015). The excretion rate for long-chain PFAAs varies substantially between animal species, and it is much slower in humans than in laboratory animals. Additionally, for some PFAS, the excretion rate is very different in males and females of the same rodent species, likely due to differences in the extent of secretion and reabsorption by organic anion transporter proteins (OATs) and possibly other transporter proteins in the kidney, reviewed in Lau (2012, 2015); Kudo (2015) and USEPA (2016h). Half-lives in rodents, nonhuman primates, and humans for the PFAS included in this section are shown in Table 17-7.

Table 17-7. Half-lives of PFCAs, PFSAs, and perfluoroethers in rodents, nonhuman primates, and humans
Notes: No information was located for PFPeA, PFDoA, PFTrDA, PFTeDA, PFPeS, PFNS, PFDS, ADONA; — indicates that data are not available; h-hour, d-day, y-year.

	Mouse		Rat		Nonhuman primate		Human	
	Male	Female	Male	Female	Male	Female	Male	Female
<i>PFCAs</i>								
PFBA	13 h ^a	2.9 h ^a	9.2 h ^a	1.8 h ^a	40 h ^a	41 h ^a	72 h ^a (O; mean)	87 h ^a (O; mean)
PFHxA	~1 h ^b		~2 h ^c	~2 h ^c	5.3 h ^c	2.4 h ^c	32 d ^e (O; GM)	—
					14-47 h ^d			
PFHpA	---	---	2.4 h ^f	1.2 h ^f	---	---	—	<50 yrs. of age-1.2 y ^g (G-U)
								All M & F >50 yrs. of age-1.5 y ^g (G-U)
PFOA	19 d ^h	17 d ^h	4-6 d ⁱ	2-4 h ⁱ	21 d ^j	30 d ^j	3.8 y (O; mean); 2.4 y (O; GM) ^k 2.3 y ^l (DW; median) 3.3 y ^m (DW; GM) 3.4 y ⁿ (DW; mean)	
							15-50 yrs. of age-4.6 y ⁿ (DW)	15-50 yrs. of age-3.1 y ⁿ (DW)
PFNA	34-68 d ^{o,p}	26-69 d ^{o,p}	30 d ^{o,p}	1-2 d ^{o,p}	---	---		<50 yrs. of age-2.5 y ^g (G-U)
								All M & F >50 yrs. of age-12 y ^g (G-U)
PFDA	---	---	24 d ^q	29 d ^q	---	---		<50 yrs. of age-4.5 y ^g (G-U)
								All M & F >50 yrs. of age-4.3 y ^g (G-U)
PFUnA	---	---	---	---	---	---		<50 yrs. of age-4.5 y ^g (G-U)
								All M & F >50 yrs. of age-12 y ^g (G-U)
<i>PFSAs</i>								
PFBS	---	---	3.1-4.5 h ^{r,s}	2.4-4.0 h ^{r,s}	15-95 h ^{r,s}	8.1-83 h ^{r,s}	26 d (O; GM) ^s	
PFPeS	---	---	---	---	---	---	---	---
PFHxS	29 d ^t	26 d ^t	29 d ^t	1.8 hd ^t	141 d ^t	87 d ^t	8.5 y (O; mean); 7.3 y (O; GM) ^k 5.3 y ⁿ (DW)	
							15-50 yrs. of age-7.4 y ⁿ (DW)	15-50 yrs. of age-4.7 y ⁿ (DW)
PFOS	40 d ^u	34 d ^u	47-67 d ^{u,v}	40-48 d ^{u,v}	132 d ^u	110 d ^u	5.4 y (O; mean); 4.8 y (O; GM) ^k 3.4 y ⁿ (DW; mean)	
			15-50 yrs. of age-4.6 y ⁿ (DW; mean)	15-50 yrs. of age-3.1 y ⁿ (DW; mean)				
<i>Perfluoroether (Replacement for PFOA in fluoropolymer manufacturing processes)</i>								

	Mouse		Rat		Nonhuman primate		Human	
	Male	Female	Male	Female	Male	Female	Male	Female
GenX	21 h ^w	18 h ^w	3 h ^x	<3 h ^x	~2 h ^y	~2 h ^y	---	---

DW-Based on decline in serum levels after exposure to contaminated drinking water ended.
GM-Geometric mean.
G-U-Mean value; based on urinary excretion in general population, with modeled menstrual excretion for F < 50 yrs. old. More uncertain than estimates based on decline in serum levels. (Not shown for PFAS with half-lives based on serum decline).
O-based on decline in serum levels in workers or retired workers after exposure ended.

^a Chang et al. (2008)
^b Iwai (2011), reported in Russell, Nilsson, and Buck (2013)
^c Chengelis et al. (2009)
^d (Noker 2001) reported in Russell, Nilsson, and Buck (2013)
^e Russell, Nilsson, and Buck (2013)
^f Ohmori et al. (2003)
^g Zhang, Beesoon, et al. (2013)
^h Johnson and Ober (1979) Kemper and Jepson (2003)
ⁱ (Lau et al. 2006)
^j Butenhoff, Kennedy, Hinderliter, et al. (2004)
^k Olsen et al. (2007)
^l Bartell et al. (2010)
^m Brede et al. (2010)
ⁿ Li et al. (2018)
^o Tatum-Gibbs et al. (2011)
^p Ohmori et al. (2003)
^q Gibbs et al. (2012)
^r Chengelis et al. (2009)
^s Olsen et al. (2009)
^t Sundstrom et al. (2012)
^u Chang et al. (2012)
^v Butenhoff (2007)
^w DuPont (2011a)
^x DuPont (2011b)
^y DuPont (2008)

As shown in Table 17-7, excretion rates in mammalian species vary among PFAS for which half-life data are available, with short-chain PFAAs and GenX generally excreted more rapidly than longer chain PFAAs. Half-lives in rodents and nonhuman primates are generally in the range of several weeks to several months for long-chain PFAAs, and about 1 hour to several days for short-chain PFAAs and GenX. However, PFOA, PFNA, and PFHxS (reviewed in Kudo (2015)) are excreted much more rapidly (hours to days) in female than male rats; this sex difference in rats also exists but is not as pronounced for PFBA, PFHxA, PFHpA, and PFBS (Kudo 2015). This difference in excretion rate is important in interpretation of rat toxicology studies of these compounds, particularly for developmental effects.

Human half-lives for PFAS are longer than in other mammalian species that have been studied, with estimates of several

years for long-chain PFAAs (PFOA, PFNA, PFOS, PFHxS); 1 year for PFHpA, and several days to 1 month for shorter chain PFAAs (PFBA, PFHxA, PFBS; Table 17-7). The estimates of human half-life shown in Table 17-7 are based on measured declines in serum PFAS levels in the same individuals over time after a source of elevated exposure, such as occupational exposure or ingestion of contaminated drinking water, ceases. Such estimates are less uncertain than population-based estimates from modeling of PFAS intake and biomonitoring data for serum PFAS levels from different sets of individuals from the general population at different time points. Half-life estimates based on urinary excretion are available for several PFAAs, including some with no serum-based half-life estimates ((Zhang, Beesoon, et al. 2013) shown as G-U in Table 17-7); these urinary estimates are less certain because they include modeled estimates of menstrual excretion in women of childbearing age and do not consider fecal excretion or blood loss other than menstruation (for example, blood donation). It should be noted that there are large inter-individual variations in human half-lives, which may arise from physiological factors (for example, differences in renal transport by OATs; (Yang, Glover, and Han 2010).

Because of the large species and sex differences in excretion rates, the internal dose resulting from a given administered dose varies widely among species and, in some cases, males and females of the same species. Therefore, interspecies (for example, animal-to-human) comparisons must account for the large interspecies half-life differences with approaches such as use of internal dose (serum level) as the dose metric, interspecies toxicokinetic extrapolation based on the ratio of half-lives in humans and animals, or use of physiologically based pharmacokinetic models.

17.2.3.1 Toxicokinetics Relevant to Developmental Exposures

Toxicokinetics relevant to developmental exposures to PFAAs are important because developmental effects are sensitive endpoints for toxicity of long-chain PFAAs in rodents, and prenatal exposure to some long-chain PFAA was associated with decreased fetal growth in some human epidemiology studies. Developmental exposures have been studied in rodents for several PFAAs, but not in nonhuman primates. PFAAs cross the placenta to reach the developing fetus in both humans and rodents (reviewed in Lau (2012) and Kudo (2015)), and are transferred to milk, resulting in exposure via lactation (Luebker, Case, et al. 2005; White et al. 2009; Kato 2015). In humans, long-chain PFAAs have been detected in cord blood (for example, (Wang et al. 2019) and amniotic fluid (Stein et al. 2012; Zhang, Sun, et al. 2013).

In humans, the greatest exposures to PFAAs in breast milk occur during the first few months of infancy because both PFAA concentrations in milk and the breast milk ingestion rate on a BW basis (ml/kg/day) are highest then; PFAA levels in milk may be lower in mothers who previously nursed other infants (Tao, Kannan, et al. 2008; Haug et al. 2011; Thomsen et al. 2010). Serum concentrations of long-chain PFAAs in breast-fed infants increase several-fold from the levels at birth during the first few months of life, followed by a decline in older infancy and early childhood (Fromme et al. 2010; Mogensen et al. 2015; Verner et al. 2016b, a) (MDH 2018b, 2019a); reviewed in NJDWQI (2015); (2017a), (2018a). Because of their higher rate of fluid consumption on a BW basis, exposures to infants who consume formula prepared with PFAS-contaminated water are also highest during the first few months of life (USEPA 2011a). Goeden, Greene, and Jacobus (2019) presented a model that predicts transplacental transfer and exposure to breast-fed and formula-fed infants for long-chain PFAAs in drinking water.

17.2.3.2 Relationship of Human Exposures to Serum Levels

Clearance factors (CL) that describe the relationship between oral exposures or dose (ng/kg/day) and steady-state serum levels (ng/L) in humans have been developed for PFOA (Lorber and Egeghy 2011; USEPA 2016d) and PFOS (USEPA 2016c):

$$\text{Dose [ng/kg/day]} \times \text{CL [L/kg/day]} = \text{serum concentration [ng/L]}.$$

These clearance factors, which indicate bioaccumulative potential, are based on average values for human PFAS half-lives and volumes of distribution (Vd);

$$\text{CL [L/kg/day]} = \text{Vd [L/kg Body Wt]} \times [\text{Ln}2/\text{half-life in days}].$$

Where Ln2 is the natural log of 2.

When combined with mean daily U.S. water ingestion rates (USEPA 2011a), the CLs can be used to predict the expected average increase in serum levels (above the “baseline” serum level from non-drinking water sources) that results from ongoing exposure to a given drinking water concentration of PFOA or PFOS (Bartell 2017; NJDWQI 2017a; Post, Gleason, and Cooper 2017). For PFOA, this average serum:drinking water ratio is greater than 100:1 (NJDWQI 2017a); this ratio is consistent with data from exposed populations and toxicokinetic modeling (Emmett et al. 2006; Hoffman et al. 2011; Bartell 2017). The CL for PFOS predicts an average serum:drinking water ratio of about 200:1 ((NJDWQI 2018a);(Post, Gleason, and Cooper 2017) (Lu and Bartell 2019), and available toxicokinetic data also support an estimated ratio of 200:1 for PFNA

(NJDWQI 2015) Lu and Bartell, 2019) and PFHxS (Lu and Bartell, 2019). It should be noted that PFAA serum:drinking water ratios vary among individuals using the same source of contaminated drinking water, due to inter-individual differences in daily water consumption rates (L/kg/day) and/or physiological differences relevant to toxicokinetics.

17.2.3.3 Isomer-Specific Toxicokinetics

Some PFAAs exist as a mixture of linear and branched isomers; the isomer profile varies depending on the manufacturing process used (telomerization yields primarily linear PFAS; electrochemical fluorination yields a mixture of linear and branched PFAS; Section 2.2.5.2. Toxicokinetics may differ among isomers of the same PFAA in rodents (Loveless et al. 2006; De Silva et al. 2009) and humans (Zhang, Beesoon, et al. 2013; Gao et al. 2015; Beesoon et al. 2011).

17.2.4 Human Epidemiology Studies

Many U.S. general population studies are based on data from NHANES, and other general population studies come from various worldwide locations. These include studies of specific subpopulations such as pregnant women, infants, children, or the elderly, as well as evaluations of associations of prenatal exposures with effects later in life. Data on communities exposed through contaminated drinking water come primarily from the C8 Health Study evaluations of approximately 70,000 Ohio and West Virginia residents exposed to PFOA in drinking water for at least 1 year at concentrations of 50 ng/L to >3,000 ng/L, including evaluations by the C8 Science Panel (Frisbee et al. 2009; C8 Science Panel 2020). This panel consisted of three prominent environmental epidemiologists charged with determining whether there are “probable links” (defined as “given the scientific evidence available, it is more likely than not that a connection exists between C8 exposure and a particular human disease among class members”) between PFOA exposures in this study group and disease. However, such health effects studies are not available from communities with drinking water contaminated with either the other PFAS discussed in this section or the complex mixtures of PFAS present in AFFF. Finally, health effects of several long-chain PFAAs, including PFOA, PFOS, and PFNA, have been studied in occupationally exposed workers (Khalil 2015). Because these workers were primarily male, relatively few women were included in these studies.

Exposure assessment in most but not all of these studies is based on blood serum levels of PFAS as an indicator of internal dose. The studies often evaluate associations between health endpoints and multiple PFAS detected in blood. Serum levels of long-chain PFAAs are indicators of long-term exposures (Section 7.1.2) that reflect individual differences in both exposure (for example, daily water consumption) and rate of excretion. Therefore, serum levels are less uncertain as indicators of exposure than external parameters such as drinking water concentration. In contrast to long-chain PFAS, there is little epidemiological information on short-chain PFAS because they are infrequently detected in blood serum due to their more rapid excretion. Exposure assessment in some of the C8 studies of communities with PFOA exposure from an industrial source is based on serum PFOA levels estimated from modeling of drinking water and air PFOA concentrations over time, rather than measured serum levels (Savitz et al. 2012; Winquist and Steenland 2014b, a; Dhingra, Lally, et al. 2016; Dhingra, Darrow, et al. 2016) Herrick (Herrick et al. 2017). Finally, exposure is based on job classification, rather than serum PFAA measurements in some occupational studies of PFOA (Gilliland and Mandel 1993; Leonard 2003; Lundin et al. 2009; Raleigh et al. 2014), PFNA (Mundt et al. 2007), and PFOS (Alexander et al. 2003; Olsen et al. 2004; Alexander and Olsen 2007; Grice et al. 2007).

As is the case for epidemiologic studies of environmental contaminants in general, the human studies of PFAAs are observational, in contrast to toxicology studies, which are experimental. Additionally, most epidemiology studies of PFAAs are cross-sectional, although some use other designs (prospective, retrospective, case-control). In cross-sectional studies, exposure and outcome are evaluated at the same point in time. Such cross-sectional studies cannot reveal whether increased exposure led to the health endpoint or vice versa, and reverse causality (for example, when a physiological change affects serum PFAS levels, rather than the serum PFAS levels causing the physiological change) has been hypothesized by some researchers as partially or totally explaining some of the associations in the epidemiological literature, including reduced birth weight and decreased kidney function. In general, publications of epidemiology studies report results in terms of associations with the endpoints of interest based on statistical analysis. When there are multiple studies of associations of an environmental contaminant such as PFAA(s) with a health endpoint, results often differ among studies. The differing results can arise from difference in the study design (for example, sex, age, ethnicity of population studied; magnitude and/or duration of exposure; method for assessment of endpoint of interest), size of population studied (may be too small to detect statistically significant associations), method used for statistical analysis, consideration of potential confounding factors, or chance. Therefore, conclusions about whether the overall body of evidence supports an association are based on scientific judgment. Such conclusions may differ among scientists who review the same body of data, and the conclusions are often phrased carefully to convey the nuances of the opinions being stated. Such observational studies are not designed to prove causality for health effects, and conclusions about evidence for causality are

therefore based on criteria, such as the Hill criteria (Lucas and McMichael 2005) related to the overall body of relevant scientific information (for example, consistency, dose-response, biological plausibility, potential for reverse causality). As is the case for associations, when conclusions about causality are presented in the scientific literature, they are often carefully worded to convey nuances and may differ among scientists reviewing the same body of data.

17.2.4.1 Noncancer Health Endpoints

This section summarizes information for various categories of noncancer health endpoints: Changes in systemic markers, Fetal growth, Immune system effects, Thyroid effects, and Other effects.

Systemic Markers

For PFOA and PFOS (Khalil 2015; USEPA 2016d, c; NJDWQI 2017a) (NJDWQI 2018a; ATSDR 2018e, draft), PFNA (NJDWQI 2015; ATSDR 2018e, draft), and PFDeA (ATSDR 2018e, draft), the cited reviews concluded that associations are generally consistent for increases in total cholesterol and/or low-density lipoproteins. Australia Government DOH (2018) concluded, based on a review of key reports and published systematic reviews, that an association of both PFOA and PFOS with small changes in cholesterol is generally observed. Additionally, the C8 Science Panel concluded that there is a “probable link” between PFOA and clinically defined high cholesterol (C8 Science Panel 2012a). Rappazzo, Coffman, and Hines (2017) concluded that the evidence for an association of prenatal or childhood exposure to PFAS with increased cholesterol is generally consistent; studies reviewed found associations with PFOA, PFOS, PFNA, and/or total PFAS. Regarding causality, NJDWQI (2017a) concluded that the evidence supports multiple criteria for a causal relationship between increased serum cholesterol and PFOA, while Australia Government DOH (2018) concluded that it cannot be established whether PFOA or PFOS causes increased cholesterol based on currently available data.

Most reviews have concluded that PFOA (Gleason, Post, and Fagliano 2015; Khalil 2015; USEPA 2016d; NJDWQI) (ATSDR 2018e, draft) and PFNA (NJDWQI 2015) are generally associated with increases in certain liver enzymes, particularly alanine aminotransferase (ALT). NJDWQI (2017a) concluded that there is some evidence to support a causal relationship between PFOA and ALT. In contrast, most evaluations of PFOS have found weaker or no evidence for associations with increased liver enzymes (Gleason et al., 2015; (Khalil 2015; NJDWQI 2018b) NJDWQI (2018a); (USEPA 2016c). However, (ATSDR 2018e, draft) concluded that “increases in serum enzymes and decreases in serum bilirubin, observed in studies of PFOA, PFOS, and PFHxS, are suggestive of liver damage.” Australia Government DOH (2018) concluded that an association of PFOA and PFOS with elevated levels of the liver enzyme ALT was observed in many studies.

Various reviews have concluded that there is some evidence or limited evidence for an association of increased serum uric acid and/or hyperuricemia with exposure to PFOA, PFOS, and/or PFNA (Gleason, Post, and Fagliano 2015; Khalil 2015; NJDWQI 2015) (2017a), (2018a; Australia Government DOH 2018).

Fetal Growth

Exposure to PFOA and PFOS were associated with relatively small changes in measures of decreased fetal growth (for example, birth weight, head circumference) in most studies, while some studies did not find such an association. A systematic review and meta-analysis by Johnson et al. (2014) found that there is “sufficient” human evidence that developmental exposure to PFOA reduces fetal growth in humans and provided a quantitative estimate of the decrease in birth weight per ng/ml serum PFOA. The main analysis included nine studies in which maternal or umbilical cord serum PFOA levels were measured in pregnant women. These studies met other inclusion criteria defined by the researchers; study subjects were from the general population in various locations. An additional analysis included a large study from the C8 Health Study population with exposure from contaminated drinking water in which maternal serum levels were retrospectively modeled. PFOA was associated with decreased birth weight in most of the studies from the general population but not in the study of the more highly exposed community. Inclusion of the study from the C8 Health Study population, in which serum PFOA levels during pregnancy were modeled from pre-pregnancy serum PFOA data, reduced the magnitude of decreased birth weight per ng/ml serum PFOA.

Several other reviews also evaluated the associations of PFOA and PFOS with decreased fetal growth. Bach et al. (2015) concluded that PFOA and PFOS are associated with decreased birth weight in most studies, but that associations in some studies were not statistically significant, and that the existing information is insufficient to determine whether or not there is an association. Khalil (2015) concluded that there is inconsistent evidence for association of decreased birth weight and PFAS. A later meta-analysis by (Negri et al. 2017), which included more recent studies not considered by Johnson et al. (2014), also reported a quantitative relationship between decreased birth weight and serum PFOA and PFOS levels. A recent

meta-analysis by Steenland, Barry, and Savitz (2018) considered additional studies not included in the two earlier meta-analyses, including the large studies from the C8 Health Study in which serum PFOA levels during pregnancy were modeled from pre-pregnancy serum PFOA data. Although Johnson et al. (2014) concluded that results from studies without measured serum data during pregnancy are too uncertain to include in a metanalysis, Steenland, Barry, and Savitz (2018) concluded that use of modeled or pre-pregnancy serum data may actually be preferable to serum levels measured during pregnancy because these exposure estimates would not be affected by potential reverse causality or confounding related to expansion of maternal plasma volume during pregnancy or renal glomerular filtration rate. Additionally, Steenland, Barry, and Savitz (2018) concluded that the decrease in birth weight in studies based on late pregnancy serum PFOA levels was larger than in those based on preconception or early pregnancy serum PFOA levels. They concluded that these findings are consistent with confounding or reverse causality as an explanation for the observed association of PFOA and decreased birth weight. A systematic review and modeling effort by Verner et al. (2015) found that PFOA is associated with decreased birth weight, and that a portion (less than half) of the reduction in birth weight results from confounding by associations of PFAS with decreases in both birth weight and maternal renal glomerular filtration rate (that is, reverse causality). USEPA (2016d, 2016c) concluded that PFOA and PFOS are associated with decreased fetal growth, and ATSDR (2018e) p.25, concluded that “evidence is suggestive of a link between serum PFOA and PFOS and small decreases in birth weight; the decrease in birth weight is <20 g (0.7 ounces) per 1 ng/mL increase in blood PFOA or PFOS level.” Australia Government DOH (2018) concluded that PFAS exposure was often associated with generally small decreases in weight and length at birth in general population studies.

Immune System Effects

Of the several potential effects of PFAS on immune function, the discussion below focuses on associations with antibody response to vaccines, including in children, because this endpoint has been evaluated and reviewed most extensively. A systematic review by the National Toxicology Program (NTP 2016, p.1) concluded that PFOA and PFOS are “presumed to be an immune hazard to humans” based on a high level of evidence from animal studies and a moderate level of evidence from human studies for suppression of antibody response. ATSDR (2018e) concluded that “evidence is suggestive of a link between serum PFOA, PFOS, PFHxS, and PFDeA (meaning PFDA) levels and decreased antibody responses to vaccines.” USEPA (2016d, 2016c) stated that there is an association between PFAS and decreased vaccine response and noted that serum concentrations of multiple PFAS are often correlated in the relevant studies. Rappazzo, Coffman, and Hines (2017) found that there is generally consistent evidence for association of PFAS with this effect in children. (NJDWQI 2017a)(2018a) concluded for PFOA that associations and decreased vaccine response are consistent among studies, and for PFOA, while decreased vaccine response was consistently observed, evidence is limited because most of the vaccine types were evaluated in only one or two studies. Pachkowski, Post, and Stern (2019) concluded that there is evidence that PFOS is associated with a decrease in some vaccine antibody responses following vaccination. Chang et al. (2016) concluded that a consistent association with vaccine response in general has not been demonstrated for PFOA and PFOS, and that some associations for specific vaccines are “striking in magnitude” but require replication in other studies. Australia Government DOH (2018) , pg.11 concluded, based on review of key reports and systematic reviews, that “the strongest evidence for a link between PFAS and clinically important immunological effects is for impaired vaccine response.” They note both that the overall human evidence is weak, but that animal data suggests that “PFAS may alter immune function at concentrations found in humans with environmental and occupational exposures.” (p. 11) Finally, Khalil (2015) stated that PFAS exposure has been associated with immunotoxicity, including decreased vaccine response, but that the data are inconsistent.

Thyroid Effects

Evaluations of PFAAs and thyroid disease have reached varying conclusions. Although stating that the overall database was mixed, the C8 Science Panel determined a “probable link” for PFOA and thyroid disease (C8 Science Panel 2012c). ATSDR (2018) p.25 concluded that “epidemiology studies provide suggestive evidence of a link between serum PFOA and PFOS and an increased risk of thyroid disease.” USEPA (2016h) concluded that the increased risk for thyroid disease in women appears to be associated with PFOA, while there is weaker or no evidence in men. For PFOS, USEPA (2016g) concluded that there is limited support for an association of incidence or prevalence of thyroid disease with PFOS, including large studies of representative samples of the general U.S. adult population. (NJDWQI 2017a) 2018a) found limited evidence for association of PFOA and thyroid disease, while associations of PFOS with thyroid disease were not noted, and Khalil (2015) found that the data are inconsistent. Australia Government DOH (2018) concluded that “there are no consistent associations between any particular PFAS and thyroid hormones,” and that there is limited evidence of an association between PFOA and thyroid disease in women but not in men. Rappazzo, Coffman, and Hines (2017) stated that conclusions about PFAS and thyroid disease in children cannot be reached with certainty due to the small number of studies and variable results. Coperchini et

al. (2017) found that hypothyroidism was the most consistent thyroid effect for PFOA, and for PFOS to a lesser extent, with women and children most susceptible. Ballesteros et al. (2017) stated that although there is a small number of studies with comparable data, there is some consistency in evidence for increased thyroid-stimulating hormone (TSH) with PFHxS and PFOS in pregnant women, and with PFNA TSH in teenage boys; associations with thyroid disease were not noted. More recently, a very large study (n = ~ 63,000) evaluated thyroid diseases in a Swedish community in which one-third of the population had previous residential exposure to very high levels of PFOS (8,000 ng/L) and PFHxS (17,000 ng/L) in drinking water. (Andersson et al. 2019). A consistent pattern of increased risk of hypothyroidism or hyperthyroidism was not found in men or women with residential exposure to the contaminated water.

Other Effects

The C8 Science Panel also found probable links for PFOA with ulcerative colitis (C8 Science Panel 2012b) and pregnancy-induced hypertension (C8 Science Panel); PIH was also associated with PFOS in the same two studies that linked it with PFOA (Stein, Savitz, and Dougan 2009; Darrow, Stein, and Steenland 2013). ATSDR (2018e) concluded that “there is suggestive epidemiological evidence for an association between serum PFOA and PFOS and [PIH] and/or pre-eclampsia.”

For many other epidemiological endpoints that have been studied, generally consistent associations were not found and/or the available data are too limited to make firm conclusions.

It is notable that associations for several of the effects mentioned above (serum lipids, liver enzymes, vaccine response, birth weight) were observed even within the exposure range prevalent in the general population (without specific exposures from environmental sources), as well as at higher exposures. For several of these effects, the dose-response curves (for example, serum lipids, liver enzymes) are steepest at very low exposures with a much flatter slope approaching a plateau at relatively low serum concentrations (for example, ~40 ng/L for PFOA and cholesterol).

17.2.4.2 Carcinogenicity

Several evaluations of the epidemiological evidence for carcinogenicity are available for PFOA and PFOS, while such evaluations have not been conducted for other PFAAs. The C8 Science Panel (2012d) found a “probable link” of PFOA with testicular and kidney cancer based on an increased incidence of these cancers in the Ohio and West Virginia communities with drinking water exposure as well as data from other human and animal studies. Although some other occupational studies of PFOA, such as Raleigh et al. (2014), did not find increased incidence of these tumors, increased kidney cancer was reported in workers exposed to PFOA in the West Virginia industrial facility (Steenland and Woskie 2012). In consideration of these findings, IARC (2016) classified PFOA as “possibly carcinogenic to humans” (Group 2B) based on limited evidence that PFOA causes testicular and renal cancer, and limited evidence in experimental animals. Based on reviews of key reports and systematic reviews, the Australia Government DOH (2018), p.70 concluded that “the evidence on cancer risk is limited;” that it is possible that PFOA is associated with an increased risk of kidney and testicular cancer; and that the evidence does not support PFAS being a major contributor to cancer burden in workers or exposed community populations. As discussed in Section 9.1.3.2, PFOA, PFOS, and GenX chemicals were described as having suggestive evidence for human carcinogenicity by USEPA (2016d, 2016c, 2018g) and (NJDWQI 2017a - PFOA) (NJDWQI 2018a - PFOS) based primarily on animal data.

In contrast to PFOA, studies of cancer incidence in large populations with exposure to PFOS-contaminated drinking water are not available. Arrieta-Cortes et al. (2017) concluded that while associations with cancer were not observed in the available occupational and general population studies of PFOS, such associations cannot be ruled out because problems with the studies may have precluded detection of associations if they were present. They therefore concluded that there is “inadequate evidence of carcinogenicity” based on the human data. Chang et al. (2014) stated that “many positive associations with PFOA exposure were detected in community settings” but were not confirmed in studies of workers with much higher exposures, although increases in certain cancers in some occupational studies are noted within the paper. They concluded that a causal association between PFOA or PFOS and human cancer is not supported by the currently available epidemiological evidence.

17.2.5 Animal Toxicology Studies

Many scientific considerations and decision points are involved in developing human health toxicity factors from animal toxicology data. In the hazard identification component of the toxicity factor development, the toxicological endpoint selected as the basis for the reference dose should be determined to be well established (that is, supported by multiple studies), related to an adverse health outcome, and relevant to humans based on mode of action considerations. Peroxisome proliferator-activated receptor- α (PPAR- α) is a nuclear receptor found in many human and animal tissues that is involved with numerous physiological processes (Corton (Corton, Anderson, and Stauber 2000; Michalik et al. 2006). The role

of PPAR- α in the effects caused by PFAS and the human relevance of effects in rodents that are mediated by PPAR- α have been a focus of research on the mode of action for the toxicological effects of PFAAs (Lau 2012; Post, Gleason, and Cooper 2017). In the dose-response evaluation portion of toxicity factor development, the selected endpoint must provide the data needed to determine a point of departure (that is, benchmark dose [BMD], NOAEL, or LOAEL). To appropriately account for the large differences in PFAA half-lives among species, and among sexes of the same species in some cases, dose-response evaluation for long-chain PFAAs is most appropriately based on internal dose, as indicated by serum level, rather than external (administered) dose. Finally, in development of RfDs, uncertainty factors appropriate to the specific study and endpoint are selected and applied to the point of departure to account for factors such as sensitive human subpopulations, interspecies differences, shorter-than-chronic exposure duration, extrapolation from a NOAEL to a LOAEL, and potentially more sensitive toxicological effects (Section 8.3 and the ITRC tables posted as an Excel file of the basis for PFOA and PFOS values).

Toxicological effects that have been reported as statistically significant in mammalian laboratory animal studies for each PFAS, with relevant citations, are presented in Table 17-8 (provided as a separate Excel file). The sections following the table present general discussions of systemic, reproductive and developmental, and carcinogenic effects of these PFAS.

17.2.5.1 Systemic Effects

All of the PFAS included in Table 17-8 (provided as a separate Excel file) for which data are available caused increased liver weight in the rodent and nonhuman primate species studied. For most of these PFAS, increased liver weight was accompanied by hepatocellular hypertrophy. Developmental (in utero or lactational) exposures to some PFAAs caused increased liver weight in rodent offspring. Many PFCAs, as well as PFOS and GenX, caused additional hepatic effects that are more severe in nature such as hepatocellular necrosis and/or vacuolation in rodents and nonhuman primates, or hepatic lipid accumulation in rodents. For PFOA (Butenhoff et al. 2012; NJDWQI 2017a)) and PFOS (Butenhoff et al. 2012; NJDWQI 2018a), these hepatic effects increased in severity with longer duration of exposure and may represent a progression to neoplastic changes, including hepatic adenomas. Additional effects reported for some PFAS include bile duct toxicity in rodents and increased serum levels of liver enzymes in rodents and/or nonhuman primates.

Some PFAAs and FECAs caused decreased serum cholesterol in rodents and/or nonhuman primates. The increased cholesterol in humans associated with much lower exposures to some PFAS may be attributable to interspecies differences, such as differences in activity of relevant receptors involved with cholesterol metabolism. However, these contrasting observations in rodents and humans may also arise from differences in the fat content of a typical low-fat laboratory diet and the higher fat diet in the humans who were studied (Tan et al. 2013; Rebholz et al. 2016), or to dose-related differences in this response, because the doses in the toxicology studies are much higher than human exposure levels.

Some long-chain PFAAs caused immune system toxicity (Table 17-8, provided as a separate Excel file). Decreased antibody response to antigens has been identified as a sensitive endpoint for PFOS toxicity (Lilienthal et al. 2017; MDH 2019a; ATSDR 2018e, draft) (NJDWQI 2018a) (Pachkowski, Post, and Stern 2019).

The majority of PFAS covered herein have not been tested for neurobehavioral effects. Of those PFAAs that have been evaluated in rodents, exposure-related effects were not observed for PFBA and PFHxA, while exposure of adult rodents to PFOS and PFDA caused effects including changes in learning, memory, activity, and habituation or other effects indicative of cognitive defects. Additionally, developmental exposures to PFOA, PFOS, and PFHxS caused persistent neurobehavioral effects in mice.

17.2.5.2 Reproductive and Developmental

Reproductive effects in males and females and developmental effects of several PFAS have been evaluated in rodents (Table 17-8, provided as a separate Excel file), but these effects have not been studied in nonhuman primates. In addition to the considerations common to developmental toxicity studies in general, the much faster excretion of several PFAS in female rats than in males must be considered when interpreting results of the rat reproductive and developmental studies.

Dosing of pregnant females with PFAAs results in gestational exposure to the fetus and also to the offspring during lactation. Cross-fostering studies of PFOA (White et al. 2009) and PFOS (Luebker, Case, et al. 2005) in which dosed dams fostered pups from control dams and vice versa showed that effects can result from exposures during either gestation or lactation.

Although malformations have been reported in a few rodent studies of PFOA and PFOS, effects such as full litter resorptions, decreased litter or number of live pups at birth, decreased survival of neonates, and decreased fetal and neonatal weight have been more frequently and consistently found. These developmental effects may result from toxicity to the placenta, as

has been observed for PFOA (Suh et al. 2011) and PFOS (Lee et al. 2015). With PFOS at relatively high doses, neonatal mice and rats appeared normal at birth but died within a few hours; the genesis of this phenomenon is not understood (multiple studies reviewed in NJDWQI (2018a)).

Decreased growth of offspring and/or delays in reaching developmental milestones was observed for several PFAS in rodent studies (Table 17-8, provided as a separate Excel file). For PFBS (Feng et al. 2017) and PFNA (Das et al. 2015), BW decrements persisted until adulthood. PFOA caused delays in ossification of bones and eruption of teeth (Lau et al. 2006; Yahia et al. 2010). Developmental markers such as eye opening and/or reaching sexual maturity were also delayed by some PFAAs, while noting that sexual maturity was conversely accelerated in male mice by PFOA (Lau et al. 2006). Persistent neurobehavioral effects in mice resulted from developmental exposures to several long-chain PFAS.

Certain developmental effects of some PFAAs persisted into adulthood. These include decreased size of uterus and ovaries, accompanied by decreased number of follicles and corpora lutea, and changes in reproductive and thyroid hormone levels in female mouse offspring exposed to PFBS (Feng et al. 2017). Developmental exposures of mice to PFOA caused persistent delays in mammary gland development (White et al. 2009) and persistent liver toxicity (Quist et al. 2015) at doses lower than those that caused other systemic and developmental effects; these endpoints have not been evaluated for other PFAS.

17.2.5.3 Chronic Toxicity and Tumorigenicity

PFAAs have generally not been found to be mutagenic or genotoxic (Lau 2015).

Of the PFAS included in Table 17-8 (provided as a separate Excel file), chronic studies that evaluated carcinogenicity and other effects of long-term exposure have been conducted in rats only for PFHxA, PFOA (two studies; one in males only), PFOS, and GenX. PFHxA did not increase the incidence of tumors in either sex of rats. PFOA increased the incidence of benign tumors, including testicular Leydig cell adenomas in both studies, and hepatic adenomas and pancreatic acinar cell adenomas in the study that included only males. In the chronic PFOS study, benign tumors were increased, including hepatic adenomas in females, and thyroid follicular cell adenomas in males only in the high dose “recovery group” (dosed for the first year only and evaluated at the end of the 2-year study). GenX increased the incidence of both hepatocellular adenomas and carcinomas in females, and the incidence of combined pancreatic acinar cell adenomas and carcinomas and testicular Leydig cell adenomas in males.

IARC (2016) classified PFOA as “possibly carcinogenic to humans” (Group 2B) based on limited evidence that PFOA causes testicular and renal cancer, and limited evidence in experimental animals. Based on the USEPA (2005a) Guidelines for Carcinogen Risk Assessment, USEPA (2016d, 2016c, 2018k) and NJDWQI (2017-PFOA, 2018-PFOS) described PFOA, PFOS, and GenX as having suggestive evidence for human carcinogenicity. For PFOA, USEPA (2016d) and ATSDR (2018e) concluded that the hepatic tumors are unlikely to be relevant to humans, while human relevance was not discounted for the testicular and pancreatic tumors. For PFOS, USEPA (2016g) and NJDWQI (2018a) not discount human relevance of the hepatic tumors. USEPA (2005a) and NJDWQI (2017b) developed cancer slope (potency) factors for PFOA based on the incidence of testicular Leydig cell tumors in rats. USEPA (2016h) noted that, while the mode of action for these tumors is not known, a nonlinear mode of action is likely because PFOA is metabolically inert.

17.2.6 Data Gaps and Research Needs

Although many studies relevant to health effects of PFAAs have become available in the last few years, important data gaps remain for most of the PFAAs and FECAs discussed here, as well as for many additional PFAS used in commerce or found in AFFF.

Human half-lives and other toxicokinetic data are not available for some PFAS found in drinking water and other environmental media. This information is critical for adequately assessing the bioaccumulative potential and relevant routes of exposure (for example, placental and breast milk transfer), and for extrapolation of animal toxicity information to humans.

Available data suggest that reactive intermediates can form in the metabolic pathways that convert PFAA precursors to PFAAs within the body. Additional information on the formation and potential toxicity of these reactive intermediates is needed.

Although the C8 Health Study provides a large body of epidemiological data from communities with exposure to PFOA in drinking water, such data are not available from communities with drinking water contaminated with PFOS, other PFAAs, or the complex PFAS mixtures found in AFFF. Health studies in communities exposed to PFAS from AFFF use at nearby military sites were funded in the 2018 federal budget (Walton 2018), and these studies could provide such information.

Additional toxicology data are needed for some PFAAs found in environmental media, including drinking water. For example, there are very limited toxicology data for PFHpA, and no information was located for PFPeA. Additionally, although humans are exposed to multiple PFAS, very little toxicological data are available for mixtures of PFAS. Multigeneration studies are important for assessment of reproductive and developmental effects, and they are available for only a few PFAS. PFHxS is a PFAA with a long human half-life that has been found in human serum and in drinking water impacted by both industrial discharges and AFFF. Although developmental effects of PFHxS are of concern, there are currently no multigenerational developmental studies for PFHxS. Available information from rodent studies suggests that developmental exposures to some long-chain PFAS (PFOA, PFOS, PFHxS) cause permanent neurobehavioral effects, but these data are limited. Additional studies are needed on neurobehavioral effects of PFAS, particularly from early life exposure.

Studies that provide data on chronic effects, including carcinogenicity, are available for only four PFAS (PFHxA, PFOA, PFOS, GenX), and such studies are needed for PFHxS, PFNA, ADONA, and other PFAS to which humans may be exposed. All of the chronic studies were conducted in rats, and chronic studies in a second species such as mice would provide valuable information, particularly for those PFAS that are rapidly excreted in female rats.

The mode(s) of action for the toxicological effects of PFAAs are not fully understood and continue to be the focus of ongoing research. Although not the focus of this section, data on bioavailability of PFAS from environmental media other than drinking water (for example, soil) are limited, and such information can be useful in assessing exposures at contaminated sites.

Challenges related to the use of toxicity information from surrogates for PFAS for which no toxicity data are available are discussed in Section 9.1.1.2. There is a need to develop approaches for addressing groups and mixtures of PFAS, such as the relative potency approach described by Zeilmaker et al. (2018).

Finally, OECD (2018) identified 4,730 PFAS-related CAS numbers, including compounds with many different structures, including some that have not been used commercially. The majority of these PFAS, including those in commercial use, have very limited or no toxicity data (Wang, Cousins, et al. 2015; Wang, DeWitt, et al. 2017), indicating a critical data gap in health effects information for PFAS. Approaches currently under development at EPA and the National Toxicology Program (NTP) may prove useful for screening of a large number of PFAS with rapid assays that evaluate parameters related to toxicokinetics and toxicity (USEPA 2018k). Additional information is found on the EPA CompTox website (USEPA 2020; Williams et al. 2018) and from the NTP Rapid Evaluation and Assessment of Chemical Toxicity (REACT) Program (DeVito 2018).

If this effort is successful, the results could be used, along with data on human exposure, for prioritization of PFAS for more detailed toxicological studies (USEPA 2018k).

17.3 Additional Information for Risk Assessment

17.3.1 Human Health Exposure Assessment

Figure 9-5 illustrates predominant exposure pathways. In the following sections information is presented for exposures by environmental medium. Information about site risk assessment is in Section 9.

17.3.1.1 Soil

Soil exposure scenarios are possible at a site. Some of the PFAAs, such as PFOA and PFOS, are mobile and persistent in soil. As indicated in Section 5, PFAS distribution in soils is complex, reflecting several site-specific factors and individual PFAS-specific factors.

Sorption and retardation generally increase with increasing perfluoroalkyl tail length, and functional groups contribute to the degree to which a PFAS has the affinity to leach from soil to groundwater. A detailed discussion of the fate of PFAS in soil is provided in Section 5. If PFAS are retained in soil, they are available for contact by receptors, resulting in soil exposures.

PFAS are not well absorbed through the skin (ATSDR 2015; USEPA 2016g, h). Therefore, 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 to PFAS.

17.3.1.2 Potable Water

Potable water can be a major exposure pathway. When drinking water exposures are occurring, the drinking water pathway

typically represents the dominant exposure in comparison to other exposure pathways (for example, via food), even when PFAS concentrations in drinking water are relatively low (Post, Gleason, and Cooper 2017; Bartell 2017). PFAS levels in young children (up to the age of 6) are higher than in adolescents and adults consuming the same drinking water source, as discussed and cited in Section 7.1.2. This is most likely due to the higher levels of water ingestion per unit of body mass at these ages. Even if bottled water is supplied for drinking water purposes, potential exposures may occur to PFAS in potable water if it is used for non-drinking water purposes (for example, showering, bathing, hand washing dishes). Although the dermal absorption potential from water is low and in most cases is expected to be insignificant, exposure may occur. In addition, if PFAS is present in potable water used for food preparation (in commercial or residential settings), PFAS will be transferred to foods, resulting in dietary exposures.

17.3.1.3 Groundwater

The same potential exposure pathways described above for potable water apply to groundwater when used as a potable source. In addition, construction workers may contact PFAS in shallow groundwater (if within the depth of construction activities), although dermal absorption potential from water is low. If PFAS-impacted groundwater is used as irrigation water for crops, homegrown produce, or animal watering, PFAS in groundwater may be transferred to biota (plants or animals), resulting in dietary exposures.

As indicated in Section 6.3, 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. However, sorption and partitioning might restrict leaching rates from the vadose zone and reduce the advection-driven transport velocity of PFAS in groundwater, depending on specific properties of the PFAS. These processes might limit plume development and discharge to surface water and might also provide time for transformation of PFAA precursors. Groundwater geochemistry might dictate the extent of transformation because nearly all microbial processes identified to date are aerobic (Liu and Mejia Avendaño 2013).

17.3.1.4 Surface Water

Surface water exposure scenarios are possible because surface water may become impacted with PFAS by surface runoff or groundwater discharge. Surface water exposures can occur through drinking water or by consuming aquatic biota from contaminated water bodies. Much of the PFAAs reaching 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).

Biofilms on surface water are known to accumulate PFAS (Munoz et al. 2018), as do other organic-/protein-rich particles in aquatic systems (Ahrens and Bundshuh 2014). Therefore, surface water films that contain these matrices are very likely significant repositories (and potential sources of exposure) of long-chain PFAS.

17.3.1.5 Sediment

Sediment exposure scenarios are possible because surface water may become impacted with PFAS by surface runoff or groundwater discharge, and there is likely to be partitioning to sediment and uptake to biota. However, when reaching marine waters, 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).

17.3.1.6 Air

Inhalation exposure scenarios are possible for PFAS. Dusts containing PFAS may be generated from a site where PFAS are present in soil. In addition, some PFAS (for example, FTOHs and some perfluoroalkyl sulfonamides) have higher volatilities and tend to partition into air from other media (ITRC 2018a). Certain PFAS are found in ambient air, with elevated concentrations observed or expected in urban areas nearest to emission sources, such as manufacturing facilities, wastewater treatment plants, fire training facilities, and landfills (Barton et al. 2006; Ahrens et al. 2011; Liu et al. 2015).

17.3.1.7 Diet

PFAS exposures may occur from food consumption scenarios (specifically, ingesting aquatic and terrestrial plants and animals). Crops may be impacted by PFAS if irrigated with contaminated groundwater or surface water; if impacted by soil, runoff, or atmospheric deposition; or where biosolids have been applied to soil. In addition, because some PFAS biomagnify in food webs, ingestion of contaminated biota, especially fish and animals that eat fish (for example, bears), may be a major exposure route (ATSDR 2018c) (ATSDR 2015; USEPA 2016g, h). Recreationally caught fish from areas with PFAS contamination may be a specific source of elevated exposures to PFAS such as PFOS that bioaccumulate in fish. PFAS

exposures may also occur from food packaging materials containing PFAS (see Section 17.3.1.8, Consumer Products).

Breast Milk and Infant Formula

Consumption of breast milk and infant formula are potential exposure scenarios for infants. A mother's breast milk may be impacted through exposure to PFAS-contaminated media, and infants may ingest formula prepared with PFAS-contaminated water (Fromme et al. 2010) (Mogensen et al. 2015). Higher exposures to infants are of concern because infants are sensitive subpopulations for developmental effects of PFAS, including PFOA and PFOS } (USEPA 2016g, h), as discussed in Section 7.1. Infant exposure through breast milk or formula prepared with contaminated water is higher than older adults (for example, the mother) using the same water source. The USEPA Exposure Factors Handbook (USEPA 2011a) provides detailed information on breast milk consumption rates and the higher water consumption rate of infants.

17.3.1.8 Consumer Products

Typically, exposure scenarios associated with consumer products are not included in human health risk assessments (HHRAs) for contaminated sites. However, the HHRA should acknowledge that analytical results for environmental media (including indoor air and dust) may reflect impacts from consumer products (for example, carpets and upholstered furnishings) containing PFAS that have degraded, released fibers, or volatilized.

17.3.2 Other Considerations When Calculating Exposure Point Concentrations

Other contaminants present at the site can affect the movement of PFAS, which are not easily accounted for in fate and transport models. For example, petroleum hydrocarbon 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). As discussed in detail in Section 5 and Section 10.4.1, the movement of PFAS in environmental media depends on both site-specific media properties and properties of the specific PFAS. Leaching potential is a function of both media properties (for example, pH, redox conditions) and PFAS structural properties (for example, chain length) (Gellrich, Brunn, and Stahl 2013; Gellrich, Stahl, and Knepper 2012).

It is critically important to collect site-specific soil partitioning and soil-to-groundwater pathway data for PFAS sites. Existing models and standard methods are not able to accurately predict or calculate soil-to-groundwater movement of PFAS, and therefore site-specific empirical data are necessary.

As discussed in detail in Section 5.4, the composition of PFAS can change in media. Studies have reported both biotic and abiotic transformations of some polyfluorinated substances (precursors), which may form PFAAs (Buck et al. 2011). Precursors that are ingested can be transformed in the body to PFAAs (USEPA 2016g, h). However, PFAAs likely do not degrade or otherwise transform under ambient environmental conditions. PFAS composition may change in surface water because of biotic and abiotic degradation of PFAA precursors. These complex transformations are not incorporated in current fate and transport models.

17.3.3 Information about Selecting Bioaccumulation and Bioconcentration Factors

As indicated in Section 5.5 (PFAS Uptake into Aquatic Organisms) and Section 6.5.3 (Fish), certain PFAS can bioaccumulate in the food web. PFAS occur widely in biota through bioaccumulation processes. PFAAs, particularly PFOS, are typically the dominant PFAS detected in biota (Houde et al. 2011). Figure 17-1 illustrates bioaccumulation from sediment and surface water.

Section 5.5.2 provides a detailed discussion of factors affecting the bioaccumulation potential of PFAS.

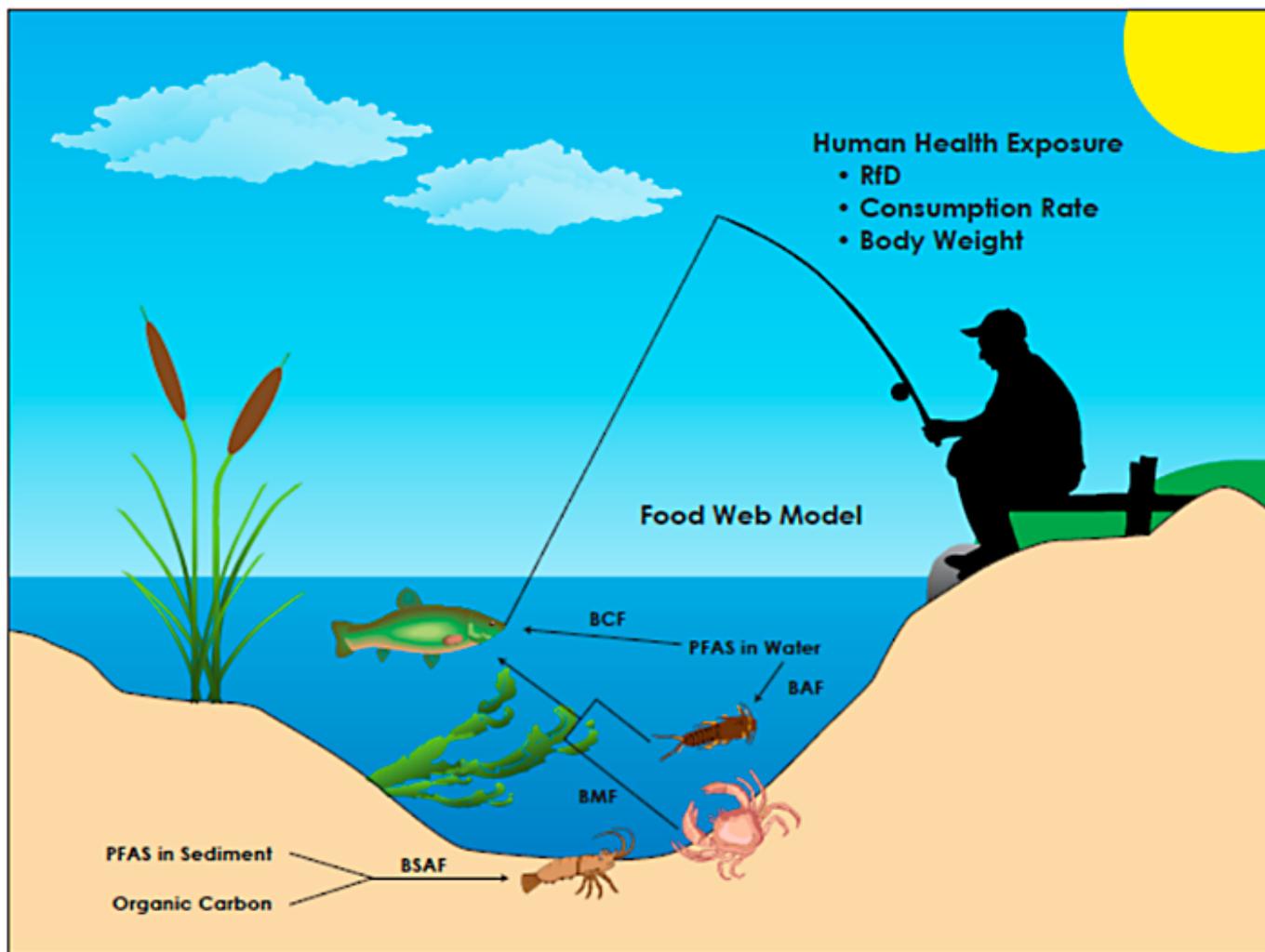


Figure 17-1. Bioaccumulation of PFAS from sediment and surface water. (BAF–bioaccumulation factor; BCF–bioconcentration factor; BSAF–biota-sediment accumulation factor; RfD–reference dose. (Source: J. Conder, Geosyntec. Used with permission.)

Section 6.5.3 (Fish) provides a detailed discussion of bioaccumulation of PFAS in fish. Accumulation of PFAS in fish has been documented, particularly for PFOS, longer chain PFCAs (with eight or more fluorinated carbons), and perfluorodecane sulfonate (PFDS) (Houde et al. 2011; Martin et al. 2013; Conder et al. 2008). 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). PFOS BAFs in field-based studies are presented in Table 5-2 (provided as a separate Excel file).

Trophic level biomagnification in food webs (Figure 17-1) can occur for some PFAS (Franklin (Franklin 2016; Fang et al. 2014) as discussed in further detail in Section 5.5.3.

Sections 5.6 and 6.5.1 discuss partitioning of PFAS to plants. Plant uptake and bioaccumulation

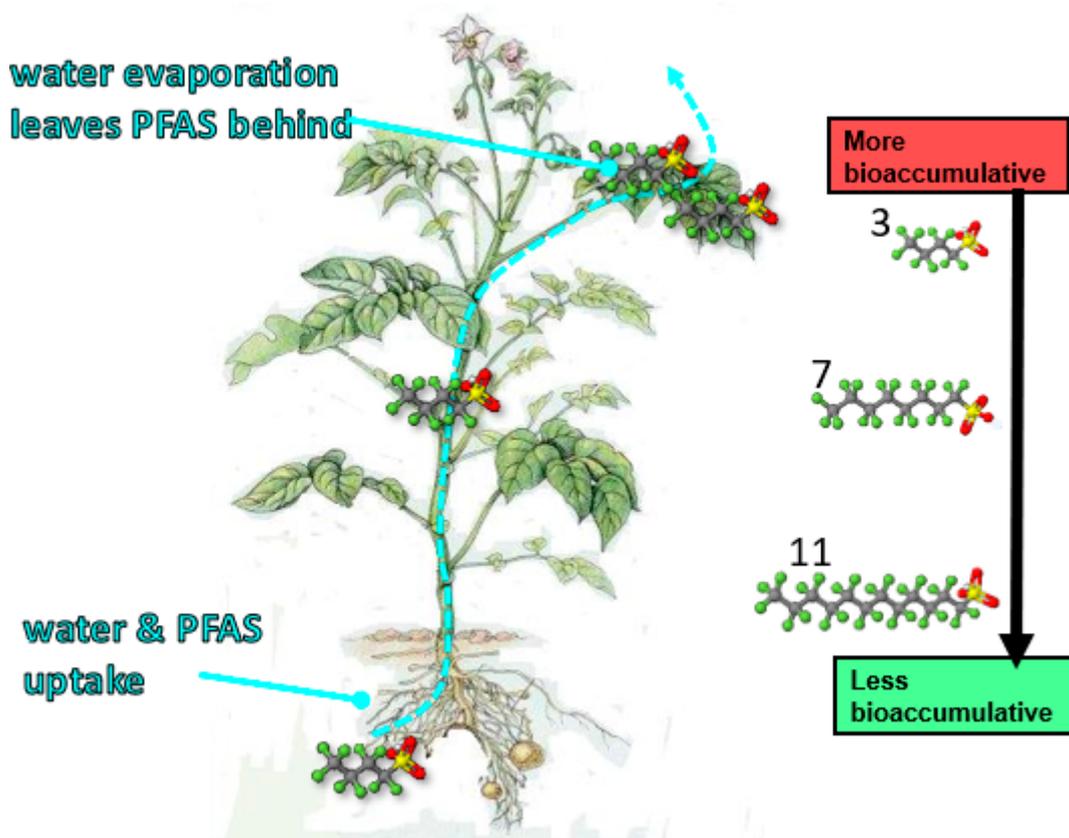


Figure 17-2. Bioaccumulation of PFAS in plants.

Source: J. Conder, Geosyntec. Used with permission.

and partitioning within the plant appear to depend on PFAS chemical structure and the plant species. Figure 17-2 illustrates bioaccumulation of PFAS in plants. 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 (Blaine et al. 2013; Blaine, Rich, Sedlacko, Hundal, et al. 2014; Yoo et al. 2011; Scher et al. 2018; Gobelius, Lewis, and Ahrens 2017). Table 5-2 (provided as a separate Excel file) contains BCFs and BAFs for 14 different PFAS for a variety of plant species. In general, most plant BCFs and BAFs fall between a range of 0.1 and 10.

As indicated in Section 4.2.8 (Octanol/Water Partition Coefficient (K_{ow})) and Section 5.5.2 (Bioaccumulation), it is difficult to measure K_{ow} for PFAS due to their complex chemistry, and because many PFAS have both lipophobic and hydrophobic properties. Therefore, BAFs rely on calculations from empirical data instead of modeling (Haukås et al. 2007).

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Acronyms

AACO	Army Aviation Centre Oakey
AA-QS	annual average quality standards
ADONA	trade name for 4,8-dioxa-3H-perfluorononanoate
AERMOD	American Meteorological Society/EPA Regulatory Model
AFCEC	Air Force Civil Engineering Center
AFFF	aqueous film-forming foam
ALT	alanine aminotransferase
amu	atomic mass unit
ANSES	French National Agency for Food Safety, Environment and Labor
AOF	adsorbable organic fluorine
APFN	ammonium perfluoronanoate
APFO	ammonium perfluorooctanoate
ARAR	applicable or relevant and appropriate requirement
AM	arithmetic mean
ARP	advanced reduction processes
ATSDR	Agency for Toxic Substances and Disease Registry
BAF	bioaccumulation factor
BARC	bottom antireflective coatings
BCF	bioconcentration factor
BERA	baseline ecological risk assessment
BMD	benchmark dose
BMF	biomagnification factor
BMP	best management practices
BSAF	biota-sediment accumulation factor
BuFASA	<i>N</i> -butyl perfluoroalkane sulfonamide
BuFASE	<i>N</i> -butyl perfluoroalkane sulfonamido ethanol
BuFASAA	<i>N</i> -butyl perfluoroalkane sulfonamido acetic acid
BV	bed volume
BW	body weight
C	carbon
C8	historical name for PFOA
C&D	construction and demolition
CAA	Clean Air Act
CAC	colloidal activated carbon
CalEPA	California Environmental Protection Agency
CAP	chemical action plan
CAS	Chemical Abstracts Service
CBPR	community-based participatory research
CCL	Contaminant Candidate List
CCV	continuing calibration verification
CDC	U.S. Centers for Disease Control and Prevention
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act

CFR	Code of Federal Regulations
CHP	catalyzed hydrogen peroxide
CIC	combustion ion chromatography
CL	clearance factor
CMC	critical micelle concentrations
CNT	carbon nanotube
COOH	carboxylic acid functional group
CSF	cancer slope factor
CSM	conceptual site model
CWA	Clean Water Act
Da	dalton (unit of mass)
DDT	dichlorodiphenyltrichloroethane
DNAPL	dense nonaqueous phase liquid
DOC	dissolved organic carbon
DQO	data quality objective
DW	drinking water
DWR	durable water repellent
EAO	emergency administrative order
EBCT	empty bed contact time
ECCC	Environment and Climate Change Canada
ECF	electrochemical fluorination
ECHA	European Chemicals Agency
ECOS	Environmental Council of the States
ECT	Emerging Compound Treatment Technologies, Inc.
EIS	extraction internal standards
EPC	exposure point concentration
ERA	ecological risk assessment
ERB	equipment rinse blank
ESS	Environmental Sequence Stratigraphy
ESTCP	Environmental Security Technology Certification Program
EtFASA	<i>N</i> -ethyl perfluoroalkane sulfonamide
EtFASE	<i>N</i> -ethyl perfluoroalkane sulfonamido ethanol (var: <i>N</i> -ethyl perfluoroalkane sulfonamide ethanol)
EtFASAA	<i>N</i> -ethyl perfluoroalkane sulfonamido acetic acid (var: <i>N</i> -ethyl perfluoroalkane sulfonamide acetic acid)
ETFE	ethylene tetrafluoroethylene
EtFOSA	<i>N</i> -ethyl perfluorooctane sulfonamide
EtFOSE	<i>N</i> -ethyl perfluorooctane sulfonamido ethanol (var: <i>N</i> -ethyl perfluorooctane sulfonamide ethanol)
EU	European Union
F	fluorine
F53B	chlorinated polyfluorinated ether sulfonate (PFOS substitute for plating)
F3	fluorine-free foams
FAA	Federal Aviation Administration
FAQ	frequently asked questions
FASA	perfluoroalkane sulfonamide
FASE	perfluoroalkane sulfonamido ethanol (var: perfluoroalkane sulfonamide ethanol)
FASAA	perfluoroalkane sulfonamido acetic acid (var: perfluoroalkane sulfonamide acetic acid)

FCM	food contact materials
FCS	food contact substances
FD	field duplicate
FDA	U.S. Food and Drug Administration
FECA	fluorinated ether carboxylate
FEP	perfluorinated ethylene-propylene
FFFC	Fire Fighting Foam Coalition
FFFP	film-forming fluoroprotein foam
FHxSA	perfluorohexane sulfonamide
f_{oc}	fraction of organic carbon
FOSA, or PFOSA	perfluorooctane sulfonamide
FOSE	perfluorooctane sulfonamido ethanol (var: perfluorooctane sulfonamide ethanol)
FOSAA	perfluorooctane sulfonamido acetic acid (var: perfluorooctane sulfonamide acetic acid)
FP	fluoroprotein (used in the context of firefighting foam formulations that contain a fluorinated surfactant)
FRB	field reagent blank
FRM	Federal Reference Method
FSANZ	Food Standards Australia and New Zealand
FTA	fire training area
FTCA	fluorotelomer carboxylic acid
FTOH	fluorotelomer alcohol
FTSA or FTS	fluorotelomer sulfonate, fluorotelomer sulfonic acid
FtTAoS	fluorotelomer thioether amido sulfonate
FTUCA	fluorotelomer unsaturated carboxylic acid
FWQC	federal water quality goal
GAC	granular activated carbon
GEF	Global Environment Facility
GenX	trade name for a polymerization processing aid formulation that contains ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoate
GM	geometric mean
HA	health advisory
HDPE	high-density polyethylene
HFPO-DA	hexafluoropropylene oxide dimer acid
HHRA<	human health risk assessment
HI	hazard index
HQ	hazard quotient
IARC	International Agency for Research on Cancer
ICV	initial calibration verification
IDA	isotope dilution analysis
IDW	investigation-derived waste
IRIS	Integrated Risk Information System
ITRC	Interstate Technology and Regulatory Council
IX	ion exchange
K_d	bulk partitioning coefficient
K_{oc}	organic carbon partitioning coefficient
K_{ow}	water/octanol coefficient
LC	liquid chromatography
LCS	lab control sample

LDPE	low-density polyethylene
LEAF	Leaching Environmental Assessment Framework
LHA	lifetime health advisory
LHWA	Little Hocking Water Association
LNAPL	light nonaqueous phase liquid
LOAEL	lowest observed adverse effect level
LOEC	lowest observed effect concentration
LOQ	limit of quantitation
MA DEP	Massachusetts Department of Environmental Protection
MAC-QS	maximum acceptable quality standards
MALDI-TOF	matrix-assisted laser desorption/ionization time-of-flight
MCL	Maximum Contaminant Level
MDH	Minnesota Department of Health
MeFASA	<i>N</i> -methyl perfluoroalkane sulfonamide
MeFASE	<i>N</i> -methyl perfluoroalkane sulfonamido ethanol (var: <i>N</i> -methyl perfluoroalkane sulfonamide ethanol)
MeFASAA	<i>N</i> -methyl perfluoroalkane sulfonamido acetic acid (var: <i>N</i> -methyl perfluoroalkane sulfonamide acetic acid)
MeFOSA	<i>N</i> -methyl perfluorooctane sulfonamide
MEP	Multiple Extraction Procedure
MPCA	Minnesota Pollution Control Agency
MRL	minimum risk level
MRM	multiple reaction monitoring
MSD	matrix spike duplicate
MSW	municipal solid waste
MWCO	molecular weight cut-off
NaPFO	sodium perfluorooctanoate
NAPL	nonaqueous phase liquid
NCOD	National Contaminant Occurrence Database
NESHAP	National Emissions Standards for Hazardous Air Pollutants
nEtFOSA	<i>N</i> -ethyl perfluorooctane sulfonamide
NF	nanofiltration
NFPA	National Fire Protection Association
NGWA	National Groundwater Association
NHANES	National Health and Nutrition Examination Survey
NHDES	New Hampshire Department of Environmental Services
NJ DEP	New Jersey Department of Environmental Protection
NJDWQI	New Jersey Drinking Water Quality Institute
NMeFOSAA	<i>N</i> -Methylperfluorooctane sulfonamidoacetic acid
NOAEL	no observed adverse effect level
NOEC	no observed effect concentration
NOM	natural organic matter
NOx	nitrogen oxides
NPCA	Norwegian Pollution Control Agency
NPDES	National Pollutant Discharge Elimination System
NPL	National Priorities List
NTP	National Toxicology Program
NWQC	national water quality criteria

NYDEC	New York State Department of Environmental Conservation
O&M	operation and maintenance
OAT	organic anion transporter protein
OECD	Organisation for Economic Co-operation and Development
OEHHA	Office of Environmental Health Hazard Assessment (California)
OH	hydroxide ion, or hydroxyl group (Helmenstine 2018)
OSB	oriented strand board
PA DEP	Pennsylvania Department of Environmental Protection
PAC	powdered activated carbon
PAF	perfluoroalkanoyl fluorides
PAH	polycyclic aromatic hydrocarbon
PASF	perfluoroalkane sulfonyl fluoride
PBSF	perfluorobutane sulfonyl fluoride
PBT	persistent, bioaccumulative, and toxic
PCA	principal components analysis
PCBs	polychlorinated biphenyls
PFA	perfluoroalkoxy polymer
PFAA	perfluoroalkyl acid
PFAI	perfluoroalkyl iodides
PFAS	per- and polyfluoroalkyl substances
PFBA	perfluorobutanoate, perfluorobutanoic acid, perfluorobutyrate, perfluorobutyric acid
PFBS	perfluorobutane sulfonate, perfluorobutane sulfonic acid
PFC	perfluorocarbon (C_nF_{2n+1} , for example, perfluorooctane) <i>Do not use this acronym for any other description including perfluorinated compound or perfluorochemical.</i>
PFCA	perfluoroalkyl carboxylate, perfluoroalkyl carboxylic acid
PFDA	perfluorodecanoate, perfluorodecanoic acid
PFOA	perfluorooctane carboxylate
PFDoA, or PFDoDA	perfluorododecanoate, perfluorododecanoic acid
PFDoS, or PFDoDS	perfluorododecane sulfonate, perfluorododecane sulfonic acid
PFDS	perfluorodecane sulfonate, perfluorodecane sulfonic acid
PFECA	perfluoroalkyl ether carboxylic acid
PFEI	perfluoroethyl iodide (aka fluorotelomer iodide)
PFESA	per- or poly- fluoroalkyl ether sulfonic acid
PFHpA	perfluoroheptanoate, perfluoroheptanoic acid
PFHpS	perfluoroheptane sulfonate, perfluoroheptane sulfonic acid
PFHxA	perfluorohexanoate, perfluorohexanoic acid
PFHxS	perfluorohexane sulfonate, perfluorohexane sulfonic acid
PFMOAA	perfluoro-2-methoxyacetic acid
PFNA	perfluorononanoate, perfluorononanoic acid
PFNS	perfluorononane sulfonate, perfluorononane sulfonic acid
PFOA	perfluorooctanoate, perfluorooctanoic acid, perfluorooctane carboxylate
PFOS	perfluorooctane sulfonate, perfluorooctane sulfonic acid
PFOSA, or FOSA	perfluorooctane sulfonamide
PFPA	perfluorophosphonic acid
PFPE	perfluoropolyether
PFPeA	perfluoropentanoate, perfluoropentanoic acid
PFPeS	perfluoropentane sulfonate, perfluoropentane sulfonic acid

PFPIA	perfluorophosphinic acid
PFSA	perfluoroalkyl sulfonate, perfluoroalkane sulfonic acid
PFSiA	perfluoroalkyl sulfinic acid
PFTeDA, or PFTA	perfluorotetradecanoic acid
PFTeDS, or PFTrS	perfluorotetradecane sulfonate, perfluorotetradecane sulfonic acid
PFTrDA, or PFTriA	perfluorotridecanoic acid
PFTrDS, or PFTriS	perfluorotridecane sulfonate, perfluorotridecane sulfonic acid
PFUnA, or PFUnDA	perfluoroundecanoate, perfluoroundecanoic acid
PFUnS, or PFUnDS	perfluoroundecane sulfonate, perfluoroundecane sulfonic acid
pg/m³	picogram per cubic meter
pH	negative log of hydrogen ion concentration (measure of acidity)
PHxSF	perfluorohexane sulfonyl fluoride
PIGE	partice-induced gamma-ray emission spectroscopy
PIH	pregnancy-induced hypertension
PNEC	predicted no-effect concentration
POD	porewater observation device
POE	point of exposure
POET	point of entry treatment
POP	persistent organic pollutant
POPRC-14	14th meeting of the POPs Review Committee
POSF	perfluorooctane sulfonyl fluoride
POU	point of use
PPAR-α	peroxisome proliferator-activated receptor- α
ppb	parts per billion
PPE	personal protective equipment
ppm	parts per million
ppt	parts per trillion
PPRTV	Provisional Peer-Reviewed Toxicity Values
PTFE	polytetrafluoroethylene
PUF	polyurethane foam
PVDF	polyvinylidene fluoride
PWS	public water system
QAPP	quality assurance project plan
QL	quantitation limit
QPD	qualified products database
QPL	Qualified Product Listing
QSAR	quantitative structure-activity relationship
QSM	Quality Systems Manual
qTOF/MS	quadrupole time of flight-mass spectrometry
RCRA	Resource Conservation and Recovery Act
REACH	European Chemicals Regulation
RfD	reference dose
RL	reporting limit
RML	removal management level
RO	reverse osmosis
RSC	relative source contribution
RSL	regional screening level (Note: In many commercial venues RSL means “restricted substances list.”)

RSSCT	rapid small-scale column testing
s.d. or SD	standard deviation
SDS	Safety Data Sheet
SDWA	Safe Drinking Water Act
SERDP	Strategic Environmental Research and Development Program
SIP	sorbent-impregnated polyurethane foam
SL	screening level
SMART	specific, measurable, attainable, relevant, and timely (goal)
SMZ	surface-modified zeolites
SNUR	Significant New Use Rule
SPE	solid-phase extraction
SPLP	Synthetic Precipitation Leaching Procedure
SSD	species sensitivity distribution
STAR	Spill Tactics for Alaska Responders
TANA	Technical Assistance Needs Assessments
TARC	top-layer antireflective coatings
TBC	to-be-considered values
TCEQ	Texas Commission for Environmental Quality
TCLP	Toxicity Characteristic Leaching Procedure
TDS	total dissolved solids
TEQ	toxic equivalency quotient
TFE	tetrafluoroethylene
TMF	trophic magnification factor
TO	Toxic Organic (method)
TOC	total organic carbon
TOP	total oxidizable precursor
TRRP	Texas Risk Reduction Program
TRV	toxicity reference value
TSH	Thyroid-stimulating hormones
TSCA	Toxic Substances and Control Act
UCMR	Unregulated Contaminant Monitoring Rule
UF	ultrafiltration
mg/kg	micrograms per kilogram
UL	Underwriters Laboratories
U.S.C.	United States Code
USDOD	United States Department of Defense
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
VDEC	Vermont Department of Environmental Conservation
VDH	Vermont Department of Health
VOC	volatile organic compound
ww	wet weight
WWTP	wastewater treatment plant
ZVI	zero-valent iron

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Glossary

A

Adsorption

The mechanism whereby ions or compounds within a liquid or gas adhere to a solid surface upon contact. The term also refers to a method of treating wastes in which activated carbon is used to remove organic compounds from wastewater.

Anion

A negatively charged ion.

Arithmetic mean

The sum of a collection of numbers divided by the number of numbers in the collection, commonly referred to as the “average”.

B

Biochar

A carbon-rich, porous solid synthesized by heating biomass, such as wood or manure, in a low-oxygen environment (pyrolysis).

Biomaterials

Materials derived from plants or animals created for use as sorption materials.

C

Cation

A positively charged ion.

Coagulation

The process of destabilizing a colloid or suspension that unbalances the forces that separate the particles, often by neutralizing the charges on the particles and allowing the particles to clump or settle.

E

Electro precipitation/electrocoagulation

The use of an electrical current to enhance the coagulation and precipitation of ionic compounds. The electrical current may attract the compounds to an anode or cathode, or create coagulating ions from a sacrificial anode, or both.

Empty bed contact time (EBCT)

A measure of the time during which water to be treated is in contact with the treatment medium in a contact vessel, assuming that all liquid passes through the vessel at the same velocity. EBCT is equal to the volume of the empty bed divided by the flow rate (Sacramento State University 2019).

F

Flocculation

A process in which the suspended particles of a destabilized colloid or suspension form groups or clumps (known as a “floc”). Coagulation and flocculation work together to separate solids and liquids containing colloids and suspensions.

Fluorotelomer substance

A polyfluoroalkyl substance produced by the telomerization process.

G

Geometric mean

The central tendency or typical value of a set of numbers, derived by multiplying the numbers in a set then finding the n th root of the product, where “ n ” is the number of values in the set.

H

Head

The part of a molecule that is a charged functional group attached at one end of the carbon chain tail.

I

Incineration

Thermal destruction process typically characterized by oxidation at temperatures in excess of 1,000°C.

Isomers

Chemicals with the same chemical formula, but different molecular structures.

M

Membrane fouling

Loss of production capacity of a membrane due to accumulation of compounds or biogrowth on the membrane.

Micelles

Particles in which long hydrocarbon tails, repelled by the water molecules and attracted to each other, make up the interior, whereas the negatively charged heads coat the surface and interact with the surrounding water molecules and positive ions (Ege 1999).

Mineralization/decomposition/destruction

The breakdown of a chemical compound into its constituent elements and carbon dioxide and water.

Moiety

A specific group of atoms within a molecule that is responsible for characteristic chemical reactions of that molecule (Helmenstine 2019).

O

Organoclays

A naturally occurring clay mineral that is organically modified to incorporate cations and enhance the sorption capability.

P

Perfluorinated chemical

Subset of PFAS. Have carbon chain atoms that are totally fluorinated. Examples are perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS) (Buck et al. 2011).

Perfluoroalkyl substance

Fully fluorinated alkane (carbon chain) molecule. They have a chain (tail) of two or more carbon atoms with a charged functional group (head) attached at one end.

Permeate

The water treated by a membrane filtration technology, which has passed through the membrane, and from which PFAS have been removed. The contaminants not passing the membrane accumulate in the filtrate, which also does not pass through the membrane.

Polyfluorinated chemical

Subset of PFAS. Have at least one carbon chain atom that is not totally fluorinated (Buck et al. 2011).

Polyfluoroalkyl substance

The molecule has a nonfluorine atom (typically hydrogen or oxygen) attached to at least one, but not all, carbon atoms, while at least two or more of the remaining carbon atoms in the carbon chain tail are fully fluorinated.

Polymer

Large molecules formed by combining many identical smaller molecules.

R

Reactivation

The process of treating regenerated GAC to restore treatment properties.

Redox

Chemical reduction-oxidation processes and conditions that can result in the alteration of a chemical compound.

Regeneration

The act of restoring some of the sorption capacity of a sorptive media (that is, activated carbon or ion exchange) by removing the adsorbed matter. For carbon, regeneration is a thermal oxidation process.

S

Stabilization

A process to reduce mobility of compounds in the environment through physical or chemical means.

Surfactant

A surface-active agent that lowers the surface tension of a liquid.

T

Tail

The part of a molecule that is a chain of two or more carbon atoms.

Thermal desorption

Thermal treatment process intended to remove the contaminants from a solid medium (such as soil, sediment, carbon) and drive them into the vapor phase.

Z

Zwitterion

An ionic compound containing both positively and negatively charged groups with a net charge of zero.

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LASTFIRE

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