Technical/Regulatory Guidance

Per- and Polyfluoroalkyl Substances Technical and Regulatory Guidance

[DECEMBER 2021]

Prepared by
The Interstate Technology & Regulatory Council
PFAS Team

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Table of Contents

PFAS HOME

This Interstate Technology and Regulatory Council (ITRC) online document includes the resources that the ITRC PFAS Team has developed since it began work in 2017.

- PFAS Fact Sheets
- PFAS Technical and Regulatory Guidance Document
    - External Data Tables
- Training Resources
    - Quick Explainer Videos
    - Longer PFAS Training Module Videos
    - Archived Roundtable Sessions
    - PFAS Training Page

You can reach this PFAS Home page from any of the pages on this web site with the Home button at the top of screen.

PFAS Technical and Regulatory Guidance Document

Updated December 2021

⇐ **ONLINE DOCUMENT**: On this web page, use the Table of Contents shown in the left-hand navigation column to select a specific section of interest

- Full Guidance Document PDF download coming soon!
- Find the References, Glossary and Acronyms with these links or at the footer of the web

External Data Tables

In many of the sections of the PFAS Guidance Document the team has developed tables that provide additional data and information to support the topics in the sections. These tables are linked here, along with identity of the section with which the table is associated.

- Fact Sheets: PFAS Water and Soil Regulatory and Guidance Values Table Excel File
- Fact Sheets: Basis for PFOA and PFOS Regulatory Values in Drinking Water Table Excel File
- Section 2: Figure 2-4 PFAS Family Tree PDF
- Section 2: USEPA Analytes List-PFAS Classifications PDF

- Section 3: AFFF Characteristics Excel File
- Section 3: AFFF Transition to F3 Case Studies Excel File
- Section 4: Physical and Chemical Properties Table 4-1 Excel File
- Section 5: Aquatic Organisms BCF-BAF Table 5-1 Excel file
- Section 5: Plants BCF-BAF Table 5-2 Excel File
- Section 7.2: Ecotoxicology Data Summary Excel File
- Section 8: PFAS Regulatory Programs Summary Excel File (*Coming Soon*)
- Section 11: Analytical Methods Excel File
- Section 11: PFAS Data Usability Table PDF
- Section 12: Table 12-1 Liquids Treatment Methods Table PDF
- Section 12: Table 12-2 Solids Treatment Methods Table PDF
- Section 12: Integrated Water Treatment Flow Chart PDF
- Section 14: Risk Communication Social Factors Vision Board PDF
- Section 15: Water Treatment Case Studies Excel File
- Section 17.2: Table 17-8 Toxicological Effects Excel File

Training Resources

Quick Explainer Videos

The PFAS Team developed brief explainer videos to accompany the fact sheets. The following links will redirect you to ITRC's PFAS Explainer Videos on YouTube:

- ITRC PFAS Team Introduction
- PFAS Naming Conventions
- PFAS History and Use
- PFAS Fate and Transport
- PFAS Remediation
- PFAS Lab Analytical Methods
- Aqueous Film Forming Foam

Longer 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

The PFAS Roundtable Sessions offered a unique opportunity to interact directly with PFAS experts from around the country on a different group of topics for each session. Each Roundtable is archived for On Demand listening and includes a Q&A Digest of all questions asked for the event, including those that were not addressed during the live class.

- Roundtable Session 1 – Naming Conventions, Sampling and Analytical Techniques, and History and Uses of PFAS (July 2020)

    - Roundtable Session 1 Digest
- Roundtable Session 2 – Physical & Chemical Properties, Site Characterization, Fate and Transport (October 2020)
    - Roundtable Session 2 Digest
- Roundtable Session 3 – AFFF and Treatment Technologies (April 6, 2021)
    Roundtable Session 3 Digest

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PFAS Fact Sheets

This page includes links for the ITRC PFAS fact sheets. The fact sheets are available as PDF files. Several tables of supporting information are published separately so that they can be updated periodically by ITRC. The fact sheet user should visit this page to access the current versions of the files.

The references list and an acronyms list are available on the website.

- Naming Conventions (updated August 2020)
- Regulations (updated August 2020)
    - PFAS Water and Soil Values Table Excel file– (updated February 2022)
        - The Water Table includes the available PFAS water values established by the USEPA, each pertinent state, or country (Australia, Canada and Western European countries)
        - The Soil Table includes the available PFAS soil values established by the USEPA, each pertinent state, or country (Australia, Canada and Western European countries)
    - Basis for PFOA and PFOS Values Tables Excel file (updated March 2020)
        - The PFOA Table summarizes the differences in the PFOA values for drinking water in the United States.
        - The PFOS Table summarizes the differences in the PFOS values for drinking water in the United States.
- History and Use (updated August 2020)
- Fate and Transport and Physical and Chemical Properties (updated August 2020)
    - Physical and Chemical Properties Table 4-1 for select PFAS Excel file (updated October 2021)
- Sampling Precautions and Laboratory Analytical Methods (updated August 2020)
- Site Characterization and Media-Specific Occurrence (updated August 2020)
- Treatment Technologies and Methods (updated August 2020)
- Aqueous Film-Forming Foam (updated August 2020)
- Human and Ecological Health Effects and Risk Assessment (published August 2020)
- Risk Communication (published August 2020)
- Stakeholder Perspectives (published August 2020)

PFAS Explainer Videos

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- PFAS Remediation
- PFAS Lab Analytical Methods
- Aqueous Film Forming Foam

Updated December 2021

1 Introduction

A PFAS introduction Video is available.

Per- and polyfluoroalkyl substances (PFAS) constitute a large family of fluorinated chemicals, exceeding several thousand that might be in commercial use or the environment, that vary widely in their chemical and physical properties. 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 environmental media at trace levels across the globe. PFAS have relatively 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 to detect a limited number of PFAS 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.

Broadly speaking, PFAS are characterized as having carbon atoms linked to each other and bonded to fluorine atoms, by which the fluorination imparts properties to the molecule. The carbons may be partially fluorinated (polyfluorinated) or fully fluorinated (perfluorinated). Modifying characteristics, such as addition of a functional group, other substitutions (for example, chlorine), and partial fluorination, are described in Section 2.2 along with evolving definitions of PFAS.

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?	• Naming Conventions and Use • Chemistry, Terminology, and Acronyms • PFAS Uses • PFAS Releases to the Environment • Firefighting foams (AFFF)
How do they behave in the environment?	• Physical and Chemical Properties • Environmental Fate and Transport Processes • Media-Specific Occurrence
Why are we concerned about PFAS?	• Human and Ecological Health Effects • Basis of Regulations • Site Risk Assessment • Surface Water Quality
How do we evaluate PFAS in the environment?	• Site Characterization • Sampling and Analytical Methods • Case Studies
How do we remediate PFAS?	• Treatment Technologies
What are the major concerns of communities and Tribes and how do we share what we know about PFAS?	• Stakeholder Perspectives • Risk Communication

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.

Updated May 2021

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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 a **Naming Conventions and Physical and Chemical Properties** training video and a **Production, Uses, Sources and Site Characterization** training video with content related to this section.

This section provides a basis for the discussion of PFAS in the environment by presenting foundational information about its discovery, commercial use, health and environmental awareness, chemistry, and terminology.

In 1938, Roy J. Plunkett at the DuPont Company's Jackson Laboratory discovered polytetrafluoroethylene (PTFE) while conducting commercial experiments with chlorofluorocarbon refrigerants (Science History Institute 2017).

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/or friction reduction to a range of products. These products have applications 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 1999; Buck et al. 2011; KEMI 2015; USEPA 2017).

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 chemical substances (USEPA 2018). A recent inventory of PFAS identified more than 4,700 PFAS with Chemical Abstracts Service (CAS) Registry Numbers 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 2015). An industry survey, reported in Buck et al. (2021), noted that only 256 of the 4,700 PFAS with CAS Registry Numbers are commercially relevant, with others of lesser environmental significance but potentially still occurring in the environment. Publicly available health and toxicity studies are limited to only a small fraction of PFAS, and modern commercially available analytical technologies typically identify and quantify only about 50–60 PFAS, but these lists are increasing.

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 certain long-chain perfluoroalkyl carboxylates, long-chain perfluoroalkane sulfonates and their precursors, including two widely produced, commonly encountered, and most studied compounds: perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) (USEPA 2016; WA DER 2017).

PFAS have followed a similar pattern of emergence and awareness exhibited by many other anthropogenic environmental contaminants. Figure 2-1 provides a general timeline of PFAS emergence and awareness that includes categories of 1) synthesis/development, 2) commercial production, 3) health concerns, 4) environmental detection, and 5) reduction/alternatives.

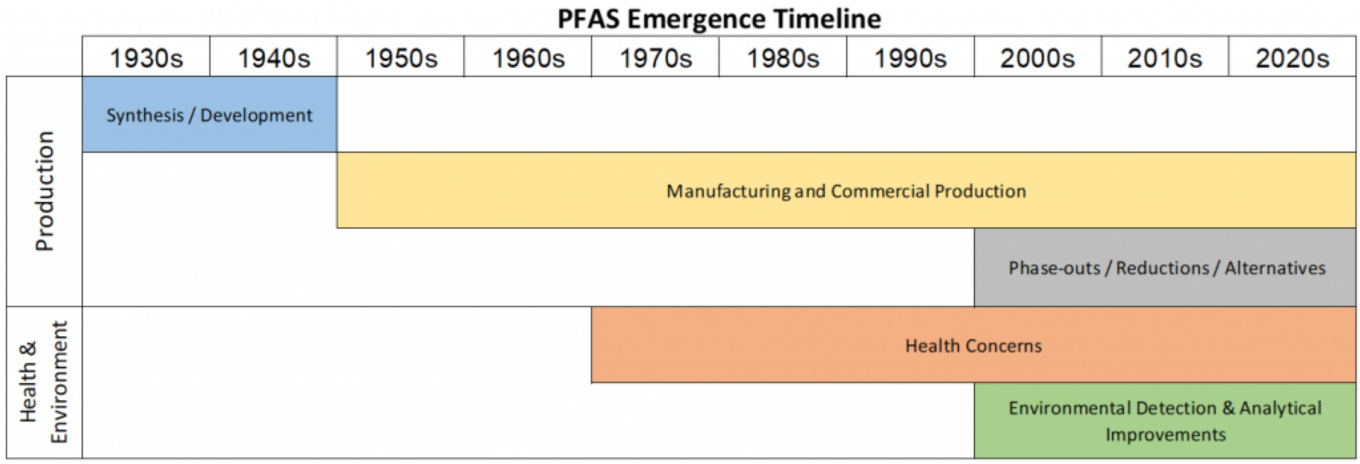

Figure 2-1. General timeline of PFAS emergence and awareness.

Graphic provides general indication of PFAS emergence and awareness by decade. Specific activities and events are described in more detail within this chapter. "Reductions/alternatives" include other PFAS that have replaced legacy chemistry.

Source: J. Hale, Woodard & Curran. Used with permission

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

Updated August 2021.

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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. However, potentially significant environmental releases of other PFAS historically or currently used in the manufacturing process (for example, PFAAs, GenX, ADONA) have occurred, but can be limited or eliminated with effective engineering controls. Such considerations may help to focus investigation resources on major sources.

Figure 2-2 illustrates a conceptual PFAS lifecyle 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 are 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 have been impacted by PFAS. The relative significance of these exposures will also vary widely.

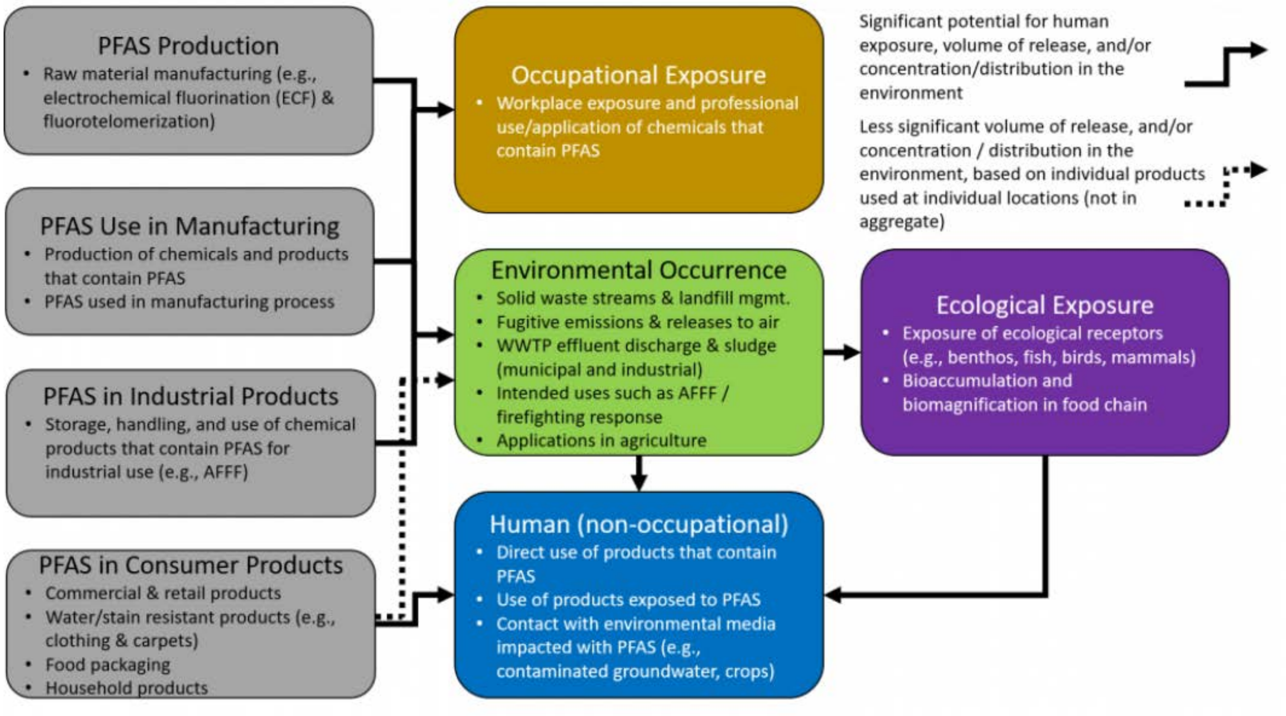

Figure 2-2. Generalized PFAS uses and relative exposure and environmental impact potential from PFAS life cycle.

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 source or 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 some applications 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, nonpolymer PFAS used in Class B firefighting foam may impact a moderate area near the source, exhibiting higher groundwater concentrations, in contrast to air emissions of nonpolymer PFAS from fluoropolymer manufacturing, which are more widely dispersed but at lower concentrations.

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 1999). Many fluoropolymers may be resistant to degradation. For example, in one study, PTFE did not significantly degrade under certain incineration conditions (Aleksandrov et al. 2019). However, research suggests side-chain fluorinated polymers are likely to break down to nonpolymer PFAS over time (Li et al. 2018). For example, commercial fluorotelomer-based polymers (a kind of side-chain fluorinated polymer) have been documented to biodegrade under environmental conditions (Washington et al. 2015) and to abiotically degrade by hydrolysis under environmental and consumer-use conditions (Washington and Jenkins 2015).

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.

There is no universally accepted definition of PFAS. However, in general, PFAS are characterized as having carbon atoms linked to each other and bonded to fluorine atoms at most or all of the available carbon bonding sites. An early and widely recognized technical definition of PFAS is provided by Buck et al. (2011), who defined PFAS 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_nF2_{n+1} –."

The definition of PFAS continues to evolve to reflect continued study of these compounds and takes different forms depending on the operational criteria used and the intended scope and application of the included list of chemicals. For example, the definition of PFAS used in one study (OECD 2018) expanded the Buck et al. (2011) definition to include chemicals that contain the – C_nF_{2n} – moiety in addition to the C_nF_{2n+1} – moiety, which encompasses chemicals with both ends of the carbon-fluorine chain connected to a hydrogen or a functional group, as well as cyclic analogs of linear PFAS. In another example, the state of Maine defines PFAS as substances that include any member of the class of fluorinated organic chemicals containing at least one fully fluorinated carbon atom (Maine State Legislature 2021). An emerging subject of discussion is whether the presence of an aromatic component in a chemical's structure still constitutes classification as PFAS. Support for such classification inclusion includes cases where a perfluorinated compound could result from reaction or biotransformation.

The USEPA's CompTox Chemicals Dashboard provides a large publicly available resource for PFAS structures and predicted properties (Williams et al. 2017). This effort has taken two approaches to defining PFAS. The first, denoted PFASMASTER (USEPA 2020), was based on a simple join, or combination, of publicly available lists of PFAS chemicals reported by other entities, such as the OECD (2018) report. The second approach applied a small set of structure filters to the entire EPA DSSTox database (currently exceeding 900,000 substances), resulting in a list containing more than 8,000 PFAS structures, denoted PFASSTRUCTV3 (USEPA 2020); please check USEPA's CompTox Chemicals Dashboard for the most current version. The PFASMASTER file currently exceeds 9,200 substances and includes both PFAS structures (from PFASSTRUCV3) and structures and non-structurable chemicals (such as mixtures and polymers) from combining several public PFAS lists. Hence, the structure-based filters used in this effort expand the PFAS definition beyond the Buck et al. (2011) and OECD (2018) definitions and are designed to fully encompass publicly available PFAS lists, as well as to be inclusive of small, fluorinated chemicals of potential concern to USEPA.

Whereas PFAS definitions such as provided by USEPA's CompTox Dashboard are designed to be broadly inclusive, regulatory applications often must be more circumscribed and precisely worded.

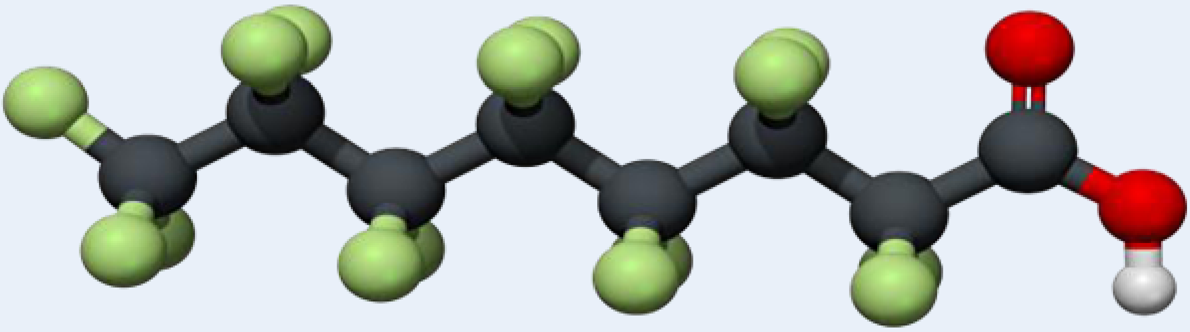
Glüge et al. (2020) acknowledged the Buck et al. (2011) and OECD (2018) definitions while also considering the definition of PFAS to include:

- substances in which a perfluorocarbon chain is connected with functional groups on both ends
- aromatic substances that have perfluoroalkyl moieties on the side chains
- fluorinated cycloaliphatic substances.

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 2-15 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 C_8 homologue group, while all of the linear and branched isomers of perfluorohexane sulfonic acid (PFHxS) would be in the C_6homologue group. The C_4-C_{12} PFSAs are a homologous series of perfluoroalkane sulfonates.

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 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

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.” “PFC” is widely used in the climate community, referring to perfluorocarbons, which are a subset of PFAS. PFC does not agents, or chlorofluorocarbons [refrigerants]). This definition distinguishes PFAS from the more generic term "PFC," which can include aromatic compounds.

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 exist 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 (Section 5) and potential human health and ecological effects (Section 7). The ionic state of individual PFAS can result in significantly different physical and chemical properties (Section 4), 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 are comprised of a wide variety of molecules with different physical and chemical properties and molecular weights with perfluoroalkyl moieties as common structural features, as note by Cousins et al. (2020), who identified specifically:

"…the PFAS class comprises distinct substances with very different structures and properties: high-molecular-weight polymers and high-molecular-weight non-polymers; neutral, anionic, cationic and zwitterionic substances; solids, liquids, and gases; highly reactive and non-reactive (inert) substances; soluble and insoluble substances; and volatile and involatile substances. In the environment, some PFAS are mobile and others immobile, and some bioaccumulate while others do not."

This variety of PFAS with diverse properties is organized in the form of a PFAS family tree (Figure 2-3) that includes 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.

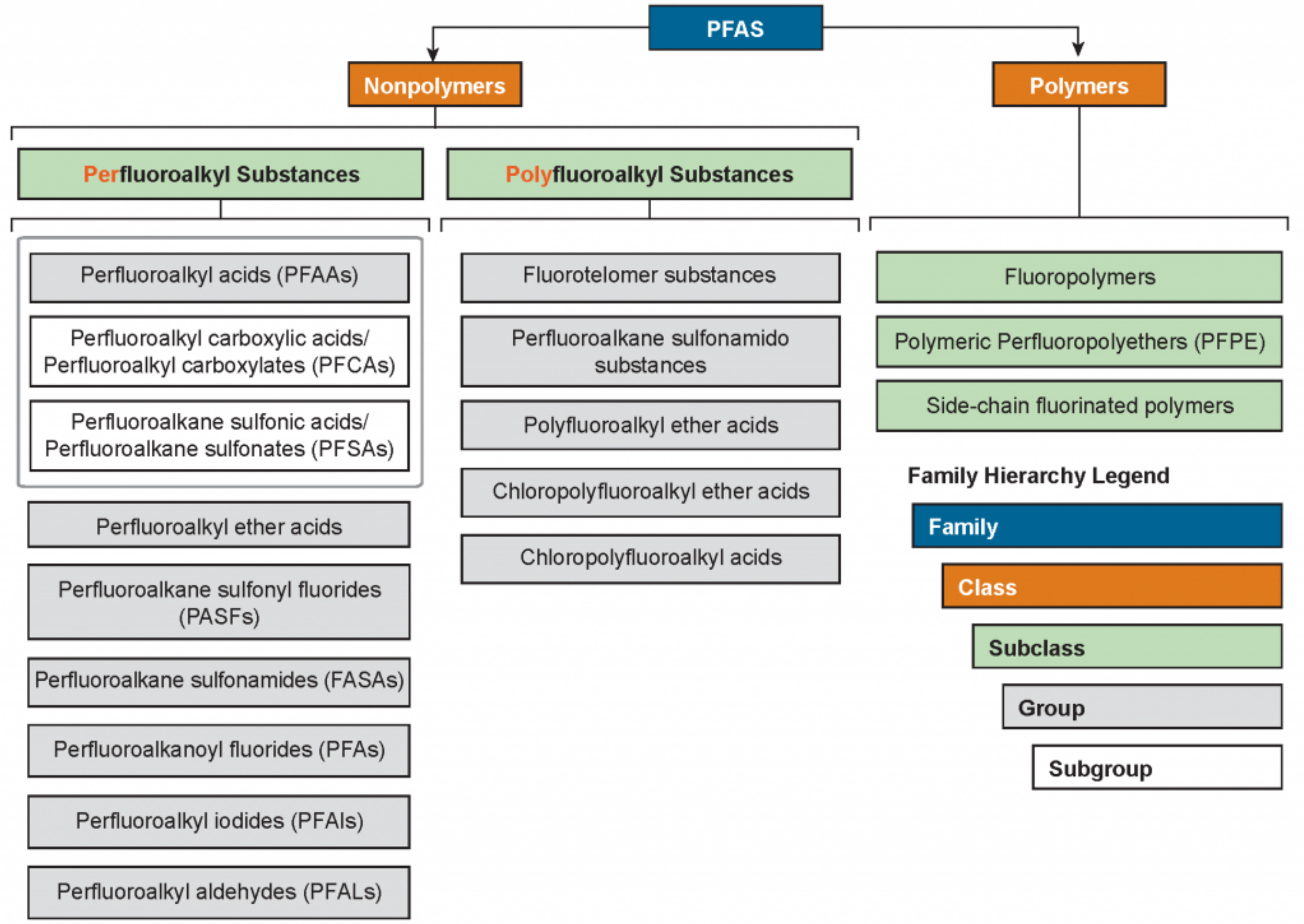
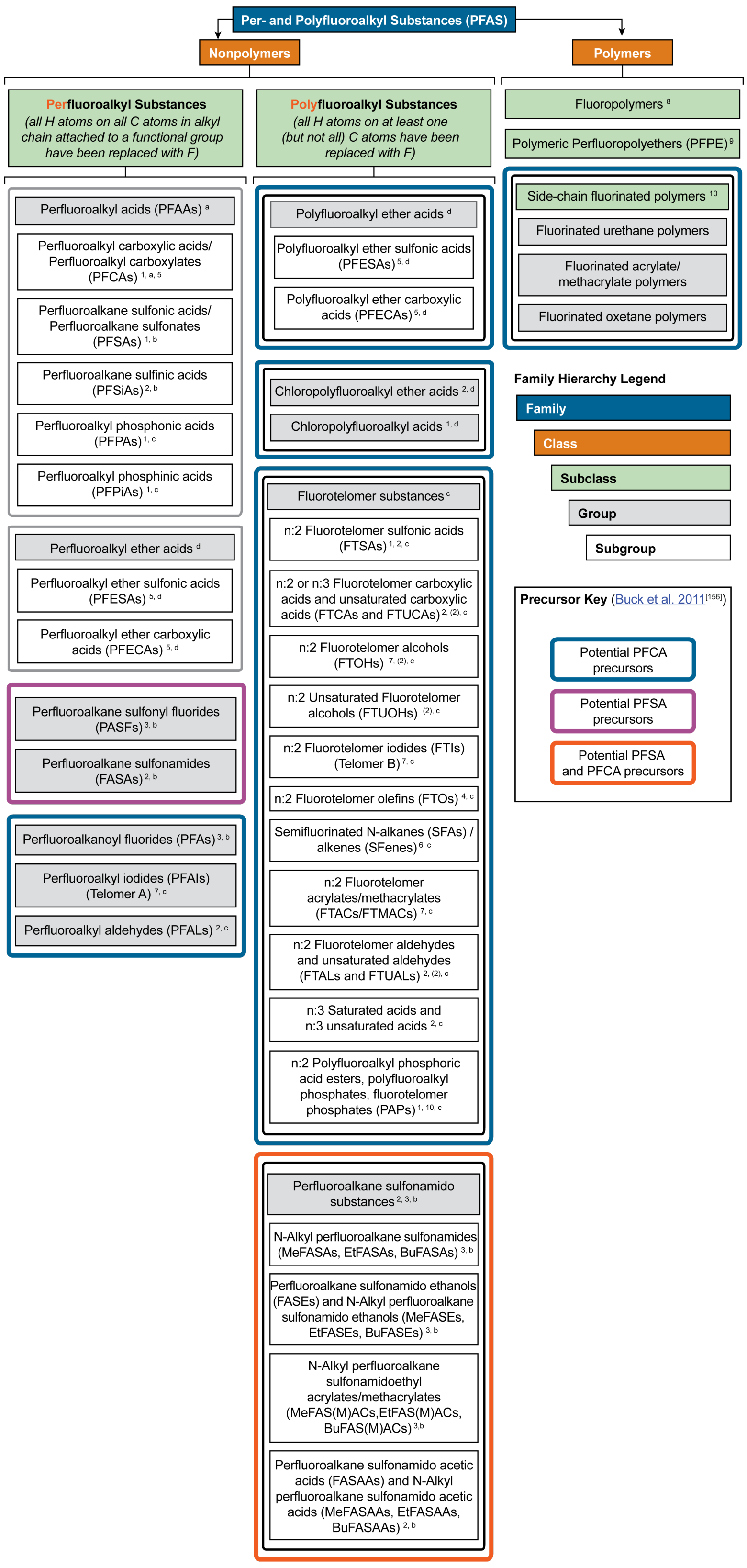


Figure 2-3. The PFAS family.

The family tree is further expanded in Figure 2-4, based on nomenclature provided in Buck et al. (2011), Organization for Economic Co-operation and Development OECD (2015), and Wang 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 associated CAS numbers but are being identified by molecular structure. Naming conventions and categories of PFAS are developed as a means to communicate, manage, and address this class of many chemicals, which can include alternate naming conventions and a variety of rationales for assigning categories.



Manufacturing Process Legend

(a) Manufactured by either ECF or fluorotelomerization
(b) Manufactured by ECF
(c) Manufactured by fluorotelomerization
(d) Other process

Notes

The acronym PFECA is utilized for both per and polyfluoroalkyl ether carboxylic acids and the acronym PFESA is utilized for both per and polyfluoroalkyl ether sulfonic acids. When using these acronyms, it is important to be clear as to the specific group of chemicals being referenced (i.e., per or poly).

The family tree is based on the PFAS definition provided in Buck et al. 2011.[156]

PFAS Use Legend

(1) Surfactants
(2) Intermediate transformation product
(3) Major raw material for ECF-based surfactants and surface protection products
(4) Raw material for surfactants and surface protection products
(5) Includes some fluoropolymer polymerization aids
(6) Ski wax, medical applications
(7) Major raw material for fluorotelomer-based surfactants and surface protection products
(8) High molecular weight polymeric plastics such as PTFE
(9) A broad class of polymers used largely as lubricants
(10) Used for surface protection

Figure 2-4. PFAS family tree.

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

A stand-alone PDF version of Figure 2-4 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.

The PFAS polymer class includes fluoropolymers, polymeric perfluoropolyethers, and side-chain fluorinated polymers (Henry et al. 2018; Buck et al. 2011; Wang 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 perfluoroocanoate (APFO) or sodium perfluorooctanoate (NaPFO), which are salts of perfluorooctanoate (PFOA). Fluoropolymers also include polyvinylidene fluoride (PVDF), which was historically made using ammonium perfluorononanoate (APFN), the ammonium salt of perfluorononanoate (PFNA) (OECD 2015; Buck et al. 2011).
- The specific fluoropolymers PTFE, FEP, ETFE, and PFA have been referred to as "polymers of low concern" in one study because they have high molecular weight and are extremely stable and PTFE has been demonstrated not to be bioavailable (Henry et al. 2018). Polymers of low concern are reported to pose little environmental or health risk once in a consumer product, and based on this, Henry et al. (2018) suggested that "polymers of low concern" should be considered separately from other PFAS when evaluating risk. However, during the manufacture of some fluoropolymers, nonpolymer PFAS are used as processing aids and may be found as impurities in some fluoropolymer products (3M Company 1999; CalEPA 2018; see Section 5.4.5). For this reason, in order to prevent potential releases of nonpolymer PFAS processing aids and short-chain polymeric byproducts/impurities, such as unreacted monomers, environmental controls are necessary during the manufacturing and further processing of fluoropolymers. However, it should be noted that another study (Lohmann et al. 2020) found that there was insufficient evidence to consider fluoropolymers as being of low concern for environmental and human health and that group of fluoropolymers should not be given a blanket exemption from regulatory review. According to Lohmann et al. (2020), the assessment and management of fluoropolymer products should consider the complete life cycle, including associated emissions during production and disposal.
- 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.

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 2-5 provides general classification and chemical structures, examples of each group and/or subgroup, and examples of the primary uses of the nonpolymer PFAS highlighted in Figure 2-3 and Figure 2-4.

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 and Fluoropolymer processing aid
Perfluorooctanoate (PFOA)	$C_7F_{15}CO_2^-$	Surfactant and Fluoropolymer processing aid

Perfluoroalkane sulfonic acids/ 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 acids

Perfluoroalkyl ether carboxylic acids (PFECAs)

Example	Chemical Structure	Uses
Hexafluoropropylene oxide dimer acid (HFPO-DA)	$CF_3CF_2CF_2OCF(CF_3)COOH$	Surfactant and Fluoropolymer processing aid

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

Family Hierarchy Legend

- Family
  - Class
    - Subclass
      - Group
        - Subgroup

Notes

The acronym PFECA is utilized for both per and polyfluoroalkyl ether carboxylic acids. When using this acronym, it is important to be clear as to the specific group of chemicals being referenced (i.e., per or poly).

Polyfluoroalkyl Substances

Polyfluoroalkyl ether acids

Polyfluoroalkyl ether carboxylic acids (PFECAs)

Example	Chemical Structure	Uses
4,8-dioxa-3H-perfluorononanoic acid (ADONA)	$CF_3OCF_2CF_2CF_2OCHFCF_2COOH$	Fluoropolymer processing aid

Fluorotelomer 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 FTCA)	$C_8F_{17}CH_2COOH$	Intermediate transformation product

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 intermediate transformation product

Perfluoroalkane sulfonamido substances

N-Alkyl perfluoroalkane sulfonamides (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 (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 (MeFASAAs, EtFASAAs, BuFASAAs)

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

Figure 2-5. Examples of some 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 Voogt, 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 2-6 for PFOS and PFOA, can be written as:

$$\mathbf{C_nF_{2n+1}\text{-}R}$$

where "C_nF_{2n+1}" defines the length of the perfluoroalkyl chain tail, "n" is $\geq$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.

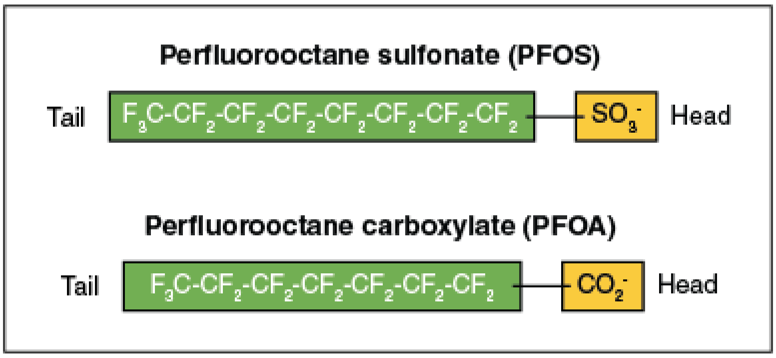


Figure 2-6. The tail and head structure of PFOS and PFOA molecules.

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 are not known to biodegrade to shorter chain PFAAs.

The PFAA group is divided into two major subgroups (as shown in Table 2-1 and Figure 2-4).

- ***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 fluorotelomer alcohols (FTOHs). An example PFCA is PFOA.
- ***Perfluoroalkane sulfonic acids*** (PFSAs), or perfluoroalkane sulfonates, also are used commercially and can be formed as terminal degradation products of select precursor polyfluoroalkyl substances, such as perfluoroalkane sulfonamido ethanols (FASEs). An example PFSA is PFOS.

Other subgroups of PFAAs are introduced below. 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. Other PFAAs include:

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

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

X	Y	Acronym	Name	Formula	CAS No.
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
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	$C_{13}F_{27}SO_3H$	791563-89-8
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	$C_{14}F_{29}SO_3^-$	343629-46-9
			Perfluorotetradecane sulfonic acid	$C_{14}F_{29}SO_3H$	1379460-39-5

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).

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 2-7 illustrates the dissociation of PFBA.

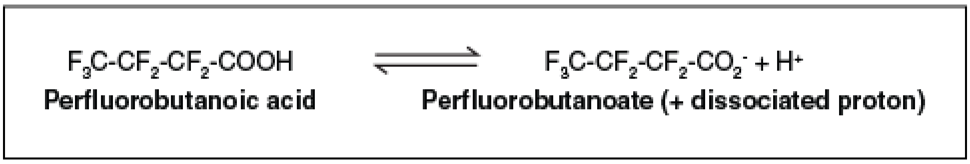


Figure 2-7. Dissociation of PFBA.

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 PFSAs 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 (USEPA 2009).*

2.2.3.2 Perfluoroalkane Sulfonamides (FASAs)

FASAs, such as perfluorooctane sulfonamide (FOSA), are products and/or intermediates from the ECF process for surfactants and surface protection products. FASAs can degrade to form PFAAs such as PFOS.

2.2.3.3 Other Perfluoroalkyl Substances

Other perfluoroalkyl substances shown on Figures 2-3 and 2-4 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 acids, including 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

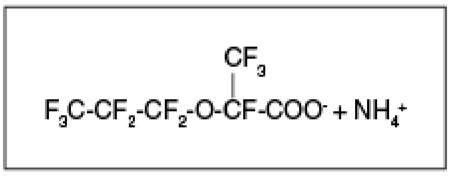
A PFECA, commonly referred to by the trade name “GenX,” has been used by one manufacturer as a replacement for APFO (PFOA) as a surfactant and polymerization aid in the production of their PTFE product. GenX actually refers to the GenX processing aid technology, while the major chemicals used include:

• 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 [$CF_3CF_2CF_2OCF(CF_3)COO^-NH_4^+$, CAS No. 62037-80-3, also known as FRD -902])

(Wang et al. 2013) (Buck 2015) (USEPA 2018).

Prior to their use in PTFE production, GenX chemicals were produced as a byproduct of other manufacturing processes (NC DEQ 2018). From the draft GenX Toxicity Assessment document ATSDR (2018), HFPO also is used to manufacture other HFPO-DA derivatives, fluoropolymers and perfluoropolyethers, and other specialty agrochemical, semiconductor, and pharmaceutical applications. 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 2-8.



$$F_3C\text{-}CF_2\text{-}CF_2\text{-}O\text{-}\overset{\overset{CF_3}{|}}{C}F\text{-}COO^- + NH_4^+$$

Figure 2-8. Example replacement chemistry structure for GenX Ammonium Salt.

In addition to linear and branched structures, certain cyclic structures have much in common with the noncyclic PFAS and are consistent with the definitions/descriptions provided above. As an example, Figure 2-9 illustrates the structure of perfluoro-4-ethylcyclohexanesulfonate (PFECHS), which some classify as a PFAS. It is used in airplane hydraulic fluids and has been found both in the environment (Kaboré et al. 2018; Howard and Muir 2010; De Silva et al. 2011; Lescord et al. 2015; Houde et al. 2016) and in human blood (Miaz et al. 2020). The characteristics of PFECHS include:

- fully fluorinated six-carbon ring
- nonaromatic
- sulfonate active group
- perfluorinated two-carbon tail

PFECHS fits the Buck et al. (2011) description by having a fully fluorinated aliphatic tail of one or more carbon atoms attached to a charged functional group head.

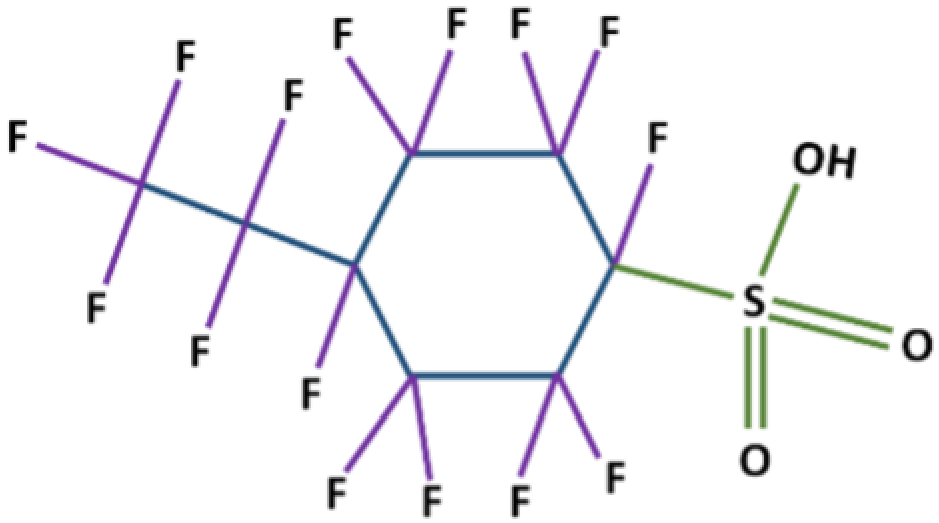


Figure 2-9. Illustration of perfluoro-4-ethylcyclohexanesulfonate (PFECHS) structure.

Source: Michigan PFAS Action Response Team's Human Health Workgroup PFECHS Whitepaper (May 15, 2020)(MPART 2020)

2.2.4 Polyfluoroalkyl Substances

Polyfluoroalkyl substances including 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. 2020). Figure 2-3 and Figure 2-4 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). Of the approximately 4,700 PFAS identified in the OECD (2018) study, about 90% were potential precursors to PFAAs.

Polyfluoroalkyl substances are distinguished from perfluoroalkyl substances by not being fully fluorinated. Instead, they are aliphatic substances for which all hydrogen atoms attached to at least one (but not all) carbon atoms have been replaced by fluorine atoms, in such a manner that they contain the perfluoroalkyl moiety C_nF_{2n+1} (Buck et al. 2011), see Figure 2-5.

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 C_nF_{2n+1} moiety are potential precursor compounds that have the potential to be transformed into PFAAs.

Figure 2-10 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.

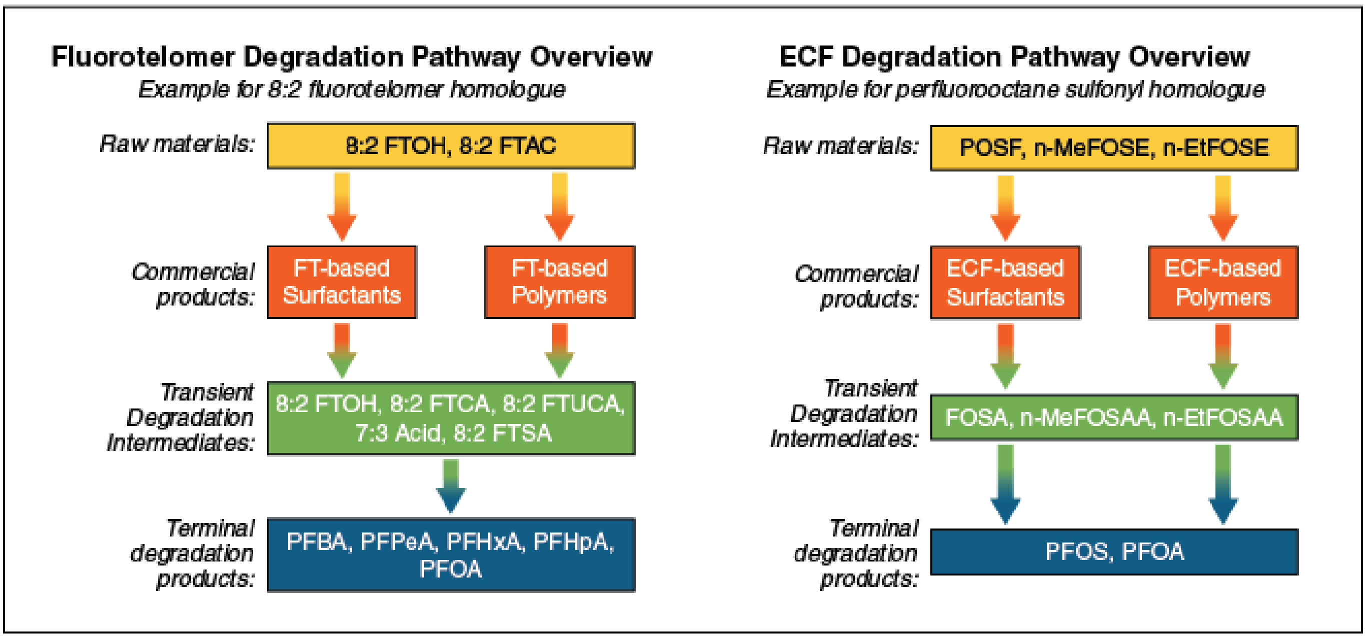
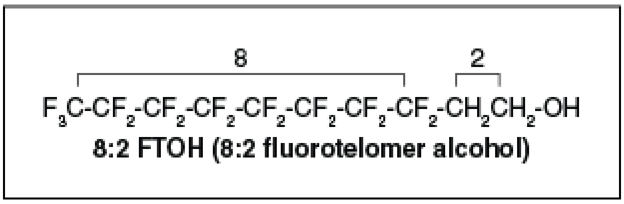


Figure 2-10. Example polyfluoroalkyl substance degradation pathways.
(Note that degradation of POSF-based products is for the terrestrial environment, but transformation into lower homologues of PFCAs and PFSAs in the atmosphere is also possible.)

2.2.4.1 Fluorotelomer Substances

Fluorotelomer substances are polyfluoroalkyl substances produced by the fluorotelomerization process. As shown in Figure 2-10, the degradation of fluorotelomer-based substances is a potential source of PFCAs in the environment, but not PFSAs (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 2-11, which also illustrates the “n:x” naming convention.



$$\overbrace{F_3C\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2}^{8}\text{-}\overbrace{CH_2CH_2}^{2}\text{-}OH$$

8:2 FTOH (8:2 fluorotelomer alcohol)

Figure 2-11. Example of a polyfluoroalkyl substance.

Some of the fluorotelomer substances most commonly detected in the environment to date are as follows (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* (FTS): The n:2 fluorotelomer sulfonic acids (n:2 FTSs) 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. FTSs 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 2-10; (Buck et al. 2011; Mejia-Avendaño et al. 2016) 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.

Other fluorotelomer (FT) substances are shown in Figure 2-5.

2.2.4.2 Perfluoroalkane Sulfonamido Substances

The subgroups of perfluoroalkane sulfonamido substances shown in Figure 2-4 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 CH_2 groups in the head of the molecule attached to the sulfonamido spacer (Figure 2-12). 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 2-10, 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 raw materials used for surfactant and surface treatment products that include N-methyl perfluorooctane sulfonamide (NMeFOSA) and N-ethyl perfluorooctane sulfonamide (NEtFOSA) (Buck et al. 2011)
- *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 2-12 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 2-10) (Buck et al. 2011)
- *N-alkyl perfluoroalkane sulfonamidoethyl acrylates/methacrylates* (MeFAS(M)ACs,EtFAS(M)ACs,BuFAS(M)ACs)

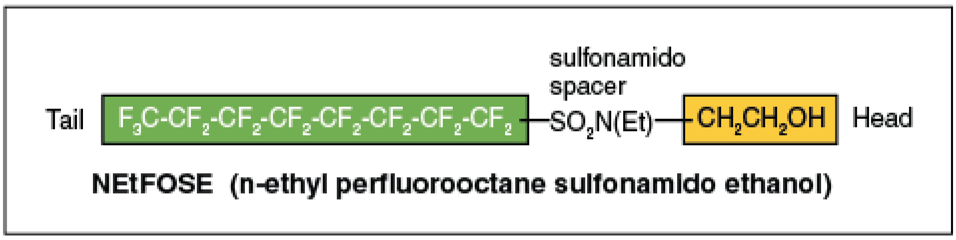


Figure 2-12. Example of a perfluoroalkane sulfonamido ethanol (FASE).

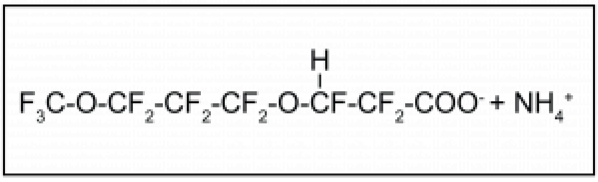
2.2.4.3 Other Polyfluoroalkyl Substances

Other polyfluoroalkyl substances shown in Figure 2-4 include:

- polyfluoroalkyl ether acids, including polyfluoroalkyl ether sulfonic acids (PFESAs) and polyfluoroalkyl ether carboxylic acids (PFECAs)
- chloropolyfluoroalkyl ether acids
- chloropolyfluoroalkyl acids

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.

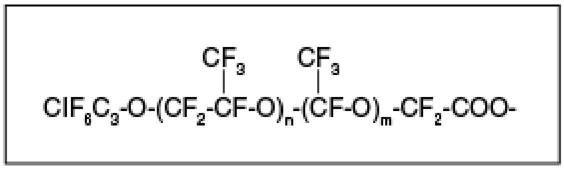
One replacement compound for the use of PFOA as a polymerization aid in the production of PTFE is a polyfluoroalkyl ether carboxylic acid: ammonium 4,8-dioxa-3H-perfluorononanoate ($CF_3OCF_2CF_2CF_2\text{-}OCHFCF_2COO^-NH_4^+$ (CAS No. 958445-44-8), commonly referred to by the trade name ADONA (Gordon 2011). The chemical structure is shown in Figure 2-13.



$F_3C\text{-}O\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}O\text{-}\overset{H}{C}F\text{-}CF_2\text{-}COO^- + NH_4^+$

Figure 2-13. Chemical structure for ADONA.

Other replacement polymerization compounds for the manufacture of PTFE and polyvinylidene fluoride (PVDF) include polyfluoroalkyl ether acids, also referred to as cyclic or polymeric functionalized perfluoropolyethers (PFPEs) (Wang et al. 2013). A sample chemical structure of a chloropolyfluoroalkyl ether acid is shown in Figure 2-14.



$$ClF_6C_3\text{-}O\text{-}(CF_2\text{-}\underset{}{\overset{\overset{\displaystyle CF_3}{|}}{C}}F\text{-}O)_n\text{-}(\overset{\overset{\displaystyle CF_3}{|}}{C}F\text{-}O)_m\text{-}CF_2\text{-}COO\text{-}$$

Figure 2-14. Sample chemical structure for a chloropolyfluoroalkyl ether acid.

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 2-4).

2.2.5.1 Processes

Two major processes, *electrochemical fluorination (ECF)* and *fluorotelomerization*, have been (and are) used to manufacture PFAS that contain perfluoroalkyl chains: side-chain fluorinated polymers, PFAAs and polyfluoroalkyl surfactants (USEPA 2003; Benskin, DeSilva, and Martin 2010; KEMI 2015; OECD 2018). The fluorotelomerization process may also be characterized as "oligomerization," as it involves, for example, 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 2-4. PFSAs are produced only using the ECF process, whereas PFCAs can be produced by both ECF and fluorotelomerization (USEPA 2003; 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 1999) 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 1999; USEPA 2003; 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 2003; Buck et al. 2011). The variable composition is caused by the process conditions, raw materials, and equipment used by the ECF process (3M Company 1999; CONCAWE 2016). Subsequent processes (for example, hydrolysis, base neutralization) are then used to refine the compounds (USEPA 2003).

Historically, the ECF process was primarily used to produce POSF which was then used to make PFOS-based materials. PFOS is often a terminal degradation product of POSF-based compounds. ECF was also used to produce perfluorooctane carbonyl fluoride which was then used to produce PFOA and other 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 PFAS-based products, such as those based on PBSF (3M Company 2018).

Fluorotelomerization

A typical fluorotelomerization process involves the reaction of perfluoroethyl iodide (PFEI, CF_3CF_2-I) with tetrafluoroethylene (TFE, CF_2=CF_2) to yield a mixture of even-numbered carbon linear perfluoroalkyl iodides (C_nF_{2n+1}-I, n= 4, 6, 8, 10, etc.), commonly known as "Telomer A." Telomer A is then reacted with ethylene to make "Telomer B" (fluorotelomer iodide, $C_nF_{2n+1}CH_2CH_2$-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).

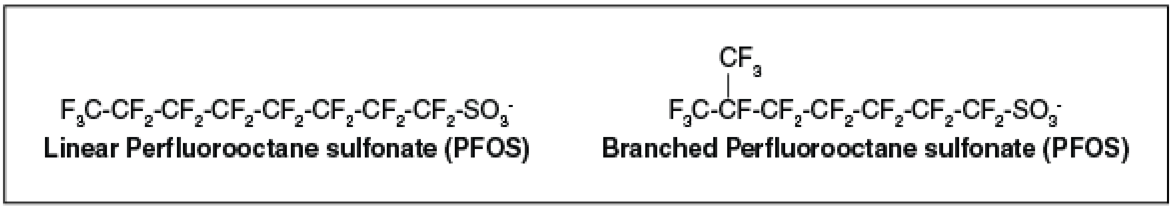
As part of the USEPA 2010/2015 Stewardship Program (USEPA 2018; Section 2.4.3), eight major global fluoropolymer and fluorotelomer manufacturers phased out production of long-chain fluorotelomer-based products that were potential precursors to PFOA and other long-chain perfluoroalkyl carboxylic acids (PFCAs). Today, the major global fluorotelomer manufacturers are reported to have refined their processes and predominantly manufacture short-chain (C6) fluorotelomer-based products (American Chemistry Council 2021). 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 2-15) 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.



$F_3C\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}SO_3^-$

$F_3C\text{-}\overset{\overset{CF_3}{|}}{C}F\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}SO_3^-$

Figure 2-15. 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 10.5 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	FTS[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 sulfonic acid: for example, may be found at AFFF sites

[2] Fluorotelomer carboxylic acids: for example, 5:3 FTCA may be found in landfill leachate

[3] Under certain instances, can produce mixture of linear and branched PFCAs

Updated August 2021.

⇑

2.3 Emerging Health and Environmental Concerns

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

- discovery and/or synthesis of PFAS (Section 2.2.5), followed by growth in commercial production and use (Section 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)
  - growing awareness and concern (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 et al. 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; Kärrman 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 2018). 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 2016; USEPA 2016; ASTDR 2018). 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 2016; USEPA 2018).

ATSDR is undertaking a national, multi-site PFAS health study to evaluate how PFAS-impacted drinking water may harm health (ATSDR 2020). 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.

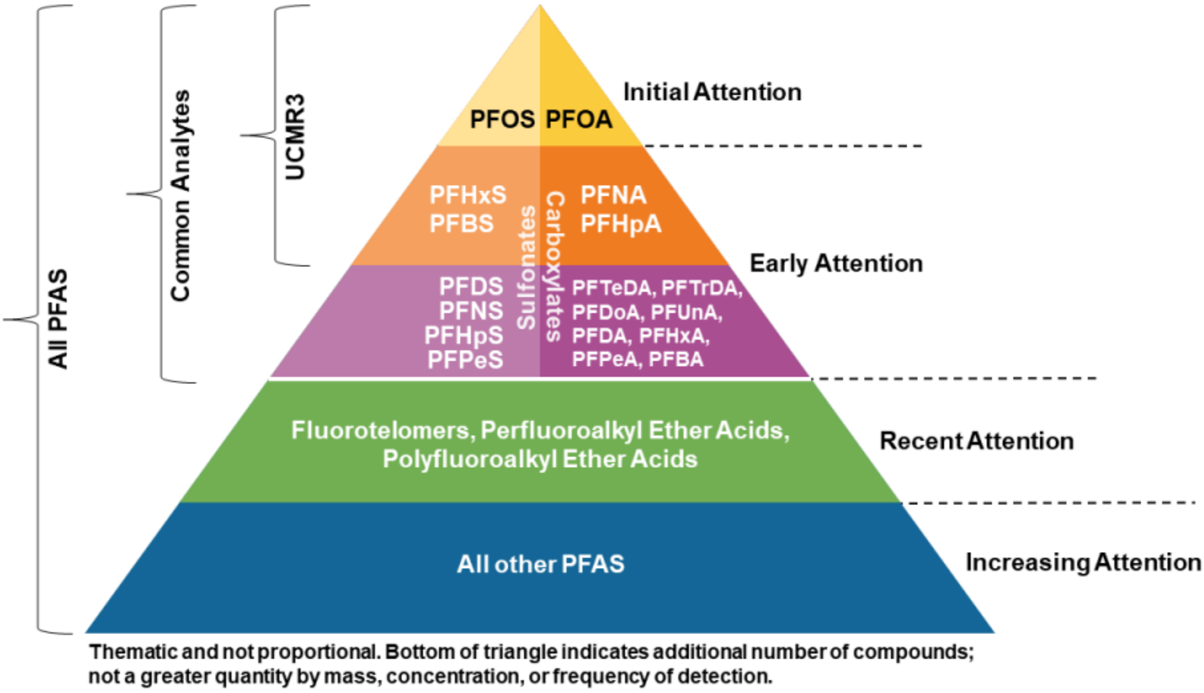
2.3.2 Analytical Developments

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 2000). 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. The number of commercial laboratories that offer PFAS analysis is increasing. Analytical methods continue to be developed and improved to test a variety of media and additional PFAS; these continue to improve our knowledge of PFAS in the environment and potential human health effects. In September 2021, USEPA announced that they, in collaboration with the USDOD, had published a draft EPA-validated laboratory analytical method (Draft Method 1633) that tests for 40 PFAS in eight environmental media (USEPA 2021). For further information on analytical methods, refer to Section 11.

The number of PFAS that can be identified and quantified by analysis has also evolved over time, with longer lists of compounds and changing commercial availability linked to 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. UCMR5 is planned for 2023–2025, and is expected include 29 PFAS. 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 2-16. Many of these PFAS are also summarized in Figure 2-5.

Other analytical methods and approaches are available to detect and quantify PFAS not included in the standard methods mentioned above, including nontarget analysis, total organic fluorine, and total oxidizable precursor assay (see Section 11).



Thematic and not proportional. Bottom of triangle indicates additional number of compounds; not a greater quantity by mass, concentration, or frequency of detection.

Figure 2-16. Emerging awareness and emphasis on PFAS occurrence in the environment

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

Since the early 2000s, three analytical methods have been developed, validated, and published by USEPA for the analysis of PFAS in drinking water. These include Methods 537, 537.1, and 533 (USEPA 2020). These methods were developed for finished drinking water from groundwater and surface water sources. According to USEPA, these methods were developed for accuracy, precision, and robustness and have been through multi-lab validation and peer review (see Section 11). USEPA notes that Method 537 was used extensively during Unregulated Contaminant Monitoring Rule 3, described above. Most recently (December 2019), USEPA published Method 533: Determination of Per- and Polyfluoroalkyl Substances in Drinking Water by Isotope Dilution Anion Exchange Solid Phase Extraction and Liquid Chromotography/Tandem Mass Spectrometry (USEPA 2019). While each method includes analytes not included in the other, the analytes targeted by Method 533 include shorter-chain PFAS and fluorotelomers (see Section 11.2.1.1). Methods 537.1 and 533 have both been validated for the analysis of HFPO-DA (a component of the GenX processing aid technology). For more information, including approaches to other media, refer to Section 11.2 (Analytical Methods/Techniques).

The PFAS analytes associated with Methods 537.1 and 533 are listed in Table 2-4 (separate PDF) and categorized according to the family tree hierarchy.

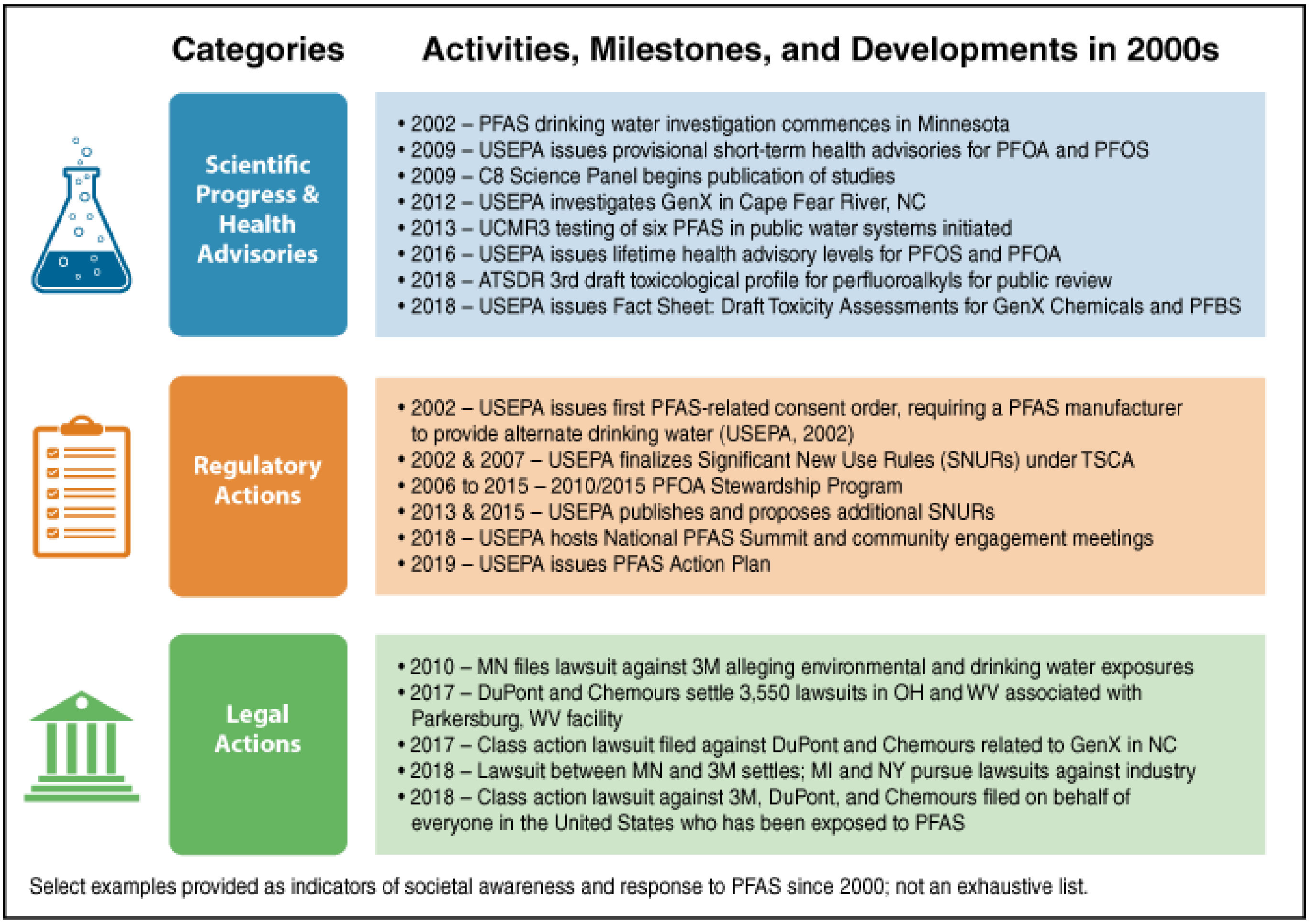
2.3.3 Detection in the Environment

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. 2007; 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 2-17. 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.



Categories	Activities, Milestones, and Developments in 2000s
Scientific Progress & Health Advisories	• 2002 – PFAS drinking water investigation commences in Minnesota • 2009 – USEPA issues provisional short-term health advisories for PFOA and PFOS • 2009 – C8 Science Panel begins publication of studies • 2012 – USEPA investigates GenX in Cape Fear River, NC • 2013 – UCMR3 testing of six PFAS in public water systems initiated • 2016 – USEPA issues lifetime health advisory levels for PFOS and PFOA • 2018 – ATSDR 3rd draft toxicological profile for perfluoroalkyls for public review • 2018 – USEPA issues Fact Sheet: Draft Toxicity Assessments for GenX Chemicals and PFBS
Regulatory Actions	• 2002 – USEPA issues first PFAS-related consent order, requiring a PFAS manufacturer to provide alternate drinking water (USEPA, 2002) • 2002 & 2007 – USEPA finalizes Significant New Use Rules (SNURs) under TSCA • 2006 to 2015 – 2010/2015 PFOA Stewardship Program • 2013 & 2015 – USEPA publishes and proposes additional SNURs • 2018 – USEPA hosts National PFAS Summit and community engagement meetings • 2019 – USEPA issues PFAS Action Plan
Legal Actions	• 2010 – MN files lawsuit against 3M alleging environmental and drinking water exposures • 2017 – DuPont and Chemours settle 3,550 lawsuits in OH and WV associated with Parkersburg, WV facility • 2017 – Class action lawsuit filed against DuPont and Chemours related to GenX in NC • 2018 – Lawsuit between MN and 3M settles; MI and NY pursue lawsuits against industry • 2018 – Class action lawsuit against 3M, DuPont, and Chemours filed on behalf of everyone in the United States who has been exposed to PFAS

Select examples provided as indicators of societal awareness and response to PFAS since 2000; not an exhaustive list.

Figure 2-17. Growing awareness and concern 2000-2019.

Updated August 2021.

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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 2006; 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 2003). 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 2000). 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 2017; 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 2000).

The paper and packaging protectors included POSF-based side-chain fluorinated polymers and phosphate diesters (Wang 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 PFSA: PFBS) (OECD 2013, Wang 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 2018).

When 3M stopped producing PFOA in the early 2000s, it is reported that the manufacture of PFOA was continued by other domestic and international producers using fluorotelomerization (USEPA 2003; Wang et al. 2014). Domestic PFOA production was later phased out by the eight major domestic producers, as described in Section 2.4.3. Global production is summarized in Section 2.4.4 and Section 2.4.5.

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 2006). 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 2003), 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 2018). There may be other manufacturing or processing companies that did not participate in the program (USEPA 2015). 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 2017). 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 2018). Products manufactured and imported prior to 2015, and materials with ongoing uses, may still contain these PFAS (USEPA 2018), 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. Additional information on current US regulatory activities can be found in Section 8.2.

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, 2015; USEPA 2017). 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).
- Additionally, the following amendments and recommendations have been made:
    - In May 2019, Annex B was amended to discontinue several of the previously allowed ongoing uses (UNEP 2019).
    - 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 2019).
    - the POPs Review Committee recommended in October 2019 to list PFHxS (and its salts and related compounds) in Annex A without specific exemptions (UNEP 2019)

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; for further information, see OECD's Country Information page on the OECD Portal on Per and Poly Fluorinated Chemicals (OECD 2017), "Risk Reduction Approaches for PFASs" (OECD 2015), and "Toward a New Comprehensive Global Database of Per- and Polyfluoroalkyl Substances" (OECD 2018). 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 2015).

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 2015). PFAS manufacture began in China in the 1980s (World Bank 2017, 2017), and PFOS production in China increased coincident with the long-chain PFAA phaseout in the United States (CONCAWE 2016; OECD 2015). 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 2017). China has developed some guidance for restriction and limitations of some PFAS (OECD 2015). 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 publicly available to document the individual PFAS and the quantity of PFAS produced over the years. This is possibly because these data are proprietary or because quantities produced did not meet USEPA reporting requirements under TSCA, but could also be 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 (2015) and Wang et al. (2014), and for PFOS and PFOS precursors from Armitage et al. (2009) and Paul, Jones, and Sweetman (2009). OECD (2015) called 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 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 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 3.11.1 and 3.13).

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 et al. 2015 RIVM 2016; OECD 2015). 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 2017), and other documentation regarding replacement PFAS chemistries is available from the Performance Fluoropolymer Partnership (2021) and American Chemistry Council (2021). Draft toxicological evaluations have been provided for public comment by the USEPA for GenX chemicals and PFBS (USEPA 2018; USEPA 2018) with the PFBS Toxicity Assessment finalized in 2021 (USEPA 2021), and the GenX Toxicity Assessment finalized in 2021 as well (USEPA 2021) . 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 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 F-53B (used as a replacement for PFOS in plating), have recently been added to USEPA Method 537.1 (USEPA 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 et al. 2015; CONCAWE 2016). Some of these fluorinated substitutes may degrade to form short-chain PFAAs. Some short-chain PFAAs, PFECAs (both per and poly), and related chemicals were manufactured as early as the 1980s, or earlier (Wang 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 et al. 2013; Wang et al. 2014; Wang et al. 2015; KEMI 2015; 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 (PHxSF, which can degrade to PFHxS 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 acids used as polymerization aids in manufacture of fluoropolymers, such as GenX chemicals (perfluoroalkyl ether acids) and ADONA (polyfluoroalkyl ether acids) used as a replacement for APFO in the manufacture of PTFE, as well as other types of perfluoroalkyl ether acids, also referred to 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 PFAS known as F-53 and F-53B in lieu of PFOS in metal plating applications.

Updated November 2021.

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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, some of which are considered essential to health, safety, or modern life (Glüge et al. 2020). Glüge et al. (2020) categorized PFAS by uses according to industry application and practical use and identified more than 200 uses for more than 1,400 individual PFAS.

Table 2-5 provides a general (not exhaustive) introduction to some of the uses of PFAS chemistries that are, or have been, marketed or used (3M Company 1999; Poulsen et al. 2005; OECD 2006; Washington State Department of Ecology 2012; OECD 2011; OECD 2013; Fujii, Harada, and Koizumi 2013; OECD 2015; Performance Fluoropolymer Partnership 2021; 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 2015). 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 2-5 distinguishes between these two major classes of PFAS and where they are used in various industries and products. Glüge et al. (2020) provided a detailed listing of PFAS by use category/subcategory, function, and properties; however, it is not organized according to polymer versus nonpolymer PFAS used in these instances.

The major industries and applications summarized in the table are described in more detail in Section 2.6.1.

Table 2-5. 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)

Industry/Application	PFAS Type	Documented Use and Examples of Some PFAS
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
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 (PFPAs 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

Industry/Application	PFAS Type	Documented Use and Examples of Some PFAS
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
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.

Updated August 2021.

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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 are 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 have been used for worker safety purposes, such as using 6:2 FTS or 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 2-18 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.

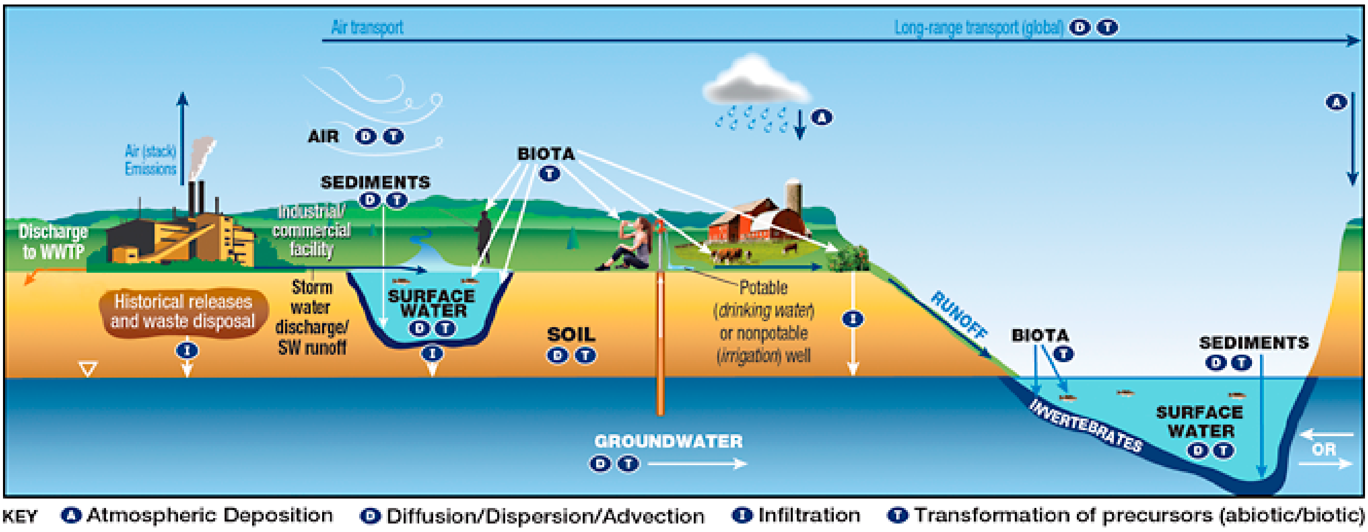


Figure 2-18. CSM for industrial sites.

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 (µg/kg) (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 lightweight 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 2018).

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 (Performance Fluoropolymer Partnership 2021; Glüge et al. 2020).

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).

Studies pertaining to PFAS in building materials continue to be published. The Green Science Policy Institute recently published a report that summarizes currently available studies for the purposes of informing those in the building and construction industry of the presence of PFAS and eliminating unnecessary uses (Fernandez, Kwiatkowski, and Bruton 2021).

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 1996).

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. Glüge et al. (2020) identified PFAS use in chrome, nickel, copper, tin, and zinc plating for lowering surface tension. 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 2012). 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 2015) or changing decorative chrome plating operations to employ the less toxic trivalent chromium. PFAS known by the trade name F-53B (11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid [11Cl-PF3OUdS or F-53B Minor], 9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid (9Cl-PF3ONS or F-53B Major]) have been used as metal plating mist suppressants in China (USEPA 2021; Bao et al. 2019). The toxicology of F-53B is reviewed in Section 17.2.6.1 (note that toxicological research may use different nomenclature for F-53B, namely 6:2 chlorinated polyfluoroether sulfonate (6:2 ClPFESA) and 8:2 ClPFESA (Munoz et al. 2019).

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 2009) (OSHA 2013) (Danish EPA 2015).

Studies show use of PFAS in these settings can result in high concentration wastewater discharges (USEPA 2009) 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).

According to a study in Michigan by the Michigan Department of Environment, Great Lakes, and Energy (EGLE), 320 metal finishers that had a history of using fume suppressants were found to have PFOS in wastewater effluent. The report noted that 15% of metal finishers were discharging to WWTPs at concentrations greater than screening criteria (12 ppt PFOS) and 5% were discharging greater than 1,000 ppt PFOS (MI EGLE 2020). Of the metal finishers discharging PFOS above screening criteria, 89% used hexavalent and/or trivalent chromium in their current or past processes. Chrome platers in Michigan were determined to be in compliance with the NESHAP and many replaced PFOS with a fume suppressant containing 6:2 FTS. Some chrome platers did not use PFOS-containing chemicals to control fumes and have not been found to be sources of PFOS to WWTPs. Nearly half of the chrome platers regulated under the NESHAP used mechanisms other than chemical fume suppression. It was concluded that current effluent containing PFOS from facilities that have complied with NESHAP originates from historical use of PFOS-containing fume suppressants.

2.6.1.4 Industrial Surfactants and Fluoropolymer Production

PFAS have been, and currently are, instrumental as surfactants in industrial and commercial production. In the recent past, some information pertaining to specific surfactant uses of PFAS has become publicly available, though much information still remains unavailable. 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, as discussed in detail in Section 2.2.2.1

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 et al. 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 et al. 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, et al. 2015; Schaider et al. 2017). See Section 8.2 for additional information regarding a voluntary phaseout of 6:2 FTOH.

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) (Schaider 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 PFAS were intentionally added to the packaging material or if they were attributed to unintentional background levels (Schaider 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 et al. 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 et al. 2005; 3M Company 2000).

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 et al. 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 et al. 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 (Kwok et al. 2013), as well as snow, soil, and groundwater (Carlson and Tupper), near ski areas may have measurable PFAS impacts.

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 2-19.

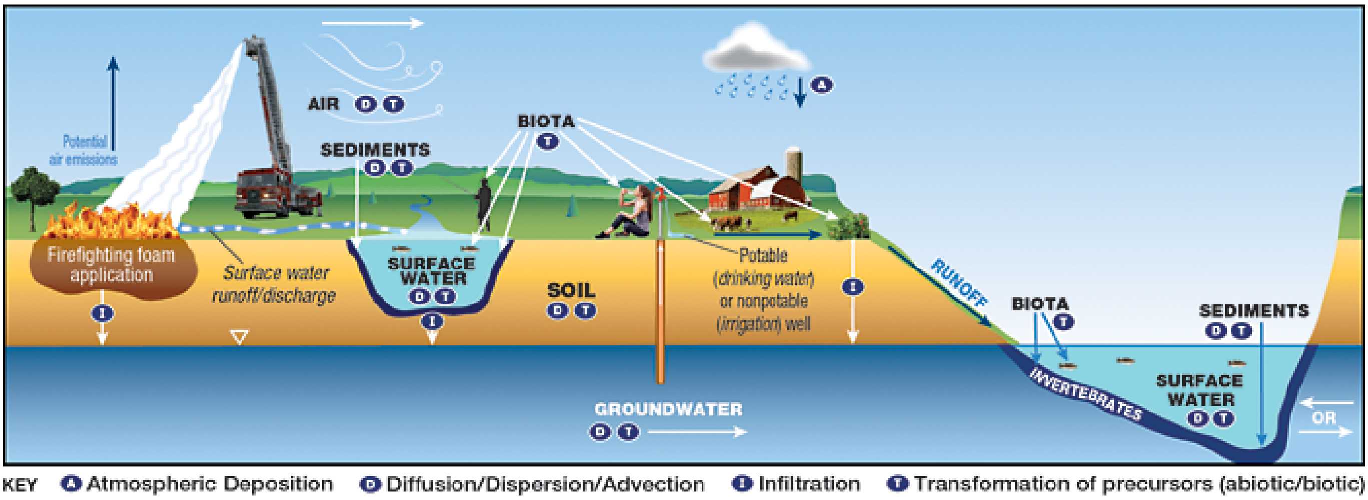


Figure 2-19. CSM for fire training areas.

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

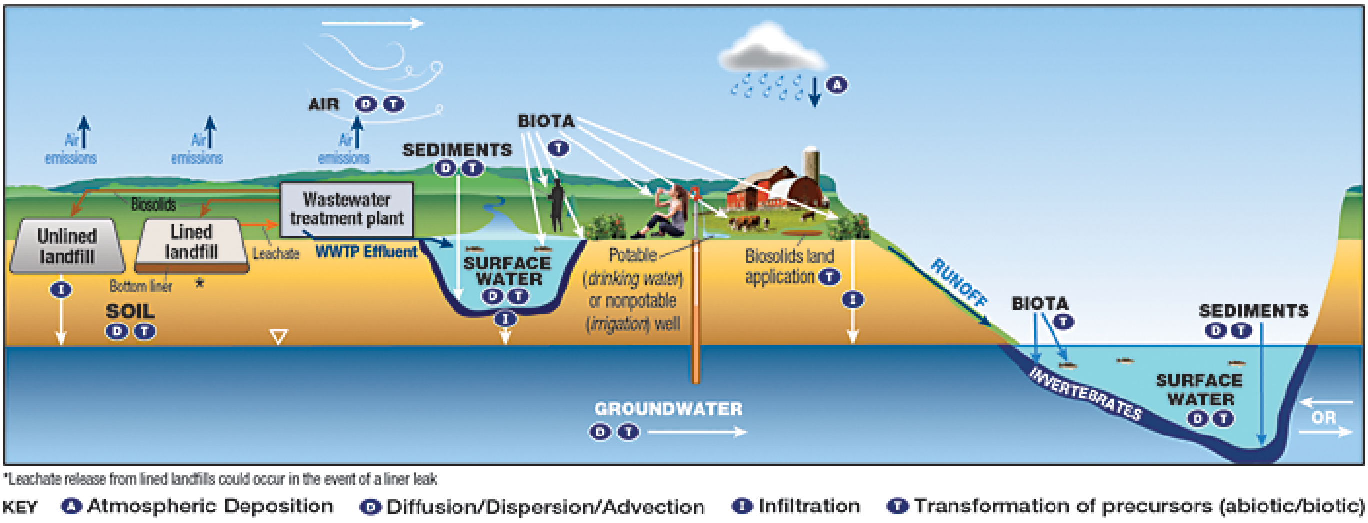
Class B firefighting foams are commercial surfactant solutions that have been (and continue to be) stored and used for fire suppression, fire training, and flammable vapor suppression at military installations and civilian facilities and airports (Hu et al. 2016), as well as at petroleum refineries and 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). Additional information pertaining to disposal of PFAS and PFAS-containing materials at MSW landfills can be found in the 2020 USEPA Interim Guidance on the Destruction and Disposal of Perfluoroalkyl and Polyfluoroalkyl Substances and Materials Containing Perfluoroalkyl and Polyfluoroalkyl Substances (USEPA 2020).

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 2-20 illustrates common elements of CSMs associated with the potential release scenarios at waste management facilities.



*Leachate release from lined landfills could occur in the event of a liner leak

Figure 2-20. 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 2-20). 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. The USEPA Interim Guidance on the Destruction and Disposal of Perfluoroalkyl and Polyfluoroalkyl Substances and Materials Containing Perfluoroalkyl and Polyfluoroalkyl Substances provides further discussion about the use of landfills for management of PFAS-containing wastes, the potential for PFAS to be released to the environment from landfills, and the additional research and data that are needed to further assess the effectiveness of managing PFAS discharges and emissions from all landfills (USEPA 2020).

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 and Graven 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 et al. 2016; CRC CARE 2017). 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. 2016; 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 2-20):

- 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 et al. 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 et al. 2016; Houtz et al. 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 *poly*fluoroalkyls 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; Yoo et al. 2009), 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 2017), 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; Washington et al. 2010). Although multiple studies have reported statistically significant data showing transformation of polyfluorinated substances to PFAAs in land-applied biosolids (Yoo et al. 2010; Sepulvado et al. 2011; Washington et al. 2010), other evidence indicates that some polyfluorinated substances remain in biosolids-amended soils for many years to decades (Yoo et al. 2010; Rich et al. 2015; Washington et al. 2018).

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 (Yoo et al. 2011). 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 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).

Updated September 2021.

⇑

3 Firefighting Foams

The PFAS Team developed an Aqueous Film-Forming Foam training video with content related to this section.

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	AFFF Characteristics
3.3	Mechanisms for Release to the Environment
3.4	AFFF Fate and Transport
3.5	Forensic Analysis of AFFF
3.6	AFFF Procurement and Inventory
3.7	Foam Systems and Operations
3.8	Emergency Firefighting Operations
3.9	Immediate Investigative and Cleanup Actions
3.10	AFFF Disposal
3.11	Firefighting Foam System Replacement
3.12	Federal, State and International Regulations and Guidance
3.13	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 subsequent sections.

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.

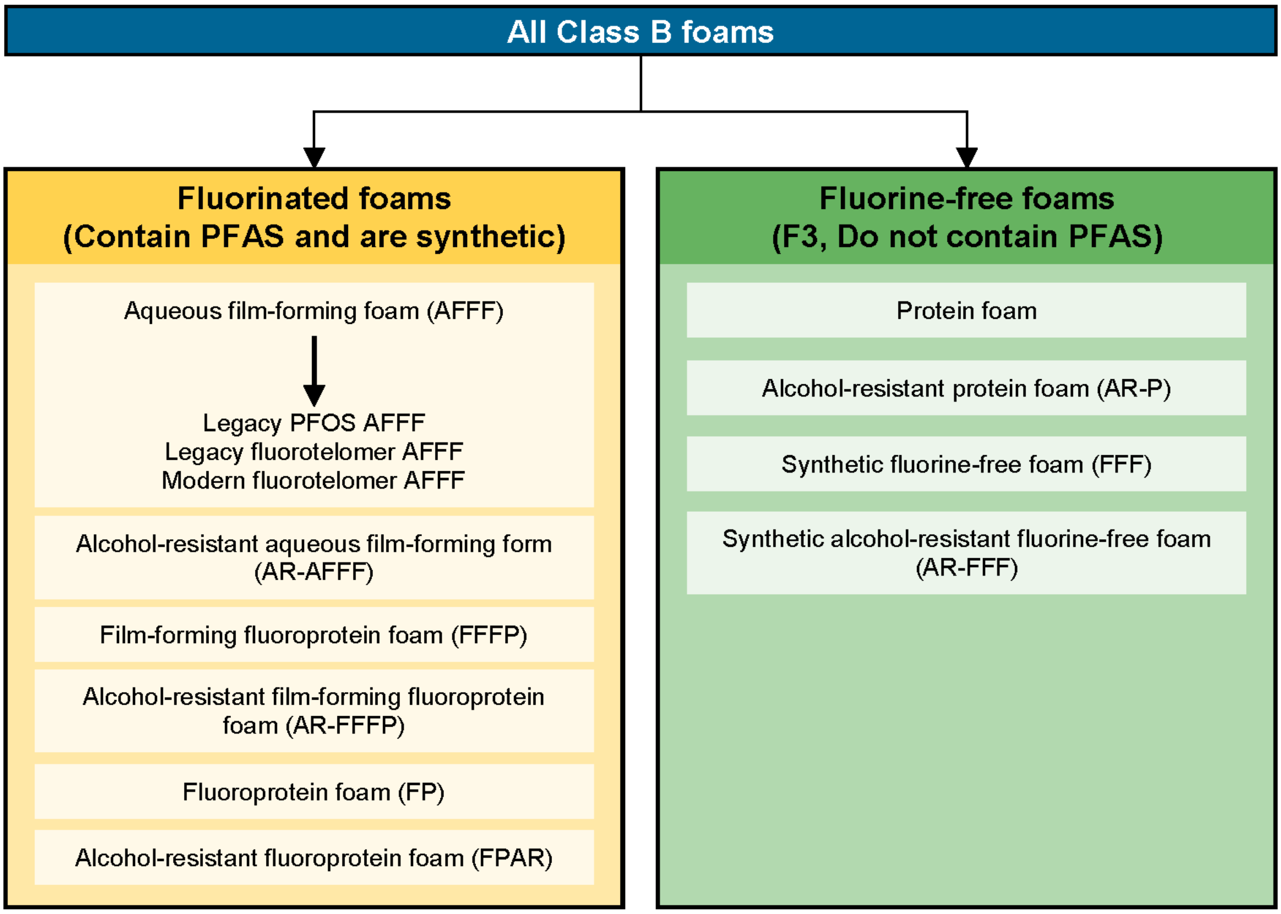


Figure 3-2. Types of Class B foams

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 electrochemical fluorination (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 perfluoroalkyl acids (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 3.10.1).

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 “Light Water” (USDOD 2014). 3M did license some companies overseas to use their products and formulations. Legacy PFOS AFFFs contain PFOS and perflouroalkane sulfonates (PFSAs) 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 Light Water 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 2018). 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 2018). 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 2016; 14 CFR 139.317). Recently, the FAA Reauthorization Act modified that requirement. More information can be found in Section 3.12.3.

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.

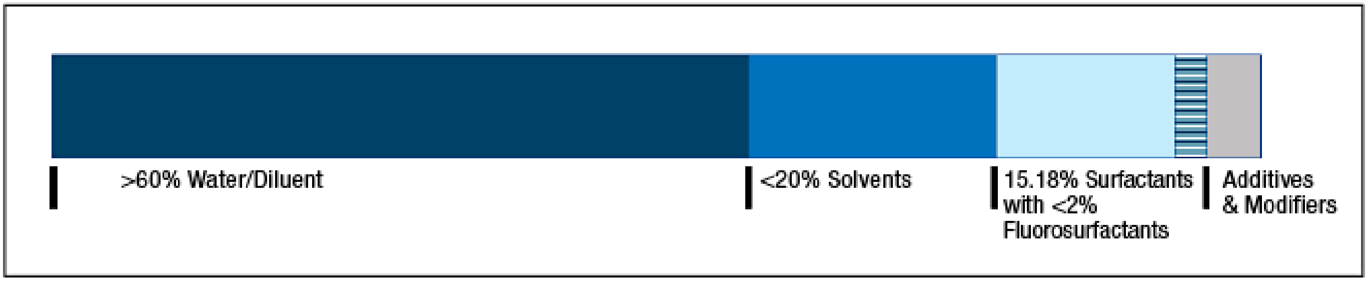


Figure 3-3. Typical composition of 3% AFFF concentrate.

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

3.2 AFFF Characteristics

As sectors and industries seek to transition from fluorinated foams to fluorine-free foams and investigation and remediation activities related to AFFF continue, an understanding of current and historical AFFF products is an invaluable asset to identify and delineate potential sources. This includes, where available:

- whether an AFFF product is/was fluorinated
- whether an AFFF product is/was considered a modern or legacy foam and if it is/was manufactured using fluorotelomerization or electrochemical fluorination
- when an AFFF product is/was approved for use and for what specific use/application and to what specific performance standard(s)
- any other pertinent and available information on the product (for example, compatibility, composition information, equipment requirements)

Table 3-1 provided as a separate Excel file, includes the above information for specific AFFF products.

3.3 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.

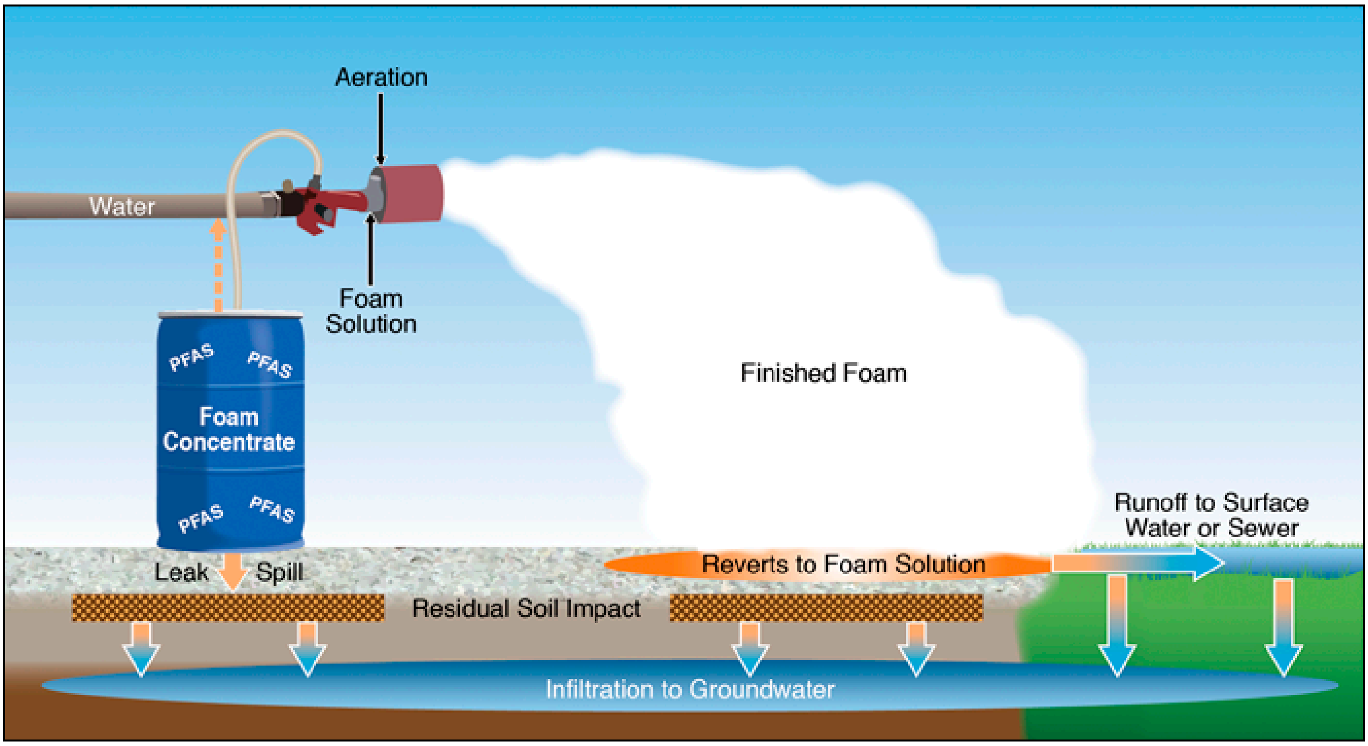


Figure 3-4. Release of firefighting foam.

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 et al. 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 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 2-19 illustrates common elements of CSMs associated with the potential AFFF release scenarios at fire training areas.

3.4 AFFF Fate and Transport

3.4.1 Physical and Chemical Characteristics

Factors that affect fate and transport of PFAS from AFFF releases, as concentrate or in mixture with water, include the chain lengths of the PFAS, their ionic states, the type of functional group(s), and the extent of fluorination. These factors strongly influence the extent of PFAS partitioning and transformation that occurs in the environment. The distribution and composition of legacy PFOS AFFF and legacy and modern fluorotelomer AFFF differ in the environment based on their different chemical constituents and physical and chemical properties (MPART 2020). It is important to consider any precursor PFAS that can degrade to PFAA over time and add to concentrations of known PFAAs in the environment, such as PFOS and PFOA. The relatively high solubilities of most PFAS in AFFF contribute to their migration rates in groundwater. Current published data and physical properties of PFAS differ and some chemical data are experimental, extrapolated, or modeled. Section 4 summarizes some of the available physical and chemical properties for PFAS. Tabulated values and references are included in Table 4-1 (provided as a separate Excel file on the fact sheets page).

3.4.2 Fate and Transport Processes

Fate and transport process information is used to address questions related to potential risk, conceptual site model (CSM), and treatment of PFAS. The mechanisms of partitioning, transport, and transformation of PFAS, which occur across different environmental media, are summarized in Table 3-2 below. Section 5 provides details and references.

Table 3-2. Fate and transport process considerations

Fate and Transport Process	**Description**	**Role in Transport**
Partitioning Refer to Section 5.2	• Competition between hydrophobic and lipophobic C-F “tail” and nonfluorinated polar and hydrophilic head groups causes partitioning to interfaces such as: soil/water water/air water/NAPL co-contaminants	• Controls distribution in environment • Preference for air-water interface influences aerosol transport and deposition, and vadose zone transport (unsaturated conditions provide significant air water interfacial area)
Advection, Diffusion, Dispersion Refer to Sections 5.3, 10.4	• PFAS diffusion in groundwater is slow but greater in air and surface water • Atmospheric transport, e.g., from AFFF applications, results in deposition to soil/surface water/surfaces • PFAS are mobilized from soil to groundwater or to surface water through runoff and leaching	• Facilitate transport of PFAS in and across media • Increase contaminant distribution. Research on the potential impacts of diffusion on PFAS persistence in natural soils is ongoing. Adamson et al. (2020) conducted a study that estimated the relative distribution of different PFAS between high and low permeability soils at AFFF fire training area
Abiotic Transformation Refer to Section 5.4.4.1	• Abiotic processes that can transform precursors under ambient environmental conditions include hydrolysis, photolysis, and oxidation	• Results in chemicals with different physical and chemical properties • May reduce risk • May affect treatment selection
Biotic Transformation Refer to Sections 5.4.4.2 and 5.4.4.3	• PFOA, PFOS, and other PFAAs are resistant to microbial degradation • Biotransformation of various precursors has been reported	• Results in chemicals with different physical and chemical properties • May reduce risk • May affect treatment selection

3.4.3 Fate and Transport Considerations for AFFF Remediation

Knowledge of the type of AFFF and the constituents released to the environment is critical for adequate site characterization and CSM development. Physical and chemical properties and environmental processes play key roles in identifying contaminant capture and collection methods and selection of treatment technologies. The effects of co-contaminants, such as petroleum hydrocarbons, on fate and transport of AFFF constituents is addressed in Section 3.3 and partitioning into NAPL co-contaminants is addressed in Section 5.2.5. Many traditional technologies, such as air stripping and soil vacuum extraction, which rely on volatilization, have been found to be ineffective for PFAS, which typically have low volatilities and are highly soluble. The stability and persistent nature of PFAS in the environment also make current bioremediation approaches ineffective.

Proven and developing treatment technologies for treatment of PFAS are presented in Section 12, which also includes details on the roles of physical and chemical characteristics and transport processes in technology selection. For example, water treatment technologies, such as GAC adsorption and ion exchange, have been proven to be effective because they rely on the surfactant and ionic properties of PFAS. Field-implemented technologies for soil include excavation and landfill disposal or mixing with sorbent for stabilization. The potential for leaching associated with disposal is reduced by stabilization. Many new technologies that rely on the unique properties of PFAS are under development.

3.5 Forensic Analysis of AFFF

Although many types of PFAS are identified in the AFFF formulations, due to the lack of analytical standards, quantitative information is not available for most of them, and only qualitative detections and area counts are reported (D’Agostino and Mabury 2014; Barzen-Hanson et al. 2017; D’Agostino and Mabury 2017; Ruyle et al. 2021). There is quantitative information on the composition of a limited number of AFFFs in several documents (Backe, Day, and Field 2013; Ruyle et al. 2021). The chemistry of AFFF is complex, consisting of anionic, cationic, zwitterionic, and neutral species; in addition, different formulations of AFFF from the same manufacturer also vary in chemistries (Backe, Day, and Field 2013; Houtz et al. 2013; Barzen-Hanson et al. 2017). AFFF includes many fluorinated and nonfluorinated surfactants. Total surfactants are thought to range from approximately 15 to 18 percent. Some references cite about 5–10% (w/w) are nonfluorinated surfactants and 0.9–1.5% (w/w) are PFAS (Backe, Day, and Field 2013; D’Agostino and Mabury 2014). These nonfluorinated surfactants have also been detected in the AFFF-impacted groundwater (García et al. 2019). For forensic analysis, evaluating the source attribution of PFAS from AFFF used for emergency response or fire training operations and understanding the manufacturing history, timing of release, potential sources, degradation products, isomer profiles, and environmental partitioning of PFAS during transport are very important (Dasu et al. 2022; Guelfo et al. 2021; Dorrance et al. 2017).

3.5.1 Manufacturing and Chemistry

PFAS are commonly produced by two manufacturing processes: electrochemical fluorination (ECF) and fluorotelomerization. For example, legacy 3M AFFF brand name Light Water was manufactured by electrochemical fluorination, and the legacy longer chain and the new replacement shorter chain (C6) fluorotelomer-based AFFFs are manufactured by the fluorotelomerization process. More detailed information on these processes is presented in Section 2.2.5, and more detailed information on AFFF as it relates to these processes is presented in Section 3.1. The final products and byproducts formed by using these two methods are different.

The ECF process results in a mixture of linear and branched fluorinated molecules of various carbon chain lengths, both even and odd carbon chains (Buck et al. 2011). The ratio of linear and branched isomers ranges from 70 to 80% linear and 20 to 30% branched isomers (Kissa 2001; Buck et al. 2011; Benskin et al. 2007). The ECF process produces varying amounts of C2–C10 PFAAs (Backe, Day, and Field 2013). Some of the ECF chemistries are based on perfluorooctane sulfonyl fluoride (POSF), a major raw material used to manufacture surfactants (such as perfluorooctane sulfonate (PFOS)), and other raw materials such as sulfonamides, sulfonamido alcohols, and related monomers (Backe, Day, and Field 2013; D’Agostino and Mabury 2014; Buck et al. 2011).

Another important manufacturing process of PFAS is the telomerization process, which mainly produces linear isomers with an even number of carbon chains as the major products, although some odd-numbered carbon chains have also been produced (Kissa 2001). The nomenclature of PFAS manufactured by the telomerization process includes n:2 fluorotelomers (see Section 2.2.4.1), where n represents the perfluorinated carbon chain length and 2 represents the nonfluorinated ethane attached to the functional group, such as alcohols, carboxylates, sulfonates, etc. (Buck et al. 2011). Fluorotelomers (FT) are predominantly produced in 4:2-, 6:2-, 8:2-, and 10:2-carbon chain lengths, although 12:2 has been seen in FT Mil-Spec AFFF (Backe, Day, and Field 2013). Fluorotelomer alcohols or iodides are commonly used as raw materials in the telomerization process to produce fluorotelomer sidechain polymers. At many of the AFFF-impacted sites, perfluorooctanoic acid (PFOA), PFOS, and perfluorohexane sulfonic acid (PFHxS) are the most prevalent PFAS detected. The phaseout of the longer chain PFAS by global manufacturers has resulted in quantifiable increase in shorter-chain concentrations and decreased concentrations of longer chains at some of the areas investigated (Ruyle et al. 2021).

3.5.2 Factors Affecting the PFAS Fate and Fractionation

PFAS forensic analysis of environmental samples is often challenging as many of the PFAS-contaminated sites consist of comingled sources. Many of the AFFF-impacted sites often contain a mix of different formulations of AFFF, either from the same manufacturing source (ECF or telomer-based), or a mix of different sources. Many of the PFAS analytes exhibit a wide range of physical and chemical properties, and hence are transported from the source zones and redistributed downstream through environmental fractionation (Lindstrom et al. 2011; McGuire et al. 2014). Higher water solubility and mobility of short-chain PFAS contribute to the relatively high concentrations of short-chain PFAAs in aqueous matrices downstream from the source areas. The isomer profiles present at the source of contamination will change and redistribute after a certain distance from the source (Adamson et al. 2020; Nickerson et al. 2021). Due to the high solid/water distribution coefficient (K_d), longer chain PFAS have a greater affinity than shorter chain PFAS to partition to sediments, sludge, and soils (Higgins and Luthy 2006; Kwadijk, Korytár, and Koelmans 2010; Schulz, Silva, and Klaper 2020). PFAS, due to their electrostatic nature, may also adsorb onto soils due to the soils' electrostatically charged surfaces (Adamson et al. 2020). Groundwater transport of PFAAs depends on the concentration, chain length, soil characteristics, partitioning behavior, and in situ precursor biotransformation followed by the redistribution of the transformation products (Guelfo and Higgins 2013; McGuire et al. 2014; Anderson et al. 2016). All these factors indicate that the PFAS fingerprint at the source could be different compared to the downstream sample locations. Hence, forensic analysis of such complex AFFF-impacted comingled sources would require consideration of many factors and multiple lines of evidence to better understand the identification and delineation of sources. These include: (1) PFAS isomer profiles and chain-length ratios, which may differ from source, based on the environmental fractionation; (2) unique source-specific markers, which require a detailed understanding of known sources to identify a source related to a sample (McGuire et al. 2014; KEMI 2015; Guelfo and Adamson 2018); and (3) high-resolution mass spectrometry (HRMS) tools to help identify and characterize a broad suite of PFAS analytes to understand the source-specific markers (D'Agostino and Mabury 2014; Barzen-Hanson et al. 2017; D'Agostino and Mabury 2017; Newton et al. 2017; Ruyle et al. 2021). In addition to HRMS analysis, application of statistical analysis tools showed great promise in identifying sources of PFAS contamination (Zhang et al. 2016; Kibbey, Jabrzemski, and O'Carroll 2020; Nason et al. 2021).

3.5.3 Summary of Forensic Analysis of AFFF

The proprietary nature of source information, complex PFAS chemistry, and lack of analytical standards pose many challenges in understanding the source identification and attribution at AFFF-impacted sites. Using only targeted PFAS analysis does not provide much information, as many of the sources contain the common, persistent PFAAs, comingled sources, and environmental fractionation, making it difficult to effectively differentiate sources using the limited list of targeted analyte data. Application of HRMS tools helps in understanding the chemistry beyond the standard PFAA analytes and shows great promise in identifying and delineating PFAS contamination. Considering multiple lines of evidence while conducting forensic investigations helps to identify PFAS source attribution and manage AFFF-impacted sites.

3.6 AFFF Procurement and Inventory

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

3.6.1 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 ≤ 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.

3.6.2 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 2016).

In fire suppression systems, the AFFF concentrate is typically stored in either an atmospheric (nonpressurized) 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 3.12

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.

3.7 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 3.11 for organizations that want to replace legacy PFOS AFFF systems with modern fluorotelomer AFFF or F3.

3.7.1 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.

3.7.2 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).

3.7.3 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.

3.8 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 3.7). 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.

> *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.*

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:

- 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.

3.8.1 Best Management Practices (BMPs)

BMPs are key to the use of AFFF in the most environmentally responsible manner with the goal of minimizing risk from their use. It is important to establish BMPs prior to use in an emergency so that BMP equipment, procedures, and training are already in place. Although firefighting personnel may be aware that the foams they are using contain chemicals, they may not be aware of the potential environmental effects of AFFF use. Training of firefighting personnel is important to ensure BMPs are discussed and employed consistently and effectively.

Example BMPs, adapted from the Fire Fighting Foam Coalition (FFFC 2016), are summarized in Table 3-3. Users should follow BMPs to protect themselves, others, and the environment when using AFFF and other foams. Further BMP guidance can be found in other documents, such as the Best Practice Guidance developed by the Fire Fighting Foam Coalition (FFFC 2016), and the US National Fire Protection Association’s NFPA 11 NFPA (2016). Users at DOD facilities have other BMPs to follow.

Section 3 provides supporting information for the BMPs presented in Table 3-3, as follows:

- Foam selection and storage are discussed in Section 3.6(AFFF Procurement and Inventory).
- Use is detailed in Section 3.7(Foam Systems and Operations).
- Planning and mitigation are covered in Sections 3.8 (Emergency Firefighting Operations) and 3.9 (Immediate Investigative and Cleanup Actions).
- Disposal is addressed in Section 3.10(AFFF Disposal).

This table addresses current operating procedures for selection, storage, use, planning and mitigation. For complete change-out and transition from AFFF to fluorine-free across an entire system, detailed consideration should be made regarding performance, compatibility, decontamination, treatment, and disposal.

Table 3-3. BMPs for AFFF (and Other Foams) Selection, Storage, Use, Planning and Mitigation, and Disposal

Life Cycle	BMP
Foam Selection	1. Public safety first. Use AFFF and other fluorinated Class B foams only in the following situations: • Class B liquid fires and/or spills with significant risks to public safety or of property loss, where specific extinguishing rates and burnback times are necessary • Facilities where AFFF is required until fluorine-free foam (F3) replacement that meets Mil-Spec has been approved
	2. Evaluate whether Class B foam is needed for a specific hazard, or if an alternative technique, such as a fluorine free foam (F3) can provide the needed level of protection. The proper agent to use for your hazard “must be evaluated well in advance of an emergency situation” (FFFC 2016).
Storage	1. Develop a foam inventory and stock tracking system documenting foam composition, date of purchase, lot number, brand, and manufacturer.
	2. “Obtain and follow manufacturers’ recommendations for foam concentrate and equipment” (FFFC 2016). The amount of foam in the system should be at least enough for the group of hazards that simultaneously need to be protected against.
	3. Designate transfer areas and store Class B foam concentrate (all foam, not only AFFF) in a covered area with secondary containment.
	4. Design storage tanks to minimize evaporation of concentrate. Label containers clearly to identify the type of concentrate and its intended concentration in solution. Keep foam within the temperature limitations provided by the manufacturer.
	5. Properly maintain foam systems to prevent accidental discharges. Conduct regular inspections of tanks, storage containers, and any associated piping and machinery. Any leaks of foam concentrate should be addressed immediately to minimize environmental impacts. Maintain records of accidental releases, including date, volume, and foam type. Be cognizant of state and local reporting requirements for releases.
	6. Corrosion is generally not an issue with foam concentrates, but exceptions exist. Manufacturers recommend stainless steel, high-density polyethylene (HDPE), or polypropylene containers for AFFF storage. Avoid using aluminum, galvanized metal, and zinc in storage tanks, piping, and handling equipment for foam concentrates (Angus Fire 2017).
	7. Ensure compatibility of foams per manufacturer specifications before change-outs. Do not mix different types or brands of foam concentrates unless all the foams are compatible. As an example, all foams that meet Mil-Spec 24385 are considered compatible.

Life Cycle	BMP
Use	1. Consider the firefighter and public safety first.
	2. Eliminate the use of AFFF and other fluorinated “Class B foams for training and testing of foam systems and equipment” whenever possible Instead, use specially designed nonfluorinated, PFAS-free “training foams available from most foam manufacturers.” (FFFC 2016).Be aware that such training foams result in longer extinguishments and less burnback protection.
	3. If the authority having jurisdiction requires testing of equipment or training of firefighters using AFFF, training foams that do not contain fluorinated compounds are preferred and, in many cases, required. All foams, regardless of type, should be captured during training and testing.
	4. Evaluate firefighting strategy to determine if Class B foam is needed or if a Class A foam or just water can succeed in fighting the fire.
	5. Provide containment, treatment, and proper disposal of foam solution. Avoid direct release to the environment to the greatest extent possible.
	6. Collect, treat, and properly dispose of runoff/wastewater from training events or live fire events to the greatest extent possible. Prevent discharge to storm drains and surface water to the greatest extent practicable.
	7. Use appropriate personal protective equipment (PPE) when handling and using AFFF and identify how to decontaminate and or dispose of PPE materials and gear that come into contact with foam.
	8. “Follow applicable industry standards for design, installation, maintenance, and testing of foam systems” (FFFC 2016).
	9. Keep records of when and where foam is used to respond to incidents, including foam type, manufacturer, brand, and amount used.
	10. Make note of any sensitive receptors (for example, streams, lakes, homes, wells) identified in the vicinity of foam use and report to environmental agencies as required.
Planning and Mitigation	1. Develop and communicate documented processes for a facility or installation with the stakeholders and regulatory agencies before a release occurs. Stakeholders may include local fire department, elected officials, landowners, interested parties, and local environmental groups.
	2. Prepare runoff collection plans, equipment, and training processes for all foam and those specific to fluorinated Class B foam use.
	3. Create mitigation plans for uncontrolled releases of foam concentrate or foam solution to minimize environmental impacts (FFFC 2016).
	4. Quickly and thoroughly clean up any contaminated environmental media after foam release following established mitigation plans.
	5. Design new firefighting systems to accommodate F3s. Consider their different properties, modes of action, and effectiveness.
	6. Prioritize education, training, and preplanning to ensure the safest and most efficient use of foam and equipment during an incident.

Life Cycle	BMP
Disposal	1. Proper disposal of foam is imperative. See Section 3.10. When available, consider disposal of AFFF inventory to state collection and disposal programs. Refer to Interim Guidance on Destroying and Disposing of Certain PFAS and PFAS-Containing Materials That Are Not Consumer Products (USEPA 2020).
	2. Terminate any donation programs for expired or unused AFFF concentrate (for example, donation to fire training school). Instead, as stated above, encourage collection/proper storage/disposal of expired or unused AFFF.
	3. Monitor developments in new treatment and disposal technologies.

3.8.2 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 2021).

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.

3.8.2.1 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.

3.8.3 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.

3.8.3.1 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.

3.8.3.2 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 2021).

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.

3.8.3.3 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.

3.9 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.

3.9.1 Visual Site Delineation

Visual site delineation refers to outlining the affected area of contamination based on visual clues, such 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.

3.9.2 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.

3.9.3 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.

3.9.4 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 3.9.2). 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).

3.9.5 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.

3.10 AFFF 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 (see Table 3-3). 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.

Disposal of AFFF concentrate represents a significant challenge for any owner of firefighting foam concentrates. The disposal of AFFF concentrates through standard disposal options may carry risks. Practitioners should be aware of possible disposal options, best management practices, and disposal hierarchy, as explained by USEPA (USEPA 2020). Manufacturers' product literature and local regulatory agencies should be consulted for information regarding the specific foam concentrate to be disposed. Some disposal options that are currently available for AFFF concentrates and AFFF-impacted natural media are presented in USEPA's recently published *Interim Guidance on the Destruction and Disposal of Perfluoroalkyl and Polyfluoroalkyl Substances and Materials Containing Perfluoroalkyl and Polyfluoroalkyl Substances* (USEPA 2020). Additional information can be found in Stoiber, Evans, and Naidenko (2020) and Aleksandrov et al. (2019).

As of August 2021, the USEPA interim PFAS destruction and disposal guidance (USEPA 2020) is published for public comment and is not final. Currently available AFFF concentrate disposal options are briefly presented below and in Table 3-4. Table 3-4 also presents advantages and disadvantages associated with each disposal method and new disposal technologies that were under development when this table was prepared. The disposal options that are currently available for materials impacted with dilute AFFF wastes are presented in Section 12, and include stabilization and burial, incineration, and deep well injection.

As stated in the USEPA interim PFAS destruction and disposal guidance (USEPA 2020), one option for addressing disposal concerns related to environmental releases of foam, byproducts, or other possible releases is to store AFFF in warehouse storage to provide time for completion of studies for destruction, disposal, or stabilization of the AFFF. Stakeholder concerns regarding AFFF waste disposal practices are presented in Section 13.1.11.

Each of the currently available disposal options presented below and in Table 3-4 has different advantages and disadvantages that the practitioner should consider when deciding how to dispose of AFFF concentrates, including availability, cost, effectiveness, and potential long-term risks associated with nondestructive disposal options.

3.10.1 Stabilization and Burial

Waste stabilization and burial is a nondestructive disposal methodology wherein waste, including AFFF concentrates, are mixed with stabilizing materials (for example, Portland cement) and buried at a landfill that is licensed to accept and manage these wastes. This disposal method is nondestructive in that the waste is not destroyed but immobilized and encapsulated to prevent exposure and reduce potential mobility. Ultimately the stabilized and buried AFFF concentrate is managed with other wastes disposed of at the same landfill through landfill best management practices (for example, liners, leachate collection, cap management, groundwater monitoring, etc.). Stabilization and burial is an accepted waste management strategy in some states, though the long-term stability of stabilized AFFF concentrate is not well understood.

Practitioners with AFFF concentrates requiring disposal should collaborate with their local or state agency waste management personnel, as applicable, to determine current availability and acceptability of stabilization and burial as a waste management practice. AFFF concentrate bound for disposal should be properly documented (for example, a proper manifest or bill of lading) as a best practice and in compliance with state and federal transportation regulations (as discussed in Section 3.6.2). After the concentrate product has been disposed of, a certificate of disposal may be generated by the disposal facility, transmitted to the product owner, and retained by the disposal facility. This certificate of disposal may be transmitted to the state regulatory agency for review and maintained on file by the product owner.

3.10.2 Incineration

Incineration is a destructive disposal technology wherein AFFF concentrate is destroyed, or mineralized, through the application of heat. Heat is applied to the AFFF concentrate at incineration facilities that have the capability to manage high temperatures and residence times required to destroy AFFF concentrate, as well as vaporized combustion products (flue gases) that are captured and/or further incinerated. Most AFFF concentrate has historically been disposed of using incineration in the United States (FFFC 2016). However, the effectiveness of incineration, and the temperature and time conditions required to achieve complete PFAS destruction, are not well understood (USEPA 2020). Legal, technical, and political challenges to incinerating AFFF exist based on gaps in research on the effectiveness of incineration (Earthjustice 2020). For example, the New York State DEC recently prepared a sampling report near one incineration facility in response to concerns about emissions from the facility (NY DEC 2021). USEPA researchers are currently studying PFAS incineration, sampling and analytical methods development, and industrial field sampling. Thermal stability of PFAS, the ability to fully capture and identify PFAS and their thermal decomposition byproducts, and the efficacy of emission control technologies are areas of targeted research (USEPA 2020). The NDAA for fiscal year 2022 (https://www.congress.gov/bill/117th-congress/senate-bill/1605) establishes a temporary moratorium on incineration of AFFF generated by DOD.

This technology is currently the only known AFFF destruction technology in widespread use, though the efficacy of incineration as an effective disposal option for AFFF concentrate is an area undergoing further study (USEPA, 2020). At the time of publication there are a number of studies ongoing to evaluate destruction temperatures and treatment time required to achieve complete AFFF destruction, the potential to generate products of incomplete combustion, flue-gas analyses to assess mobilization of AFFF concentrates, and other risk factors. Owners of AFFF concentrates requiring disposal should consider contacting their local or state agency waste management personnel, as applicable, to determine current acceptability of incineration as a disposal practice prior to disposal.

3.10.3 Deep Well Injection

Another approach currently in use for AFFF concentrate is to dispose of these materials through deep-well injection. In some cases, disposal via burial of a stabilized concentrate or deep well injection at a licensed hazardous waste management facility has been used. This disposal option eliminates discharges to surface water and shallow groundwater, similar to stabilization and burial, but does not destroy or degrade disposed wastes. Deep well injection is an available option that is being used given the currently limited number of disposal options for AFFF concentrate. Class I deep injection wells, as defined by USEPA, accept both hazardous and nonhazardous liquid wastes (USEPA 2019), including AFFF waste materials such as dilute AFFF (fire water) and AFFF concentrates. The USEPA has published guidance on the requirements for the use of deep injection wells, including siting, construction, operation, monitoring, testing, record keeping, reporting, and closure (USEPA 2019). The USEPA has also studied the risks associated with underground injection wells (USEPA 2001), and these risks are documented for consideration by generators prior to disposal of AFFF concentrates through deep-well injection.

3.10.4 Potential Future Disposal Technologies

The currently available disposal options for AFFF waste are limited and carry inherent unknowns in terms of long-term reliability. This is of particular importance when considering nondestructive disposal means such as stabilization and burial and deep well injection. These unknowns translate into short- and long-term risks for the practitioner. Additional disposal options may be available in some areas (for example, deep well injection) for AFFF concentrate wastes and AFFF-impacted materials. Alternate treatment and disposal technologies are presented in Section 12. New treatment and disposal technologies are under development by a number of research groups as presented in Table 3-4.

Table 3-4 PFAS Waste Materials Disposal Options

Current as of July 2021

Current Disposal Practice	**Advantages**	**Disadvantages**
Stabilization and Burial (Section 3.10.1)	1. AFFF concentrate mass is encapsulated and immobilized in a stable form 2. Disposal is at a licensed landfill with monitoring programs and leachate collection systems designed to ensure disposed mass remains controlled 3. Long-term management of the disposed waste is part of the overall landfill management and monitoring program	1. Disposed AFFF concentrate mass remains in place with no known and documented destruction mechanisms 2. Risks associated with comingled waste disposed of at the waste management facility 3. Long-term testing of stabilized PFAS waste materials under landfill conditions is limited. Some studies are available (CONCAWE 2016; Oliaei et al. 2013; Weber et al. 2011) 4. PFAS mass from disposed wastes can form mobile leachates, which require long-term collection, management, and disposal (Stoiber, Evans, and Naidenko 2020) 5. Some PFAS may be emitted by the landfill gas collection and management system
Deep Well Injection (USEPA, 2019; USEPA, 2020; Marine 2020) (Section 3.10.3)	1. AFFF concentrate mass is injected deep underground in previously defined tectonically stable strata 2. Waste is injected well below drinking water aquifers, reducing potential for future impacts to drinking water resources 3. Waste immobility and lack of potential for unacceptable migration must be documented prior to waste injection 4. Long-term management of the injected waste is the responsibility of the operator while the disposal facility is in operation	1. Disposed AFFF concentrate mass remains in place with no documented destruction mechanism known 2. Waste materials are injected with no modifications or additives to reduce migration potential or enhance degradation 3. Deep well injection facilities are generally operated with limited mandated monitoring to document lack of long-term waste migration 4. The long-term stability of injected wastes is undocumented
Incineration—General (Section 3.10.2)	1. Incineration (at properly licensed and operated disposal facilities) is the only disposal technology currently available that has the potential to result in the destruction of PFAS 2. PFAS destruction through incineration has been documented in laboratory studies (e.g., Aleksandrov et al. 2019; Khan et al. 2020) but known studies analyzed only for a subset of PFAS 3. PFAS destruction reduces/eliminates future risk 4. Some incineration facilities maintain successful track records of operating within permit requirements based on system performance monitoring data collection	1. The efficacy and operational requirements of incineration are currently under question and require additional study (USEPA 2020) 2. Existing laboratory experiments on the incineration of PFAS do not address the full spectrum of potential PFAS byproducts that could form during incineration (Stoiber, Evans, and Naidenko 2020; USEPA 2020) 3. Current regional and local moratoria exist in some locations against incinerating PFAS waste. Practitioners should confirm disposal vendor licensing and operational status prior to shipping AFFF concentrate for disposal
Incineration—Municipal	1. Municipal incinerators are readily available and offer a comparatively low-cost disposal option if operated at sufficient temperatures and residence times and if equipped with appropriate emissions controls	1. Municipal incinerators may not be permitted to accept AFFF concentrate for disposal 2. Temperatures, residence times and emissions controls may not be adequate to fully degrade PFAS 3. Potential for partial decomposition of PFAS to shorter carbon chain-length PFAS (USEPA 2020) 4. Existing laboratory experiments on the incineration of PFAS do not address the full spectrum of potential PFAS byproducts that could form during incineration (Stoiber, Evans, and Naidenko 2020; USEPA 2020)
Incineration—Hazardous Waste	1. Some specialized incinerators exceed minimum temperature required 2. Some are designed to handle flue gases and scrubber wastes3. Generators may be able to obtain a disposal certification from the incineration facility	1. Temperatures, residence times, and emissions controls may not be adequate to fully degrade PFAS at some standard commercial facilities 2. Potential for partial decomposition of PFAS to shorter carbon chain-length PFAS (USEPA 2020) 3. Difficulty handling high-water content wastes

Current Disposal Practice	Advantages	Disadvantages
Incineration—Cement Kiln	1. Temperatures and residence times in excess of minimum required (1100°C and 2 seconds) 2. Effective permanent capture of fluorine 3. No extra energy required above normal kiln processing	1. Potential for partial decomposition of PFAS to shorter carbon chain-length PFAS (USEPA 2020)
Experimental Disposal Technologies (Section 3.10.4)		
Electrochemical Oxidation (Le et al. 2019; Ensch et al. 2020)	PFAS is degraded in a closed-cell reactor using metallic electrodes and electrical current. Several different types of electrodes (titanium oxide, boron-doped diamond, etc.) have degraded PFAS to varying degrees of success and several studies were underway in 2020. In previous laboratory-scale studies, complete PFAS compound destruction was achieved, though at relatively low throughput rates. This disposal technology is applicable to liquid waste streams only.	
Enhanced Contact Plasma Reactor (Singh et al. 2019)	PFAS are degraded in a closed system using water, electricity, and argon gas to degrade PFAS through a series of sequential destruction steps. At laboratory scale the complete destruction of PFAS was observed within their ability to measure, limited by analytical method detection limits. Air Force Civil Engineering Center (AFCEC) and Clarkson University were field testing this technology at Wright-Patterson Air Force Base, Ohio in 2020.	
Alkaline Hydrothermal Treatment (HaLT) (Wu et al. 2019)	Perfluorooctane sulfonate (PFOS) and potentially other PFAS are degraded through the application of hydrothermal conditions (condensed water at high temperature [200–350 °C] and high pressure [2–16.5 MPa]) to solutions amended with NaOH. Initial studies document complete PFOS destruction within 90 minutes. Expanded laboratory studies continue to investigate efficacy over a broader range of PFAS compounds.	
Supercritical Water Oxidation (SERDP-ESTCP 2020)	Supercritical water oxidation at high temperature (greater than 373 °C) and high pressure (greater than 22 MPa) has been demonstrated to degrade PFAS completely. Battelle Memorial Institute has patented a process called PFAS Annihilator to apply this technology for the destruction of PFAS. In addition, an ESTCP-supported study at Duke University began in May 2020 to demonstrate the efficacy of this technology at higher throughput rates (approximately 907 kg of waste material per day).	

3.10.5 Fire Water 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; Table 3-1 provides additional information for BMPs. 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 3.10.1 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.

3.11 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 and content).

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

3.11.1 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 may be considered for use. Alternatives currently available as replacement products for legacy AFFF include products discussed in the following sections.

3.11.1.1 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 (FAA 2018).

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).

3.11.1.2 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 3.12 discusses the current state of regulations on AFFF use.

3.11.2 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 3.6.2. 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.

3.11.3 AFFF Transition Planning

Protocols around transition planning and execution of foam change-out are becoming ever more important to understand. Several factors need to be carefully considered when evaluating fluorine-free foam alternatives, including but not limited to:

- What will the foam be used for and max volume of fuel source handled?
    - Fuels fires and max volume (large atmospheric storage tanks or other)
    - Chemical fires and max volume (large atmospheric storage tanks or other)
    - Other
- What are the current performance specification requirements for the foam?
    - Mil-Spec
    - Other
- What application and application technique are anticipated?
    - Fire suppression system
    - Fire response vehicles
    - Industrial fire extinguisher
    - Other
- What water type is used for mixing?
    - Fresh water
    - Salt water
- What other types of foam characteristics should be considered? (NFPA 2020)
    - Viscosity of the foam concentrate (Newtonian and thixotropic)
    - Suitability for use with existing proportioning hardware
    - Homogeneous mixing of concentrate with water
    - Compatibility with materials in the system (for example, plastic, rubber seals, metals)
    - Stability of foam concentrate or premix solution (separation, stratification, sedimentation)
    - Suitability for use on the flammable liquids in question
    - Suitability of application method (aspirated, non-aspirated, forceful, gentle)
    - Extremes of ambient temperature that may be encountered in an incident
    - Suitability of the expansion ratios produced by existing equipment for effective firefighting performance
    - Suitability of the application rates produced by existing equipment for effective firefighting performance
    - Suitability in specific climate (extreme ambient temperatures, both high and low)

Table 3-5 (provided as a separate Excel file) is presented to provide example case studies for transition planning and execution. Case studies from the aviation industry and the oil and gas industry are provided. Case studies also vary by geography to illustrate potential variability by country. They are provided only as examples of how sites are implementing transition planning, but are not intended to represent guidance to be applied at other sites. The following items are included in the table:

- foam procurement, including selection criteria used to evaluate and select alternatives
- system decontamination and sampling, specifically how replacement versus clean-out was evaluated, how and whether sampling was conducted, and the definition of "clean"
- treatment and disposal, including type of cleaning reagent, waste streams generated, and how they were managed.

Because there are currently no federal or state standards on how much residual fluorine contamination in replacement foam is acceptable, each foam user is responsible for determining whether sampling and analysis of the replacement foam is necessary, and if sampled and analyzed, if the cross-contamination of replacement foam is considered acceptable for their use.

3.12 Federal, State, and International Regulations and Guidance

3.12.1 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 2019).

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 3-6); 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 3-6. 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 2017)
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 2018)
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)

3.12.2 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 2018). 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 2018). Users should contact their state regulatory agency for information on available take-back programs.

3.12.3 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), however, per Cert Alert 21-05, no fluorinated Milspec existed as of that date. FAA expects that the U.S. Navy will provide a specification for a fluorine-free agent by January 31, 2023, and this specification will subsequently be adopted by the FAA.. 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.

3.12.4 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 3-7.

Table 3-7. 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 Fire-fighting 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)

3.13 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.

3.13.1 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 3-8 summarizes the AFFF alternatives studies supported by SERDP-Environmental Security Technology Certification Program (ESTCP).

Table 3-8. 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	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. 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.	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	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.	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.

Updated December 2021.

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4 Physical and Chemical Properties

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

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) 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 both the quantity and robustness 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. The object of this table is to serve as a starting point for the research and selection of relevant properties by the practitioner. Selection of appropriate physical and chemical parameters for a specific use is beyond the scope of this document.

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, FTS 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/cm^3 and 974 mg/L (Table 4-1), respectively, would be predicted to behave similarly to carbon tetrachloride (with a density of 1.59 g/cm^3 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. Floating separate-phase liquid layers have been observed on the surface of aqueous PFOA and PFOS solutions at high concentrations (Costanza et al. 2019). However, the formation of these layers appears to be driven by the tendency of PFAAs to accumulate and aggregate at air-water interfaces, and not by density. See Sections 4.2.7.1, 5.2.2.2, and 5.2.4.1 for additional information on the behavior of PFAS at air-water interfaces and 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 PFSAs can form micelles and hemi-micelles, 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 2000). 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. However, recent laboratory work to measure sublimation vapor pressures of nine pure PFAS (GenX, 8:2 FTOH, 10:2 FTOH, and six PFCAs) begins to address this void (Zhang et al.

2020). Caution must be taken when using the vapor pressures for PFAAs listed in Table 4-1 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 et al. (2013)), PFSAs, PFCAs, FTCAs, FTSAs, FASEs, and FASAAs (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, converted between a number of different units, are presented in Table 4-1. Corresponding K_{aw} values and, where available, the temperature and pH at which the value is relevant, are also presented.

4.2.7 Critical Micelle Concentration

Given the difference in behavior between the "head" and "tail," traditional surfactants (surfactants that contain a hydrocarbon chain), 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 hemi-micelles 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), for PFAAs are presented in Table 4-1.

Until recently, researchers believed that PFAAs behaved like traditional surfactants and aggregated in micelles accordingly, although there were very few instances of experimental confirmation of this for PFAAs (Bhhatarai and Gramatica 2011, 2012). Some researchers have postulated that aggregations may occur at concentrations much lower than the CMC in groundwater, either due to interactions with particles and/or co-contaminants, or because of spatially variable concentrations within soil matrices (Yu et al. 2009). It is evident that there is much more research to be done on this topic, which can aid our understanding in what may be a key PFAA characteristic that influences fate and transport in the environment. This topic is further discussed in Section 5.2.

4.2.7.1 Partitioning to Fluid-Fluid Interfaces

The amphiphilic structure of PFAAs (hydrophobic tail with hydrophilic head) implies that they behave like traditional surfactants, accumulating to the fluid-fluid interfaces (for example, air-water or NAPL-water) by orienting themselves along the air-water boundary so that their hydrophobic tails are in the air while their hydrophilic head groups are in the water (Krafft and Riess 2015, Figure 4-1).

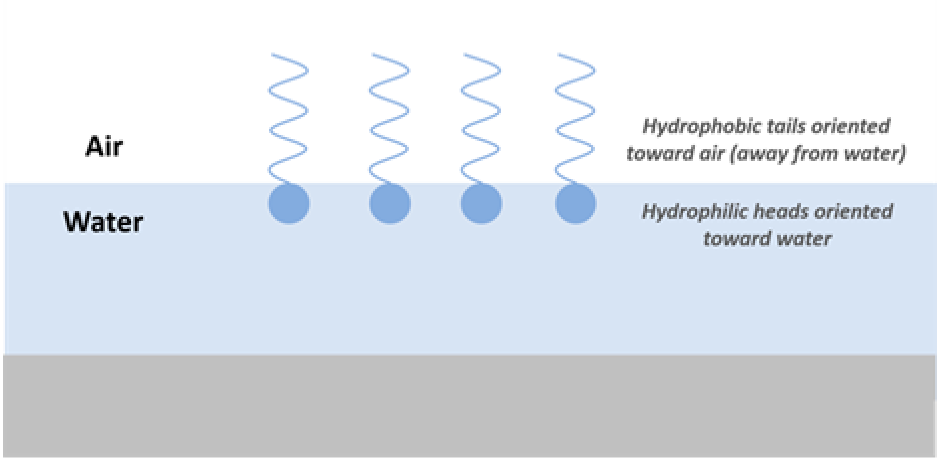

Figure 4-1. Example of expected orientation and accumulation of PFAS at air-water interface.

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

The high degree of fluorination of PFAAs imparts additional hydrophobic tendencies to the tail portions of the molecules. Because of the low polarizability of the C-F bond relative to the C-H bond, PFAAs have a stronger affinity for interfaces than that of traditional hydrocarbon surfactants (Brusseau 2018). These strong surface-active properties and propensity toward self-assembly into films is what makes PFAAs extremely effective and widely used in a variety of applications such as water/grease repellent packaging and AFFF.

Studies have shown that PFAAs are enriched at the air-water interface up to eight times that of the bulk water concentration, with enrichment factors increasing with alkyl chain length (Psillakis et al. 2009; Costanza et al. 2019; Silva et al. 2019; Schaefer et al. 2019). A similar process is thought to occur for PFAAs at NAPL-water interfaces (Brusseau 2018; Silva et al. 2019; Brusseau 2020), however, the magnitude of accumulation at the NAPL-water interface appears to be far less than at the air-water interface at environmentally relevant concentrations. Recently, Costanza, Abriola, and Pennell (2020) reported that concentrations of PFOA, PFOS, and FOSA at the air-water interface were from 2 to 16 times greater than at the NAPL-water interface when the PFAS water concentrations were below 100 mg/L. This study also estimated that, in an unsaturated soil system with a dissolved water concentration below 1 mg/L, up to 87% of the PFOS mass accumulates at the air-water interface, while less than 4% of the mass occurs at the dodecane-water interface.

The degree of affinity that PFAAs exhibit for interfaces is related to the change in surface tension that occurs between the fluids when the compound is introduced to the system. Generally, the surface tension and affinity for the interface both go down as the amount of PFAA increases in the system, although the relationship is not linear. This means that the relationship is influenced by other factors that also effect the surface tension at interfaces (for example, the ionic strength and pH of the solution). For example, Constanza et al. (2019) found that the reduction in surface tension was more pronounced as the total dissolved solids increased (for TDS = 40, 400, and 1700 mg/L), which corresponded to greater accumulation of PFOA and PFOS at the air-water interface.

The adsorption coefficient for the fluid-fluid interfacial layer, termed the K_i (also called the K_{ai} or K_{ia} for the air-water interface or the K_{ni} for the air-NAPL interface) is one metric for the affinity of a compound for fluid-fluid interfaces. However, calculation of the K_i is highly dependent on which assumed sorption model (Freundlich vs. Langmuir) is used, and values can vary by orders of magnitude at low concentrations (Schaefer et al. 2019). Because of this, it can be more useful to measure the affinity using the metric of surface excess (Γ, units of mg/m^2 or mol/m^2), which is the area-related concentration at the interface as compared to the bulk phase (Costanza, Abriola, and Pennell 2020). Because of the complicated nature of interfacial adsorption, adsorption coefficient values are not reported in Table 4-1.

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 2015). 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 PFSAs are for the acid form and are therefore not directly relevant to the anionic forms of PFCAs and PFSAs that exist within the typical range of environmental pH, although the K_{ow} for the anionic form can potentially be estimated from the K_{ow} for the neutral species (Escher et al. 2020).

K_{ow} values are often used as surrogates for other properties, such as estimating K_{oc}, the soil organic carbon/water partition coefficient; bioaccumulation; uptake in biological systems; and ecotoxicity. However, in the case of PFAS, the use of their K_{ow} values as surrogates is generally not appropriate because PFAS do not behave like other well-researched nonionic polar chemicals. For example, the use of K_{ow} as a surrogate for bioconcentration assumes partitioning to lipids in fatty tissues, but ionic PFAS such as PFOA and PFOS generally bind to proteins. 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})

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 into sediments (Dalahmeh et al. 2018). Relative to common PFAS like PFOA and PFOS, studies have suggested K_{oc} can be appropriately defined as a distribution coefficient (K_d) normalized to organic carbon content, thus implying K_{oc} specifically represents the singular process of hydrophobic interaction (Milinovic et al. 2015). Broader reviews highlight the complexity and variability of processes that may contribute to the sorption of PFAS and significant differences between laboratory- and field-scale results (Li, Oliver, and Kookana 2018). These reviews suggest simple relationships may be unreliable for predicting organic carbon partitioning for PFAS (see Section 5.2 for more discussion on partitioning). As such, the current state-of-science supports K_{oc} being reported in relatively broad ranges on a compound-specific basis. The K_{oc} values included in Table 4-1, while not an exhaustive list, are an indicator of the number of values currently available for PFAS. Discussion of the use of K_{oc}, including site-specific K_{oc}, in the prediction of PFAS transport in remedial scenarios is included in Section 10.4.1.

4.2.10 Partitioning to Biota

The extent of accumulation of PFAAs in organisms is controlled by several mechanisms, including uptake from food and from water, depuration, growth dilution, and biotransformation. These processes are described in Section 5. Within organisms, PFAA accumulation differs among tissues, depending on transport factors (for example, the ability to cross the blood-brain barrier, as discussed in Dassuncao et al. (2019) or active cellular transport (as discussed in Section 17.2.3) as well as partitioning. Partitioning is the subject of this section.

Similar to solids partitioning in the environment, the surfactant structure of PFAAs determines the types of interactions that occur within biota. Nonionic hydrophobic chemicals are known to partition into lipids within body compartments. PFAAs are amphiphilic, however, and thus are likely to interact with other organic molecules with both polar and nonpolar regions within living organisms. Many studies have found significantly different PFAA concentrations between body compartments, with the most accumulation occurring in the blood plasma, liver, and kidneys of many organisms (Labadie and Chevreuil 2011; Goeritz et al. 2013; Murakami et al. 2011). This marked difference in PFAA concentrations between bodily compartments has prompted some researchers to deem PFAAs “proteinophilic” to contrast with the description of other well-researched neutral hydrophobic environmental pollutants as “lipophilic” (Kelly et al. 2009; Labadie and Chevreuil 2011). Indeed, these differences in accumulation are likely, at least in part, due to interaction with/partitioning to proteins, which have binding pockets with varying charges that can interact with amphiphilic molecules like PFAAs. However, because the size, shape, and charge of binding pockets vary widely between proteins, there is an evident difference in PFAA binding between types of protein. Multiple studies have found strong interaction of PFAAs to serum albumin, fatty acid–binding proteins, and organic anion transporters (Chen and Guo 2009; Zhang, Ren, and Guo 2013). The magnitude of protein binding affinity differs with the type of PFAAs; Zhang, Ren, and Guo (2013) found that PFAA chain length and functional group determined the amount of binding affinity, but the relationship between binding and chain length was not linear. They also found that FTOHs (neutral charge molecules) did not bind to fatty acid–binding proteins, indicating that the charge of the functional group plays a large part in the protein interaction.

In addition to proteins, PFAAs likely interact with phospholipids (the basic building block of cell membranes). Dassuncao et al. (2019) found a positive correlation between PFAA and phospholipid content in several body compartments of pilot whales. It has been suggested that the interactions occur because of the amphiphilic nature of both phospholipids and PFAAs, which have the potential for binding at both their polar and nonpolar regions (Armitage, Arnot, and Wania, 2012). However, researchers have not found evidence that these interactions are the main determinant of tissue binding. Dassuncao et al. (2019) noted variability in the correlations between phospholipid content and tissue concentrations and concluded that the variability was likely due to the combined effect of protein and phospholipid partitioning.

For nonionic hydrophobic compounds, differences in lipid content can explain some of the variation in chemical concentration among organisms; under some conditions, individuals with higher lipid content have higher body burdens. In general, protein content differs to a much smaller extent among organisms than does lipid content, suggesting that differences in protein partitioning among individuals do not contribute strongly to differences in body burden among individuals. However, the sources of interindividual variation in PFAA body burdens is not well-understood and there is no current framework to incorporate our understanding of PFAS partitioning (for proteins and phospholipids, as well as lipids, which may still have a role) into reliable models for the prediction of bioaccumulation, biotransfer, or biomagnification.

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)

[1] When paired with an acid functional group such as a carboxylic or sulfonic acid

[2] When paired with a functional group that is hydrophilic (for example, a carboxylate)

[3] Smallest of the halogen atoms
Å = angstrom

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

4.3.2 Functional Group Properties

PFAS functional groups include carboxylates, sulfonates, sulfates, phosphates, amines, and others, as introduced in Section 2.2.2. These functional groups, including dissociated and undissociated forms, govern many fate and transport properties of PFAS. The ionic state of a compound determines its electrical charge and its physical and chemical properties, which in turn control its fate and transport in the environment. For example, the state (anionic or undissociated acid) of a given PFAS may alter aspects such as volatility and bioaccumulative potential. As further described below, due to their low acid dissociation constants (K_a), PFAAs are found in the environment in the anionic (negatively charged) state, except in very rare situations (for example, pH <3).

Functional groups of some PFAS (ionic PFAS) can dissociate into anions or cations in aqueous solution under appropriate pH conditions. For example, as discussed in Section 2.2.2, PFOA dissociates into the perfluorooctanoate anion and the hydrogen ion when dissolved in water over a wide range of pH conditions. The ion associated with the fluoroalkyl portion of ionic PFAS, other than PFAAs, can be a negatively charged anion, a positively charged cation, or a zwitterion. Therefore, PFAS can be divided into four classifications 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 2-7 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:

$$K_a = [anion^-]*[H^+]/[acid]$$

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, pK_a, where:

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

Higher pKa values indicate that an acid will dissociate less in water at a given pH than will an acid with a lower pKa. When the pH of a solution equals the pKa, 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 pKa values of 4 or less will exist in aqueous solutions at neutral pH (7) almost entirely as the dissociated acid (see Figure 4-2 for a representation of reported pKa 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.

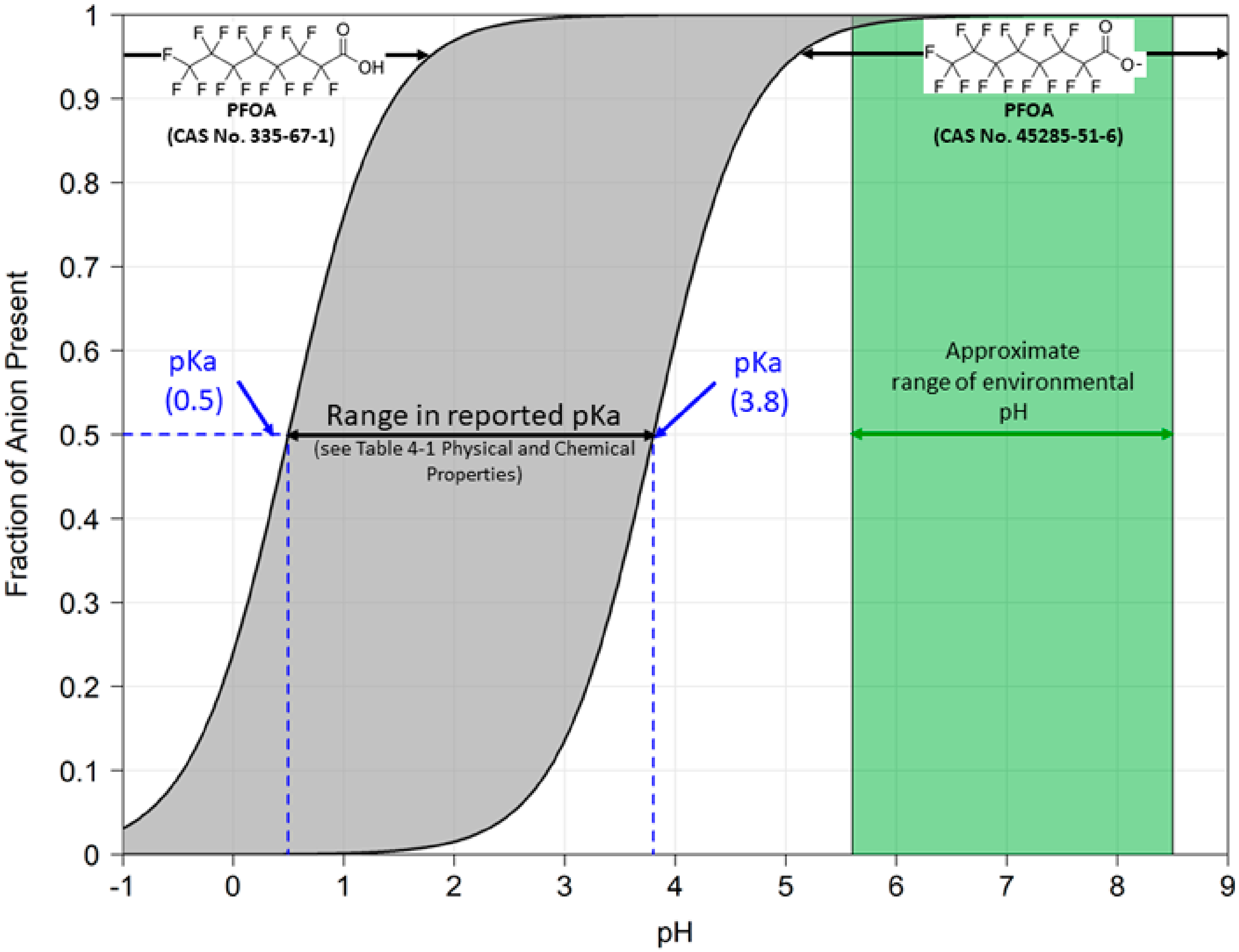

Figure 4-2. Titration curve for PFOA—relation of pKa to environmental pH.

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

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

4.3.3 Thermal Stability

Thermal stability, the degree to which a chemical remains intact under thermal stress, is an important property to predict how long a chemical will persist in the environment. PFAAs, such as PFOA and PFOS, are extremely stable, thermally and chemically, and resist degradation and oxidation. Thermal stability of PFAAs is primarily attributable to the strength of the C-F bond in the fluoroalkyl tail (Kissa 2001), but the relative stability is also determined by the specific functional group that is attached to the fluoroalkyl tail. PFCAs and PFSAs are the most thermally stable fluorinated surfactants. The temperatures at which PFAAs decompose and complete mineralization occurs is an area of active research (see Section 12.4). 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 et al. 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 Fate and Transport training video with content related to this section.

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, groundwater velocities, surface water 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). In addition, relevant transport pathways for PFAS can be similar to those for other contaminants. For example, transport of PFAS in groundwater as the result of advection is a potential concern at many sites where PFAS-containing products have been released. Although many PFAS 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 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.

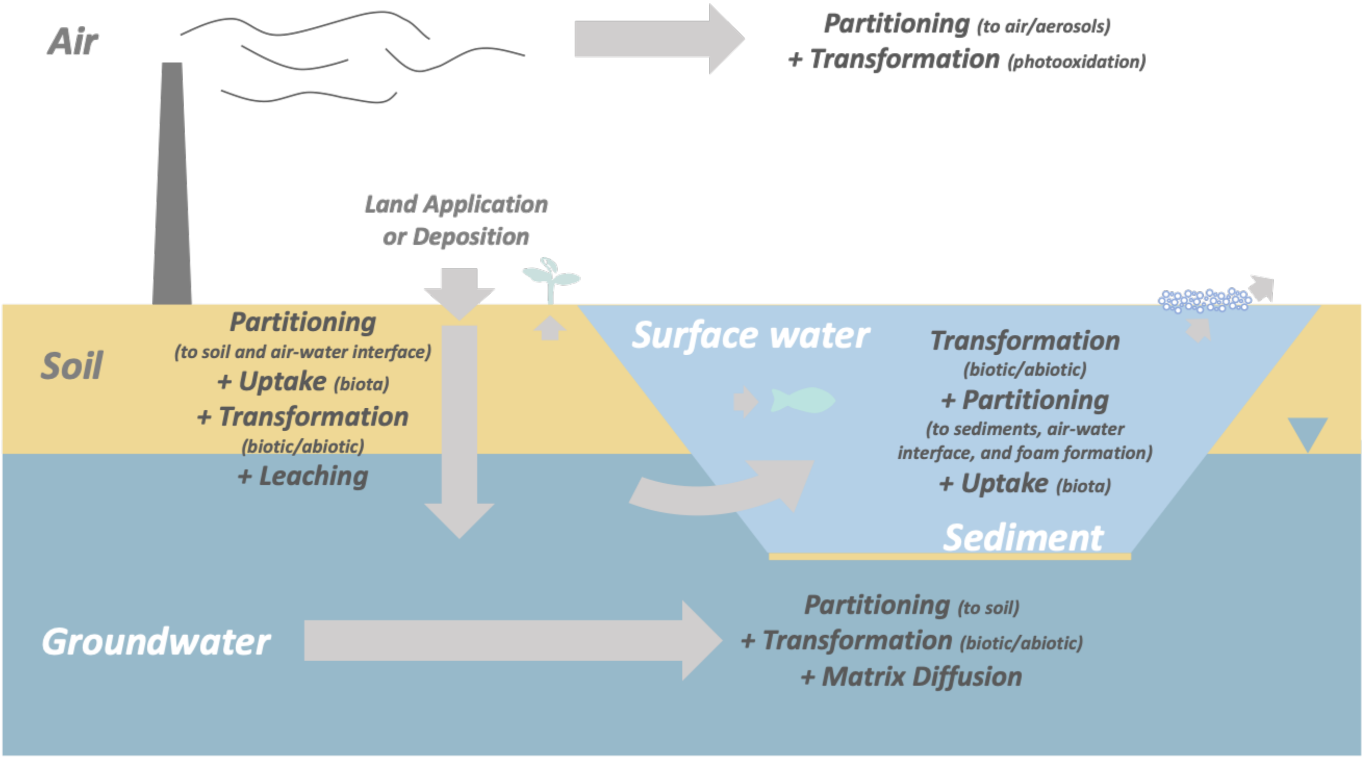

Figure 5-1. Fate and transport processes relevant for PFAS.

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 2017). 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 Micelles and Foam Formation

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

As concentrations of a surfactant increase, changes in surface tension eventually plateau at or near the critical micelle concentration (CMC) for the compound. This behavior has been observed for various PFAS (Costanza, Abriola, and Pennell 2020). Above this threshold, surfactants 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, hemi-micelles, or even simple bilayer structures (Figure 5-2). Although several studies confirm that PFAS aggregate at interfaces as concentrations approach or exceed reported CMC values (Costanza et al. 2019), more research is need on the tendency for PFAS to form traditional micelles (oil-in-water emulsions). CMCs for various PFAS are discussed in Section 4.2.7, and it is important to note that these reported values encompass a wide range, even for individual compounds. For example, the CMC for PFOS has been cited as 500–5,000 mg/L, but hemi-micelles formation for organic ions has been proposed at concentrations as low as 0.001 times the CMC (Fuerstenau 1956; Somasundaran, Healy, and Fuerstenau 1964).

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 soil organic carbon and minerals in the environment (Yu et al. 2009; Du et al. 2014) depending on the surface charge of the adsorbent surface. 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 hemi-micelles near surfaces, and this has been reported to increase the near-surface aqueous concentration of PFAS relative to that measured in bulk solution (Costanza et al. 2019). In systems where water is in contact with air, PFAS such as PFOA and PFOS have been observed to form visible separate-phase liquid floating on a water surface as concentrations exceed the presumed CMC (Costanza et al. 2019). This can contribute to PFAS enrichment at the air-water interface within surface water, particularly within the surface micro layer (SML) that is defined as the thin layer (50 µm) of water in contact with the ambient air (Section 16.5.5). This accumulation can also lead to foam formation above the surface water due to winds, waves, or other turbulent forces that introduce air into the water. In these cases, the presence of natural dissolved organic carbon within the water body can also enhance foam formation and contribute to enrichment of PFAS in these foams even at PFAS concentrations that are below reported CMCs (Schwichtenberg et al. 2020). This foam is different from AFFF because it is likely caused by the aggregation of dissolved-phase PFAS followed by agitation within a surface water body. As discussed in the Surface Water Foam Section (Section 16.5), the formation of this type of PFAS-containing foam above the surface of the water has been sampled and analyzed near or downgradient of areas where PFAS have been released (MI EGLE 2021).

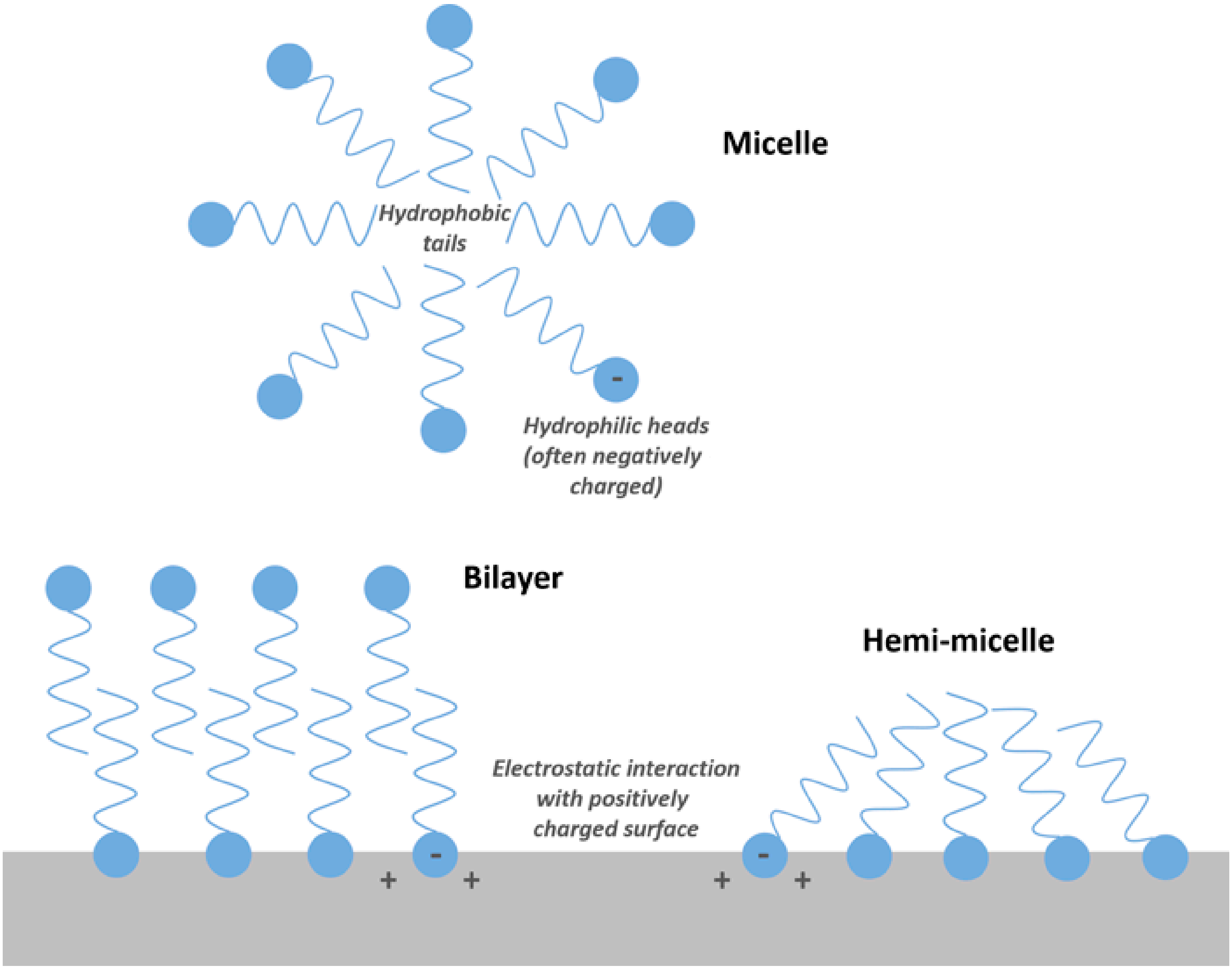

Figure 5-2. Illustration of the formation of PFAS micelles, hemi-micelles, and bilayers. Also shown is an example of aggregation at a positively charged surface. Note that the opposite effect (electrostatic repulsion of PFAS) can occur if the surface is negatively charged.
Source: D. Adamson, GSI. Used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

Table 4-1, linked in Section 4, presents the range of available organic carbon partitioning coefficients (K_{oc}) for PFAS commonly observed in the environment. K_{oc} is a soil organic carbon-normalized adsorption 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,

PFAS partitioning to solids is variable and uncertain, and depends on site-specific factors. In particular, understanding the partitioning behavior of PFCAs and PFSAs to soil organic carbon has been the subject of significant research. PFCAs and PFSAs are present as organic anions at relevant environmental pH values (see Section 4.3.2), 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 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 et al. (2017) showed a general lack of correlation 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 adsorption 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.

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 PFSAs (for example, PFBS) and PFCAs (for example, PFHxA) are less retarded than their long-chain counterparts (PFOS and PFOA, respectively). In addition, PFSAs tend to adsorb more strongly than PFCAs of equal chain length (Higgins and Luthy 2006), and branched isomers are less sorptive than linear isomers (Karrman et al. 2011).

Understanding the effects of adsorption 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. Lab-based and modeling studies have established that partitioning of PFAS cannot be easily modeled using equilibrium sorption parameters in some cases due to rate-limited sorption considerations (Guelfo et al. 2020; Brusseau 2020). In idealized systems, PFAS adsorption 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, adsorption is more likely to be subject to mass transfer effects, and temporal changes in conditions (for example, episodic releases, precipitation events, pumping wells) 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 some evidence that PFAS adsorption may be hysteretic, and desorption may occur more slowly than adsorption for certain PFAS (Higgins and Luthy 2006; Chen et al. 2016; Zhi and Liu 2018; Xiao et al. 2019). Brusseau et al. (2019) showed that PFOS exhibited nonideal adsorption/desorption behavior (tailing) and suggested that these mass transfer limitations could increase the amount of time required to reduce PFOS to low concentrations via pumping.

These findings are particularly relevant for strongly adsorbing compounds like PFOS (Chen et al. 2016) and have important implications for PFAS fate and transport, such as leaching from soil to groundwater (see Section 5.3.3). For example, nonlinear sorption implies that PFAS will adsorb more strongly at low PFAS concentrations than high concentrations. Similarly, if PFAS mass is subject to rate-limiting sorption, then desorption of a portion of the PFAS mass will occur very slowly (Xiao et al. 2019; Schaefer et al. 2021). As a result, any portion of the released PFAS that is strongly retained within sediments or the soil matrix may be more persistent but likely less bioavailable and less subject to migration. Lab-based K_d values (derived using adsorption isotherms) could also likely underestimate the impact of adsorption during fate and transport modeling (for example, by possibly underestimating the retardation factor) (Schaefer et al. 2021).

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, lower pH values in soils 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, carbonate minerals) may mitigate these impacts. Furthermore, increased levels of polyvalent cations such as Ca^{2+} ,which adsorb strongly to permanent charge sites on clay minerals, can lead to increased partitioning to soil for some PFAS (Higgins and Luthy 2006; McKenzie et al. 2015), although the effect on cationic and zwitterionic PFAS can vary widely due to charge differences in the PFAS functional groups (Mejia-Avendaño et al. 2020). In addition, PFAS partitioning due to electrostatic interactions has been shown to be nonlinear in some cases; Xiao et al. (2019) demonstrated that sorption of several zwitterionic PFAS to natural soils (for example, loams, clay loams) increased as the PFAS concentrations decreased. 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 et al. 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

As discussed in greater detail in Section 4.2, reliable data on physical properties that relate to PFAS volatilization, such as vapor pressure and Henry's Law constants, are scarce. Additionally, volatilization from water to air of acidic PFAS, such as PFAAs, is affected by pH-dependent, aqueous phase dissociation from more-volatile acidic species to less-volatile anionic species (Kaiser et al. 2010). Measured vapor pressures are available for some select PFAAs, 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), as well as FTOHs (Krusic et al. 2005). Henry's law constants for several PFAS are reported in Section 4.2.6. For some PFAS that are acidic at environmentally relevant pH, such as PFOS and PFOA, the reported vapor pressures are low and reported water solubilities are high, limiting volatilization from water to air (USEPA 2000). Other PFAS, such as FTOHs, have specific functional groups that tend to impart greater volatility. In one study performed by Roth et al. (2020), agitation of AFFF was demonstrated to release gas-phase PFAS, reportedly including PFOA. These experiments were performed in a controlled lab setting and resulted in detectable concentrations of five FTOHs and 10 PFCAs above background laboratory air concentrations. The potential for this type of partitioning to occur in field settings was not evaluated, and the veracity of the PFOA detections has been debated (Titaley, De la Cruz, and Field 2020; Roth et al. 2020).

Under certain conditions, particularly within industrial stack emissions, or during fire suppression, incineration, or combustion, PFAS can be transported through the atmosphere. This can include volatiles like FTOHs that may be present in the gas phase and anionic PFAS that may be sorbed to particulates (Ahrens et al. 2012). In the latter case, transport occurs through the association of anionic PFAS with airborne aerosols and other small particulates rather than direct partitioning to the gas phase. For example, PFOA and PFOS have been detected in airborne particulate matter in both urban and semirural areas, with PFOA dominant in the smaller, ultrafine particles and PFOS dominant in the larger, coarser fractions (Dreyer et al. 2015; Ge et al. 2017). These studies show that some PFAS can be adsorbed to particulates, likely reflecting the influence of local diffuse sources. As discussed in Section 5.3, removal of airborne PFAS can occur via wet and dry deposition processes that scavenge particle-bound PFAS or gaseous PFAS that has partitioned into water droplets (Barton, Kaiser, and Russell 2007; Dreyer et al. 2010). Wet deposition refers to the wash out of PFAS by rain droplets, where PFAS drops to the ground with no transfer of PFAS to the air (Barton, Kaiser, and Russell 2007). This has been shown to be a relevant mechanism for influencing airborne transport within a few kilometers downgradient of a major manufacturing source (Barton, Kaiser, and Russell 2007; Davis et al. 2007). Dry deposition is a naturally occurring process that depends on prevailing environmental conditions and particle characteristics. Since these deposition processes remove PFAS from the atmosphere, they can influence the location and magnitude of PFAS deposition to terrestrial and aquatic environments.

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 depend 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 behavior because many display hydrophobic and hydrophilic properties. The impacts of these properties on transport are complex and are being actively investigated. By design, many PFAS will lower the interfacial tension and 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 4-1). This behavior influences aerosol-based transport and deposition, and suggests that accumulation of PFAS at water surfaces will occur (Prevedouros et al. 2006).

This preference for the air-water interface has important implications for PFAS transport in the vadose zone, where unsaturated conditions provide significant air-water interfacial area (Brusseau 2018; Brusseau et al. 2019). This includes the potential for enhanced retention in the vadose zone and the capillary fringe, which are the subject of significant ongoing research. For example, Brusseau (2018) showed that adsorption of PFOS and PFOA at the air-water interface can increase the retardation factor for aqueous-phase transport, accounting for approximately 50% of the total retention in a model system (well-sorted sand) with 20% air saturation.

As a result, air-water partitioning may contribute to retardation of PFAS in unsaturated soils. 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 perhaps the more likely explanation was that the higher water content within these clay-rich zones (relative to other depth-discrete zones with more coarse-grained material) decreased the air/water interfacial area available for PFAS partitioning and thus decreased overall soil retention. This pattern is also consistent with the potential for negatively charged clay surfaces to reduce anionic PFAS adsorption through electrostatic repulsion. Guo, Zeng, and Brusseau (2020) highlighted the influence of soil type on air-water interfacial accumulation as a retention mechanism in a modeling study that demonstrated retardation factors for PFOS under their experimental conditions as between 233 and 1,355 in sands and 146 and 792 for finer-grained soils. This was attributed to weaker capillary forces in the sands that resulted in lower water contents and thus more air-filled pore space to promote PFAS partitioning. Note that the simulations performed by Guo, Zeng, and Brusseau (2020) examined only PFOS and did not use field-derived input parameters, so caution should be exercised when generalizing these results to the broader family of PFAS. In addition to the influence of soil type described above, ionic strength has been shown to affect air-water interfacial partitioning whereby PFAS retardation within unsaturated soils appears to be enhanced with increasing salinity (Lyu and Brusseau 2020; Costanza, Abriola, and Pennell 2020).

The tendency for PFAS to accumulate at air-water interfaces has the potential to significantly influence mass retention and soil-to-groundwater leaching, as discussed further in Section 5.3.3.

This has stimulated interest in incorporating these processes into conceptual site models, as well as predictive fate and transport models. Estimates of the air-water interfacial area and the constituent-specific air-water adsorption coefficients, as well as direct measurements of mass discharge to groundwater, can help provide a quantitative basis for these types of models (Brusseau 2019; Guo, Zeng, and Brusseau 2020). In general, air-water adsorption coefficients for an individual PFAS decrease as the concentration increases, and the process appears to be nonlinear (Freundlich-type partitioning) (Schaefer et al. 2019). Air-water adsorption coefficients also tend to increase as the number of perfluorinated carbons increases (Brusseau 2019; Schaefer et al. 2019) (see Section 4.2). This means that when PFAS are released as a multicomponent mixture, these processes will influence each compound to a different extent, with less retention of shorter chained PFAS (for example, PFBS, PFPeA) than longer chained PFAS (for example, PFOS, PFDA, PFNA) (Silva, Martin, and McCray 2021). Silva, Martin, and McCray (2021) also showed that preferential adsorption of the more surface-active PFAS within a mixed release is expected to reduce the adsorption of the other, less surface-active PFAS in the mixture. This type of competitive adsorption would influence the relative breakthrough times for different PFAS within a mixed release.

The potential retardation of PFAS in the vadose zone due to adsorption at the air-water interface is an important component that should be addressed in the conceptual site model, but the retention of PFAS is based on site-specific factors. At sites with shallow groundwater tables, or sites where the water content within the vadose zone soils is typically low, air-water interfacial partitioning may not be particularly relevant. As such, detailed site investigations are critical to understanding how these processes influence PFAS migration through the vadose zone of a specific site. For example, an extensive study of PFAS concentrations in soil at contaminated sites indicated significant retention of PFAS in the vadose zone over long periods of time, but vertical migration of PFAS to the water table was also evident, resulting in detectable PFAS in groundwater at a majority of the investigated sites (Brusseau 2020).

In addition, published studies of migration of PFAS in bedrock aquifers are scarce, but many of the processes controlling sorption in soils will be limited in fractured crystalline bedrock aquifers, resulting in potential for migration of PFAS over longer distances once plumes migrate to the bedrock aquifer.

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 onto the NAPL/water interface and resulting retardation, and greater persistence of PFAS (Guelfo and Higgins 2013; McKenzie et al. 2016; Brusseau 2018). The contribution of this process relative to other PFAS partitioning mechanisms (for example, solid phase, air-water interface) will vary based on site-specific conditions. However, several studies have suggested that the PFAS mass accumulating at the NAPL-water interface is likely to be less than that at the air-water interface in systems where all these phases are present (Brusseau 2019; Silva et al. 2019; Costanza, Abriola, and Pennell 2020).

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 the pore space of 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 PFSAs, back-diffusion of these PFAS is also likely to be a more significant process than for conventional contaminants such as chlorinated solvents. Adamson et al. (2020) reported that approximately 82% of the total mass of PFAS measured at an AFFF site was found within soils that were classified as lower permeability. This included 91% of the polyfluorinated precursor mass, most of which was encountered in the vicinity of the presumed source area. The mass distribution at this site confirmed that diffusion into lower permeability soils had occurred and demonstrated that this process can contribute to long-term retention of PFAS. The relative impact of PFAS accumulation at the air-water interface was not fully investigated in this study, as the water table was very shallow, and the unsaturated/saturated transition zone was likely disturbed during excavation. PFAS may also diffuse into site materials such as concrete. For example, Baduel, Paxman, and Mueller (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. Schaefer et al. (2019) reported experimentally derived diffusion coefficients for 9 different PFAAs and showed that aqueous diffusivity values decreased as the PFAS molar volume increased. However, this relationship was nonlinear due to the complex molecular interactions of fluorinated compounds, and the values showed reasonable agreement with some but not all comparable methods of deriving diffusion coefficients. In addition, the relative rates of diffusion of PFAS with differing charges (for example, anionic vs. zwitterionic/cationic) is a potential concern given that porous media particles may also be charged. In the study by Adamson et al. (2020) described above, 93% of the polyfluorinated mass that had diffused into the lower permeability zones was zwitterionic and/or cationic; a smaller percentage of the anionic polyfluorinated mass was found in these zones. Higher organic carbon and favorable electrostatic interactions likely contributed to further retention of PFAS. The results of this study suggest that matrix diffusion may enhance long-term retention and reduce PFAS mass discharge rates by transferring PFAS mass to less-transmissive zones.

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, Vorkamp, and Skov 2016; Lai et al. 2016; Wang et al. 2015; Dreyer et al. 2009). In contrast, ionic PFAS, such as PFOA and PFOS, characterized by low vapor pressure and high water solubility, tend to be the dominant species found in airborne particulate matter. PFOA is associated with smaller, ultrafine particles, while PFOS is 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 et al. 2016; Lin et al. 2014; Taniyasu et al. 2013; Zhao 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 2016; NH DES 2017; VT DEC 2016). Releases of ionic PFAS from factories are likely tied to particulate matter (Barton et al. 2006), which settle to the ground in dry weather and are also wet-scavenged by precipitation (Slinn 1984; Sehmel 1984).

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 2016). 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, Vorkamp, and Skov 2016; Kirchgeorg et al. 2016; Rankin et al. 2016; Wang et al. 2015; Codling et al. 2014; Wang et al. 2014; Kirchgeorg et al. 2013; Kwok et al. 2013; Benskin, et al. 2012; Cai et al. 2012, 2012, 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 and migration of 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 PFAS releases often involve surface applications (for example, AFFF and biosolids) or atmospheric deposition (Gellrich, Stahl, and Knepper 2012; Anderson, Adamson, and Stroo 2019; Galloway et al. 2020). Leaching is also potentially relevant for plant uptake as well as transport of PFAS contained in landfill waste without adequate leachate control (Benskin et al. 2012; Yan et al. 2015; Lang et al. 2017).

PFAS migration from shallow soils to groundwater is influenced by several interacting processes, which may enhance or limit PFAS leaching rates. The leaching potential will be enhanced in areas with high water infiltration rates, which may include natural water sources such as precipitation or human-made sources such as irrigation. The thickness of the unsaturated zone (depth to water table) will also affect leaching potential. These factors are consistent with other (non-PFAS) contaminants in shallow soils. Conversely, several PFAS-specific processes, as described in Section 5.2, potentially limit the extent of PFAS leaching from shallow soil to groundwater. These include partitioning of PFAS to solid phases (for example, soil particles), adsorption at the air-water interface, and partitioning to NAPL. As a result, any soil properties that enhance the potential relevance of these processes may limit soil-to-groundwater leaching. This includes elevated levels of organic carbon, increasing air content, and higher ionic strength within the vadose zone. The structural properties of the individual PFAS will also influence their transport, including the tendency for longer chain PFAAs to be less soluble and exhibit larger partitioning coefficients than shorter-chain PFAAs. In addition, several of these partitioning processes within the vadose zone have been shown to be nonlinear, which means that their relative contribution to leaching may change over time as concentrations change. Finally, site conditions that influence the degree of flushing (for example, precipitation rates and depth to groundwater) should be considered when evaluating the potential for PFAS to leach from soil to groundwater.

While our understating of these vadose zone processes continues to evolve, there are several possible implications that may be relevant for managing sites where PFAS have been released:

- These processes can affect the rate at which some PFAS migrate through the vadose zone to groundwater (breakthrough). As with hydrophobic partitioning, the relative importance of air-water interfacial partitioning is highly dependent on hydrogeologic and geochemical properties (for example, water content, salinity) of the formation (Anderson, Adamson, and Stroo 2019), as well as the air-water interfacial affinity of individual PFAS (Brusseau 2019). In general, air-water interfacial partitioning can contribute to the bulk soil retention of PFAS in a manner that is unique among organic contaminants. Time scales required for PFOS (and other PFAS that exhibit strong interfacial adsorption characteristics) to reach the underlying groundwater have been simulated to be from 1 or 2 years to several decades or longer. The extent of this retardation factor will likely vary due to climate conditions and PFOS concentrations (Guo, Zeng, and Brusseau 2020). This potential retardation could influence the selection and implementation of remedies, or even the duration of long-term management programs.

- Similar to the impact described above, retention within the vadose zone can occur because of the PFAS tendency to be associated with the air-filled pore space and (to a lesser extent) the solid phase, such that a limited portion of PFAS mass may be in the aqueous phase and subject to deeper infiltration (Guo, Zeng, and Brusseau 2020). Importantly, the interaction between solid phase sorption (hydrophobic partitioning and electrostatic interactions) and air-water interfacial partitioning could be important given that mass transfer limitations can create hysteretic desorption from soils with relatively high organic matter content (Schaefer et al. 2021).

Although some experimental and field-scale studies have reported PFAS transport by leaching (Lindstrom et al. 2011; Filipovic et al. 2015; Hellsing et al. 2016; Bräunig et al. 2017), others have observed long-term retention of longer chain PFAS on shallow soils after extended percolation (Sepulvado et al. 2011; Stahl et al. 2013; Anderson et al. 2016). In a long-term lysimeter study using a silty soil with some clay and natural rainfall, PFOA and shorter chained PFCAs and PFSAs 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, Paxman, and Mueller 2015). Due to the low (part per trillion) concentrations that are a concern in groundwater, slow leaching of PFAS from shallow soils may contribute to a persistent groundwater plume.

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 that demonstrate 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 have existed) on the global market, and the vast majority are polyfluorinated (Wang 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 5-3.

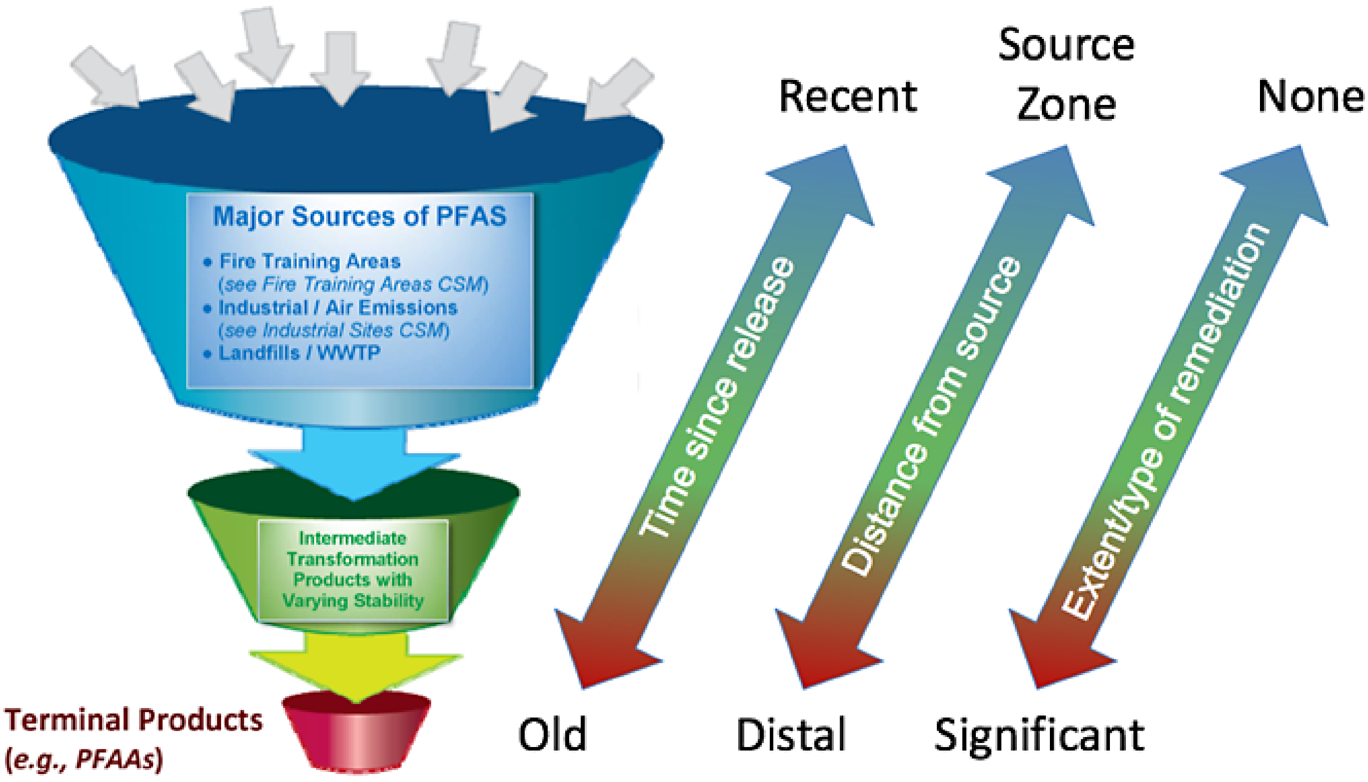

Figure 5-3. Illustration of precursor transformation resulting in the formation of PFAAs.
Source: L. Trozzolo, TRC, and C. Higgins, Colorado School of Mines. Used with permission and based on This Photo by Unknown Author is licensed under CC BY-SA.

5.4.3 Atmospheric Transformations

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

Widely measured PFCA precursors in the atmosphere include primarily FTOHs (Thackray and Selin 2017; Young and Mabury 2010; Martin et al. 2002). Wang 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 nitrous 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 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 and Stasinakis (2015) for a comprehensive review), field studies at AFFF-impacted sites (for example, Houtz et al. 2013; McGuire et al. 2014; Anderson et al. 2016; Weber et al. 2017), and most authoritatively from microcosm experiments.

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

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

In detail, most commonly studied in microcosm experiments have been the 6:2 and 8:2 FTOHs in soil, sludge, or aqueous matrices. Although observed degradation rates and intermediates are variable among these studies, ≤ C8 PFCAs have been consistently observed as terminal transformation products (Dinglasan et al. 2004; Wang et al. 2005, 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 PFSAs with variable rates and inferred pathways.

5.4.4.3 Anaerobic Biological Pathways

Few studies have been published to date conclusively demonstrating biotransformation of per- and polyfluorinated PFAS under anaerobic conditions. FTOHs were studied in two instances, demonstrating the production of stable polyfluorinated acids under methanogenic conditions with much slower kinetics relative to aerobic biotransformation (Zhang et al. 2013; Allred et al. 2015). In a recent study, PFOA and PFOS were demonstrated to be defluorinated by a specific microbial strain (*Acidimicrobium sp.* Strain A6) under conditions where ammonium is oxidized while iron is reduced, a condition known as

Feammox (Huang and Jaffé 2019). The environmental significance of anaerobic biotransformations of polyfluorinated PFAS as sources of PFAAs is uncertain.

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

Some PFAS have a propensity to bioaccumulate. That is, they are taken up and accumulate in organisms from environmental media. Moreover, some PFAS may biomagnify up the food chain; for these compounds, lower levels of PFAS are observed in tissue from organisms at the base of the food chain and in lower trophic-level invertebrates and fish and higher tissue PFAS levels are observed in predatory fish and in air-breathing animals at the top of the food chain (for example, seagulls, polar bears) (Houde et al. 2011; Gobas, Kelly, and Kim 2020; Burkhard 2021). Trophic transfer of PFAS and biomagnification appear to be higher in air-breathing organisms (aquatic-dependent birds and mammals) than in gill-breathing species (for example, higher trophic-level fish species), presumably because the respiratory elimination of PFAS via gills to water is much greater than elimination from lungs to air (De Silva et al. 2021). It should be noted that not all PFAS biomagnify, and for some (for example, PFOS), the evidence regarding biomagnification is mixed (Franklin 2016).

The major mechanisms controlling aquatic bioaccumulation of PFAS are uptake (from water and food), depuration (which includes both elimination across the gill surface and in feces) (Chen, Gong, and Kelly 2016; Zhong et al. 2019), growth dilution, and biotransformation. Within organisms, the extent of accumulation differs among types of tissues (for example, whole body, muscles, liver).

An understanding of bioaccumulation in field populations rests on evaluation of the following factors, which are common to PFAS, as well as to other contaminants:

- Exposure concentrations (concentrations of PFAS in sediments and water)
- Exposure to precursors
- Trophic level (higher trophic levels often exhibit higher concentrations)
- Movement and migration patterns, which determine the extent of exposure to contaminated areas that lie within the home range of an organism
- Bioenergetics (respiration rate, growth rate)
- Toxicokinetics (gut uptake efficiency, gill transfer efficiency, fecal elimination, biotransformation rate, differential protein binding)

Unlike nonionic polar organic compounds, which accumulate in fatty tissues, the bioaccumulation of ionic PFAS in aquatic biota is generally characterized as associated with proteins. 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 differences among tissues in type of protein explain much of the PFAS variation among tissues (Ng and Hungerbuhler 2014, 2015). Binding to phospholipids is another mechanism for PFAS accumulation (Dassuncao et al. 2019). Thus, methods and models that characterize the bioaccumulation of nonionic polar compounds by assuming partitioning to lipids (using lipid normalization) are likely to be inappropriate for PFAS (see discussion of partitioning in Section 4.2.10).

Bioaccumulation of PFAS is generally characterized using three parameters:

- Bioconcentration factor (BCF)—the direct uptake of PFAS by an organism from the water column (for example, through the gills). This is measured in the laboratory. It is defined as the ratio of the concentration in an organism to that in the exposure water (typically in units of ng/kg wet weight / ng/L, or L/kg wet weight).
- Bioaccumulation factor (BAF)—the amount of PFAS taken up from water plus the contribution of PFAS in the diet of the organism. Both the organism and its diet are simultaneously exposed to the same exposure sources. This is generally measured in the field. The units are the same as for the BCF.
- Biomagnification factor (BMF)—the increase in tissue PFAS concentration moving up the food chain, based on a specific predator/prey relationship. The BMF is measured in the field and is typically reported in units of ng/kg wet weight in predator / ng/g wet weight in prey. The trophic magnification factor (TMF) similarly describes the increase in tissue PFAS concentration with trophic level, but it is estimated using data for multiple trophic levels. It is typically calculated as a regression of log(PFAS concentration) vs. trophic level, which is usually determined using the stable isotope 15N method (Franklin 2016).

BCFs, BAFs, and BMFs are used to understand the nature of bioaccumulation; for example, they are used in the European Union REACH designation of compounds as “bioaccumulative” in the Persistent, Bioaccumulative, and Toxic (PBT) and Very Persistent and Very Bioaccumulative (vPvB) assessments. They are also used to support risk assessments and in development of surface water quality criteria (see Section 16). Publications addressing PFAS BCFs, BAFs, BMFs/TMFs are too many and too broad to cover in this document. Several publications have reviewed PFAS bioaccumulation, including but not limited to Burkhard (2021); Houde et al. (2006); Houde et al. (2011); Martin et al. (2013); Conder et al. (2020); Gobas, Kelly, and Kim (2020); and De Silva et al. (2021).

To support better understanding of PFAS bioaccumulation in aquatic species, available BCF and BAF data are provided in Table 5-1 (as a separate Excel file). BCF and BAF values for both invertebrates and fish are included. PFOS is the compound for which BCFs and BAFs are most commonly reported. This is expected because it is generally the most abundant PFAS in the tissues of aquatic organisms. The Table 5-1 Excel file consists of two sheets, the Database that reports values found in relevant literature and a Log sheet that lists each reference that was reviewed.

Table 5-1 includes BCF or BAF values reported in published studies that were compiled as of September 2021. All of the BCF studies were performed in the laboratory under controlled conditions, while the BAF studies were performed in the field. All studies were subject to quality review, which was performed in a qualitative manner. First, the table includes only BCF and BAF values that were reported in the publications. In some studies, PFAS concentrations were measured in water and biota, but BCF or BAF values were not reported. In such studies, BCF or BAF values may not have been reported due to several potential factors—for example, proper spatial and temporal matching of the data. In light of such uncertainties, BCF or BAF values were not calculated for the table. These studies are noted in the Log sheet, for the user’s consideration.

In addition, a number of studies were reviewed but not included in the Database sheet for various reasons; these studies are also indicated in the Log sheet (column “BAFs presented in Table 5-1?”), and notes on each study are provided in the column “Comment.” A quantitative ranking was not conducted, along the lines of Burkhard (2021), who developed a parallel and largely overlapping database of BAF values and classified each study into one of three data quality categories based on several factors (number of fish and water samples, temporal and spatial coordination between the water and fish sampling, and general experimental design). Burkhard (2021) concluded that “The distributions suggest that there are not big differences across the three measurement quality rankings.” This suggests that the lack of a quantitative quality review of each study in Table 5-1, along the lines provided by Burkhard (2021), is not likely to be a significant limitation to the usefulness of the information. Additional information is provided in the README sheet of the Table 5-1 Excel file.

Information on best practices for conducting laboratory bioaccumulation tests is provided by OECD (2012), USEPA (2016), and ASTM (2013). Information is also available concerning the design and interpretation of field and laboratory BAF studies (for example, Burkhard 2003; Gobas et al. 2020). These resources may be useful in guiding the interpretation of the studies included in the database.

The following sections provide overviews of the available PFAS bioaccumulation data.

5.5.1 Bioconcentration

Table 5-1 presents available BCFs for several PFAS. Variation in the reported values is observed in the BCFs and is related to the specific PFAS, exposed species, tissue type, and other factors.

Studies have indicated that chemical structure, particularly the length of perfluoroalkyl chain and the presence of functional groups (carboxylate vs. sulfonate), influence their bioaccumulation potential. Martin et al. (2003) exposed rainbow trout to individual PFAS for 12 days. The PFAS with shorter perfluoroalkyl carbon chain lengths (< 7 for carboxylates and < 6 for sulfonates) had negligible BCFs. At 8–12 carbon chain length, uptake of PFAS compounds was proportional to the carbon chain length and inversely proportional to the critical micelle concentration (CMC; the concentration at which one half of the molecules are associated as micelles). Others have also shown that shorter chain PFCAs and PFSAs (less than eight and six carbons, respectively) are not readily bioconcentrated or accumulated (Conder et al. 2008; Martin et al. 2013; Houde et al. 2011).

Martin et al. (2003) also showed that PFSAs had greater BCFs and half-lives than the corresponding PFCAs 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.

With respect to tissue types, Martin et al. (2003) showed that PFAS accumulated to the greatest extent in the blood, followed by the kidney, liver, and gall bladder. Lower levels accumulated in the gonads, followed by adipose tissue and muscle tissue. This tissue-dependent distribution has been shown in many other studies and is apparently due to PFAS having a high affinity for serum albumin and fatty acid–binding proteins (Ng and Hungerbuhler 2014, as well as to binding to phospholipids (Dassuncao et al. 2019).

5.5.2 Bioaccumulation

Table 5-1 presents available BAF data for several PFAS. As shown, BAFs may be reported using concentrations measured in whole bodies or specific tissues. BAFs reported for fish muscle or fillet are useful for human health risk assessments (for fish consumption) and for developing corresponding water quality criteria (see Section 16). Whole-body BAFs can be used in ecological risk assessments for higher trophic organisms (for example, predatory fish, piscivorous birds and mammals) and developing corresponding water quality criteria. However, Conder et al. (2020) proposed using lab-derived BCFs instead of field-based BAFs in ecological risk assessments, primarily because lab-based BCFs are less variable and generally more reliable than field-based BAFs. Furthermore, PFAS associated with freshly spiked laboratory media may be more bioavailable than in the field, potentially leading to conservative BCFs (higher than what would occur under field conditions). Field-based BAFs may be affected by the presence of precursors (Langberg et al. 2020), making risk assessments and water quality criteria based on these BAF estimates unreliable. However, site specificity of field-based BAFs may be important to consider in specific situations, such as in the refinement of site-specific risk assessments and development of site-specific water quality criteria.

When comparing BAFs among organisms, or when developing statistical summaries of BAF values, differences among tissues in the extent of accumulation must be considered. The approach that is simplest, and which probably provides the most robust approach to comparisons of BAFs among organisms, is to report BAF values on a whole-body basis, since tissue-specific BAFs may vary among species due to differences in toxicokinetics. Such data may be collected using either whole-body samples or tissue-specific measurements that can be mathematically combined to yield equivalent whole-body concentrations. In aquatic organisms, PFAS concentrations in muscle are generally within a factor of two of whole-body concentrations (Goeritz et al. 2013; Shi et al. 2015).

Bioaccumulation of some PFAS has been observed in a variety of wildlife, generally fish-eating species, across the globe as demonstrated by the large number of studies reporting wildlife PFAS residues. Bioaccumulation data are now available for a wide range of environments, including water bodies directly adjacent to or downstream of manufacturers of PFAS, industries that use PFAS in manufacturing processes, firefighting, and wastewater treatment plants, as well as urban areas and areas distant from specific sources (De Silva et al. 2021). The majority of sampling has been conducted to support risk assessments and fish consumption advisories, as well as hypotheses concerning long-range fate and transport, temporal trends, and the identification of sources. Most of the work has been performed in the Northern Hemisphere, and some authors have found that levels are lower in the Southern Hemisphere (Armitage et al. 2009; Ahrens et al. 2009; Ahrens 2011; Benskin et al. 2012). 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).

Some insights regarding PFAS bioaccumulation of PFCAs, PFSAs, and precursors are as follows:

- Similar to bioconcentration, bioaccumulation of PFAAs depends on carbon chain length (Brendel et al. 2018]). USEPA (2017) considers PFCAs with less than seven perfluorinated carbons (PFCAs shorter than PFOA) and PFSAs with less than six (such as PFBS) to less bioaccumulative. PFSAs are more bioaccumulative than PFCAs of the same carbon chain length.

- Bioaccumulation and biomagnification factors measured in the field vary widely (Franklin 2016; Gobas, Kelly, and Kim 2020; Burkhard 2021). Some PFAAs exhibit BAFs that overlap the range often used as criteria for bioaccumulation, for example by USEPA, Canada, and the European Union (1,000–5,000 L/kg).

Available BAFs in Table 5-1 validate some of the above insights. For example, in comparing BAFs for PFOA with PFOS across all species, it is clear that the BAFs for PFOA are much lower than PFOS. Moreover, comprehensive reviews (Ahrens and Bundshuh 2014; Houde et al. 2008) indicate that PFOS (8-carbon chain PFSA) is typically the most common PFAS observed in fish, as well as air-breathing animals, although in invertebrates, PFOA and PFOS can exhibit similar concentrations (~1–10 ug/kg). Ahrens and Bundshuh (2014) attributed the lower bioaccumulation of PFOA than PFOS to shorter chain (7 perfluorinated carbons in PFOA vs. 8 perfluorinated carbons in PFOS). Overall, the data in Table 5-1 indicate that for perfluorocarboxylates, BAFs increase until 11 or 12 perfluorinated carbons and decline for larger compounds.

Finally, it is important to note that PFAS precursors may contribute to the PFAS body burden. Asher et al. (2012) and Langberg et al. (2020) provided field data indicating an important contribution from precursors to PFOS concentrations in organisms via internal transformation. In addition, atmospheric measurements have shown the widespread occurrence of PFAS precursors like FTOHs and perfluorinated sulfonamide alcohols. Once absorbed by an organism, the precursor(s) may be metabolized to PFOA (for example, from 8:2 fluorotelomer alcohol) or to PFOS (for example, from N-ethyl perfluorooctane sulfonamidoethanol) (Gebbink, Berger, and Cousins 2015; Galatius et al. 2013). Additional research on how PFAS precursors may contribute their bioaccumulation in fish and wildlife is needed.

5.5.3 Biomagnification

Biomagnification factors may be used in the regulatory determination of whether contaminants biomagnify up the food chain and in food web modeling in risk assessments. Key conclusions from published literature are summarized in this section.

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).

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.

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.

Contrary to other freshwater studies, Lescord et al. (2015) did not find evidence for biomagnification in total PFAS, total PFCA, total PFSA, and PFOS. These authors observed negative relationships between trophic level, as measured using stable nitrogen isotope ratios (δ15N), and concentrations of the studied PFAS compounds (PFOS, total PFCA, total PFSA, and total PFAS) in several of the six lakes, suggesting no biomagnification in these 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.

Because the BMF or TMF is the concentration in a predator divided by the concentration in its prey, calculated BMFs can be 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). Franklin (2016) analyzed the results of 24 peer-reviewed studies reporting field-derived BMFs or TMFs for 14 PFAS. BMF values ranged over several orders of magnitude, from 0.01 to 373 (including only nonzero values). TMFs varied from 0.1 to 20 (including only nonzero values). Franklin (2016) attributed 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.

5.5.4 Characterization of Bioaccumulation in Criteria Development and Risk Assessments

In regulatory contexts, BMFs may be used to determine whether or not contaminants are considered bioaccumulative: a BMF greater than 1 indicates that a contaminant is bioaccumulative. The relationship between the BAF and BCF also provides relevant evidence.

Because consensus has not been reached regarding the extent of bioaccumulation and/or biomagnification of some PFAS, most importantly PFOS, the best approach to determining bioaccumulative status of PFAS and to conducting risk assessments is an active subject of discussion (Franklin 2016; Conder et al. 2020). Franklin (2016) made the case that "in practice, the study-to-study (and even within-study) variability of the results is so great that [field-measured BMFs and TMFs] are of very restricted usefulness for assessing bioaccumulation potential status." Franklin (2016) proposed basing the bioaccumulative status of a compound only on laboratory BCFs and on measurements of BMFs conducted under strictly monitored conditions, rather than relying on field-measured BMFs or TMFs. For fish, studies can make use of the OECD 305 protocol (OECD 2012). For terrestrial and avian species, dietary BMF determinations can be performed using laboratory rodents or cows or pigs fed with naturally contaminated feed, as well as avian species.

Similarly, Conder et al. (2020) proposed using laboratory-derived BCFs instead of field-based BAFs in ecological risk assessments, because lab-based BCFs may be less variable and generally more reliable than field-based BAFs. Moreover, lab-based BCFs are expected to provide conservative estimates of bioaccumulation, as PFAS may be more available in freshly spiked environmental media compared to aged PFAS in field samples. Furthermore, Conder et al. (2020) argued that laboratory BCFs avoid complications with the presence of PFAS precursors, which may transform into stable PFAS in field samples.

However, laboratory BCFs (studies in which organisms are exposed to contaminant in the water only) are subject to methodological limitations—for example, for substances that are highly sorptive. Furthermore, laboratory BCFs do not account for biomagnification, and for this reason will tend to provide low estimates of true BAFs. An approach similar to that proposed by Franklin (2016), namely, combining laboratory-measured BCFs with BMFs measured under controlled conditions, may be reasonable.

Furthermore, while avoiding the complications of precursors, laboratory BCFs also do not account for the contributions of precursors to tissue concentrations of PFOS. PFOS BAFs measured by Langberg et al. (2020) were the highest in Table 5-1, ranging up to about 250,000 L/kg wet weight muscle for PFOS in yellow perch. This value far exceeds values that have been measured in other sites, generally in the range of 1,000–10,000 (Table 5-1). This high value was attributed to the primary role of precursors in determining organisms' tissue concentrations of PFOS at this site. In an ecological risk assessment for such a site, a tissue concentration determined using measured water column PFOS concentrations and a laboratory-derived BCF (on average, on the order of approximately 1,000 L/kg wet weight whole body for PFOS) would significantly underestimate the true tissue concentration. Thus, if tissue concentrations are primarily determined by precursor levels in the system, then measurement of the substance in water is not appropriate in the first place. Rather, the organism exposure to the precursor(s) itself needs to be measured.

Gobas, Kelly, and Kim (2020) proposed that the bioaccumulative nature of compounds can best be evaluated by focusing on the BMF as measured using dietary-based OECD 305 studies (OECD 2012) , interpreted using a two-compartment bioaccumulation model to estimate the BCF and the BAF. The domain of applicability of the model developed by Gobas, Kelly, and Kim (2020) was limited to nonionic organic chemicals, and so would have to be modified for application to PFAS.

Bioaccumulation rates may differ between linear and branched isomers of PFAS (Conder et al. 2020), and it is hypothesized that linear PFAS are more bioaccumulative than branched PFAS (Houde et al. 2008, 2011). The use of more bioaccumulative isomers in laboratory BCF studies would result in a conservative, but potentially unrealistic, risk assessment for a field population exposed to a mixture of isomers. A full evaluation of the impact of isomer composition will require evaluation of the extent to which differences in bioaccumulation are significant, as well as the relative abundances of isomers in the environment.

Thus, in determining bioaccumulative status and in conducting risk assessments, the variability of field-measured BAFs and BMFs must be balanced against the biases and limitations associated with laboratory BCFs and BMFs. Such evaluations must be performed on a compound-specific basis, taking into account the confounding role of precursors. It is likely that a weight of evidence approach will be called for, given the uncertainties associated with PFAS bioaccumulation.

5.6 PFAS Uptake into Plants

Because PFAS contain a hydrophilic functional group, plants can be expected to take some of these compounds up through their root systems, after which they would be translocated to stems, shoots, leaves, and fruiting bodies. Plants growing closer to contaminated sources or irrigated with PFAS-containing water would be expected to accumulate higher concentrations of PFAS compared to plants more distant from the PFAS source (Gobelius, Lewis, and Ahrens 2017), 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 and that animals fed silage from land-applied fields can have elevated concentrations of PFAS 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 bioconcentration in the latter may occur through the stomata (Shan et al. 2014).

Understanding uptake of PFAS into plants is critical in evaluating the fate of PFAS among various environmental compartments, particularly along the food chains with implications for human and ecological exposures to PFAS. Human exposure may occur via consumption of PFAS-impacted produce and dairy and meat products from animals fed with PFAS-impacted plant-based feed. Potential wildlife exposure to PFAS may occur via PFAS taken up in plants at impacted sites and releases.

The following sections provide an overview of PFAS uptake pathways and mechanisms in plants and bioconcentration/bioaccumulation

5.6.1 Uptake Pathways

Wang et al. (2020) provides an extensive review of uptake and accumulation of PFAS in plants. That study forms the basis of the overview provided in this section. As described in Wang et al. (2020), uptake of PFAS has been well documented in different native and planted species to varying degrees. The majority of these studies have focused on PFOA and/or PFOS uptake by agricultural crops, although there are many other PFAS that have been shown to be subject to plant uptake. Wang et al. (2020) also reported that while most published studies were conducted under controlled lab conditions, at least 16 field studies were identified. These field studies typically have focused on point sources of PFAS, including manufacturing sites, fire training areas, wastewater treatment plants, or landfills.

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

- irrigation with impacted water
- land application of biosolids
- leachates from landfills
- impacts or releases at PFAS sites
- emissions and atmospheric deposition

Plant uptake is both PFAS- and soil-specific. PFAS with higher aqueous solubilities/diffusivities with less soil/air-water interface (AWI) retention affinity are often observed with greater uptake potential (bioavailability). For example, Wang et al. (2020) compiled bioconcentration factors (BCFs) for different PFAS that had been reported in literature studies; the bioconcentration factor is the ratio of the PFAS concentration in the plant tissue to the concentration in the soil. This compilation showed the median BCF values for PFBA and other short-chain PFAS were generally more than an order of magnitude greater than the values for long-chain PFAS like PFOA and PFOS. These patterns confirm that the physical-chemical properties of PFAS influence the extent of plant uptake. Likewise, physical-chemical soil properties (for example, organic matter content and composition, pH, salinity, temperature) affect plant uptake of PFAS, although this has not been comprehensively studied. Also, plant species and physiology (for example, transpiration rate and protein content) are important factors as discussed below.

PFAS accumulation in plants occurs primarily via root uptake from soil and water (Stahl et al. 2009; Lee et al. 2014; Wen et al. 2013; Zhang et al. 2019). Aerial uptake of PFAS from the ambient environment (vapor-phase and particle-bound) have also been reported, such as into leaves and bark (Stahl et al. 2014; Jin et al. 2018; Tian et al. 2018; Liu et al. 2019).

However, aerial uptake contributes minimally to overall PFAS accumulation in plants (Wang et al. 2020).

As noted above, availability of PFAS in soil porewater for root uptake is largely dependent on the aqueous solubility of specific PFAS (see Section 4) and controlled by interactions with the soil phases and the AWI (see Section 5.2.3). PFAS in soil porewater migrates toward plant roots by transpiration and diffusion resulting from a local concentration gradient (Lechner and Knapp 2011). Recent studies by Zhang et al. (2019) and Wen et al. (2013) indicate a concentration-dependent process in root uptake that is mediated by transport proteins in cell membranes such as aquaporins and anion channels. PFAS enter the vascular tissue after passing through the root epidermis, cortex, and endodermis via apoplastic and symplastic pathways (Blaine et al. 2013).

Once in the root xylem, PFAS are translocated to different parts of a plant, such as stem, shoots, leaves, fruits, and grains. The degree of PFAS translocation in these tissues appears to depend on the transpiration stream, with more PFAS accumulation occurring in parts with greater capacity for sorption or incorporation and receiving greater amounts of water (Krippner et al. 2015; Lechner and Knapp 2011; Gobelius, Lewis, and Ahrens 2017; Stahl et al. 2009). For example, in carrots, cucumbers, and potatoes grown in soil mixed with PFAS-contaminated sewage sludge, Lechner and Knapp (2011) found less PFOA and PFOS accumulation in peeled edible parts than in foliage, leaves and stalks., Stahl et al. (2009) found much higher PFOA and PFOS in grains than in straw of spring wheat, oat, and maize. In trees, Gobelius, Lewis, and Ahrens (2017) evaluated the distribution of PFAS at an AFFF release site and reported that total PFAS accumulation followed leaves > twigs > trunk/core or roots in birch and spruce.

5.6.2 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, 2014, 2014). The materials harvested for analysis included both inedible (for example, plant leaves) and edible portions of crops (fruit, lettuce leaves, and roots). Other BCFs and BAFs were obtained from investigations of plants exposed to PFAS from soil, groundwater, surface water, or air in close proximity to PFAS release sites (Mudumbi et al. 2014; Zhang et al. 2015; Gobelius, Lewis, and Ahrens 2017). In general, it can be observed that 1) the shorter chain (more water soluble) PFAS are taken up more readily than the longer chain homologues, and 2) the majority of the plant BCFs and BAFs fall between a range of 0.1 and 10. A BCF or BAF of 1.0 indicates no net accumulation of PFAS from soil to plant. Such a BCF or BAF indicates that the soils and the plant of interest have the same concentration of PFAS per unit weight. This, however, does not indicate that an equilibrium condition exists between soils and plants. Some plants, like lettuce, contain a large percentage of water, which may help to explain the relatively high BAF of 56.8 observed by Blaine et al. (2013). In the controlled studies of edible crops, short-chain PFCAs and PFSAs exhibited greater BAFs compared to long-chain compounds.

Blaine et al. (2013) studied the uptake of PFAAs by greenhouse lettuce and tomato grown in soils prepared to mimic an industrially impacted biosolids-amended soil, a municipal biosolids-amended soil, and a control soil (but incorporated contaminated biosolids equivalent to 10 times higher than the agronomic rates allowed for Class B biosolids), a municipal biosolids-amended soil, and a control soil. BCFs for many PFAAs were well above unity, with PFBA having the highest BCF in lettuce (56.8) and PFPeA the highest in tomato (17.1) in the industrially impacted biosolids-amended soil. BAFs for PFCAs and PFSAs were, in general, slightly higher in the industrially impacted soil than in the municipal soil (~0.3−0.8 log units). The BCFs for PFAAs in greenhouse lettuce decreased approximately 0.3 log units per -CF_2 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) 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 ofPFAS (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 (±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 2-18, Figure 2-19 and Figure 2-20.

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/m^3 (picograms/cubic meter), although concentrations of PFOA as high as 900,000 pg/m^3 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/m^3 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 2019; 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 2016; NH DES 2017; VT DEC 2016). Releases of ionic PFAS from factories are likely tied to particulate matter (Barton et al. 2006), which settle to the ground in dry weather and are also wet-scavenged by precipitation 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.

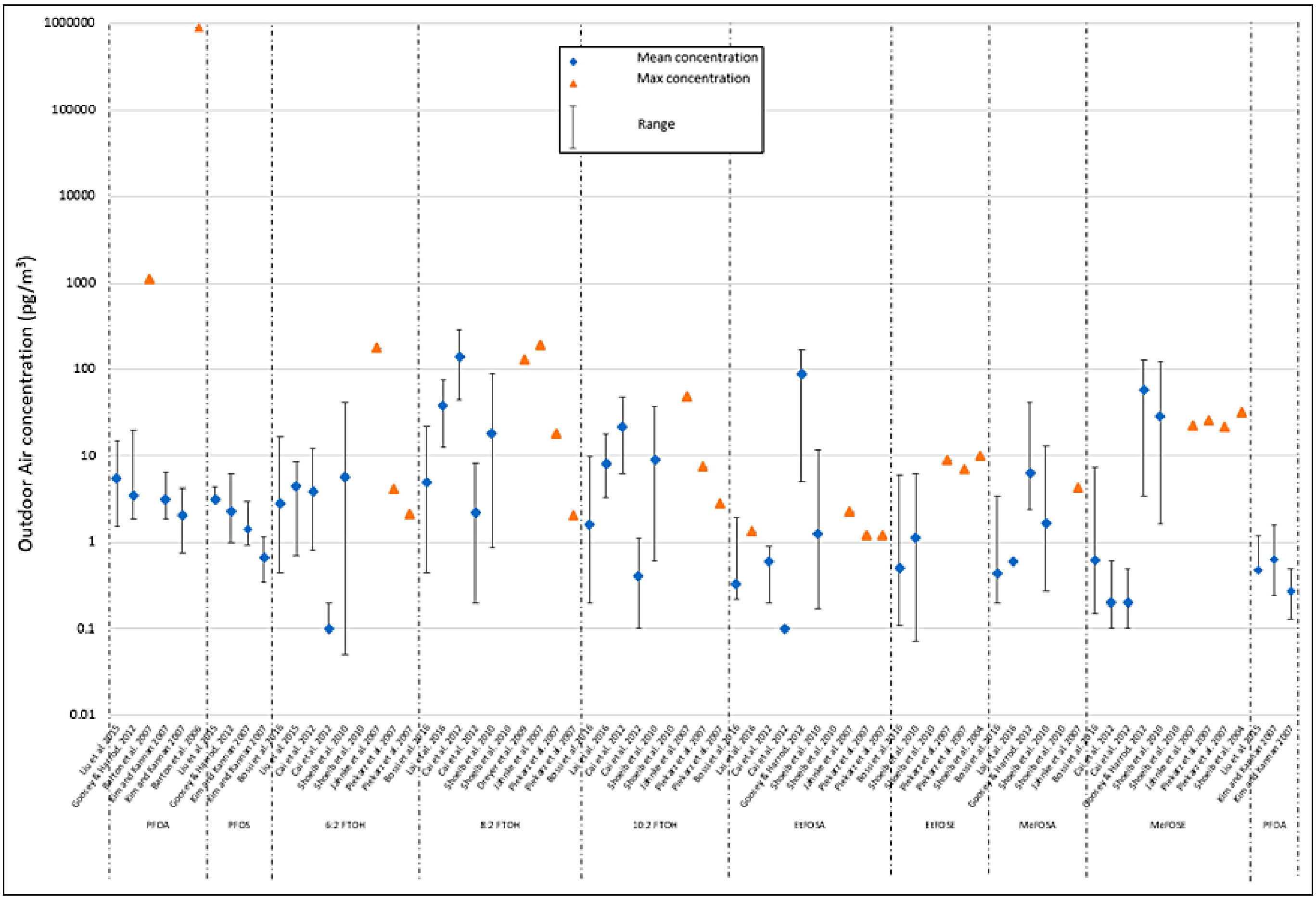


Figure 6-1A. Observed PFAS concentrations in outdoor air.

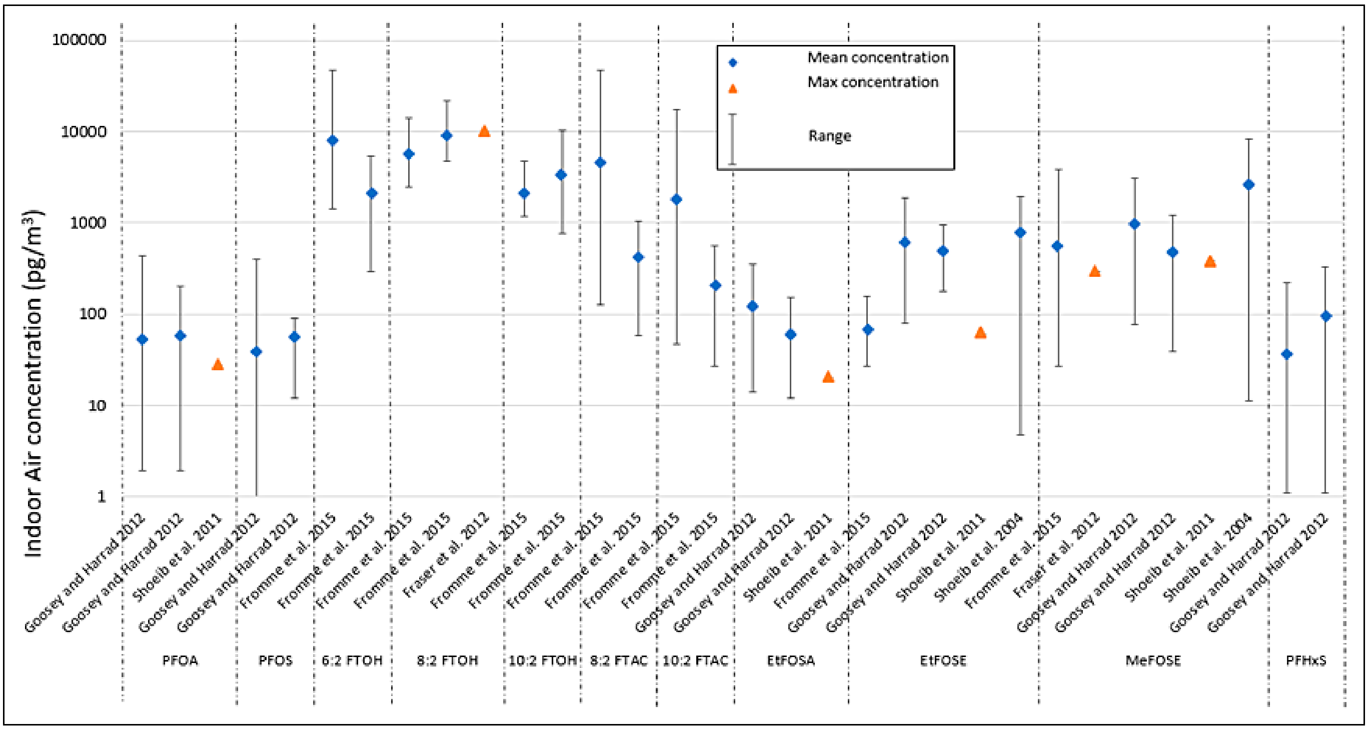


Figure 6-1B. Observed PFAS concentrations in indoor air.

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. PFAA concentrations in soil have been observed across a wide range of locations, which suggests that detection of a PFAA 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 µg/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 µg/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 the sum of PFAS in cores ranged from nondetect to 46.6 µg/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 PFAAs 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.

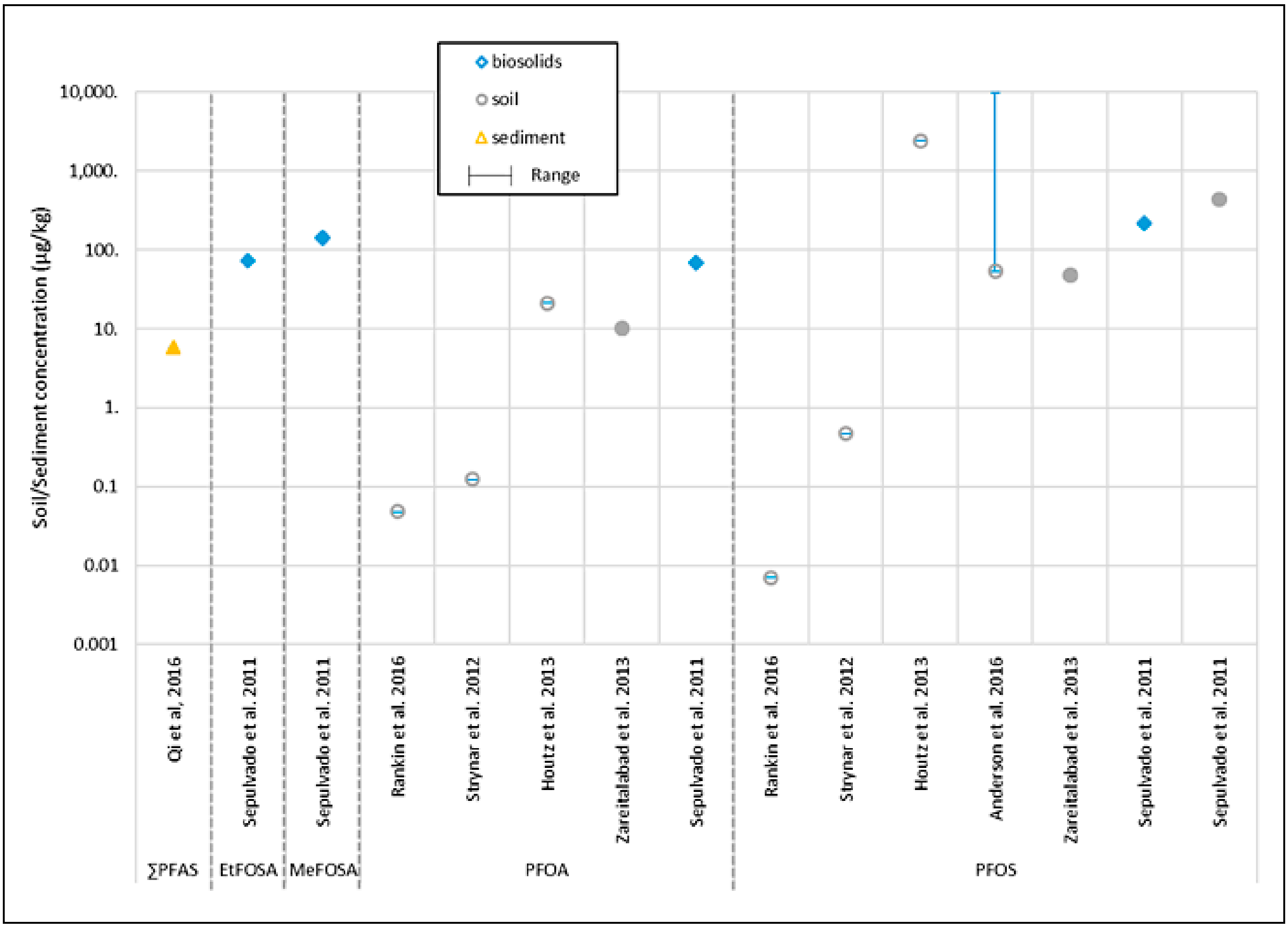


Figure 6-2. Observed PFAS concentrations in soils and sediment.

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 2017). 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 2017); 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 2018); 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.

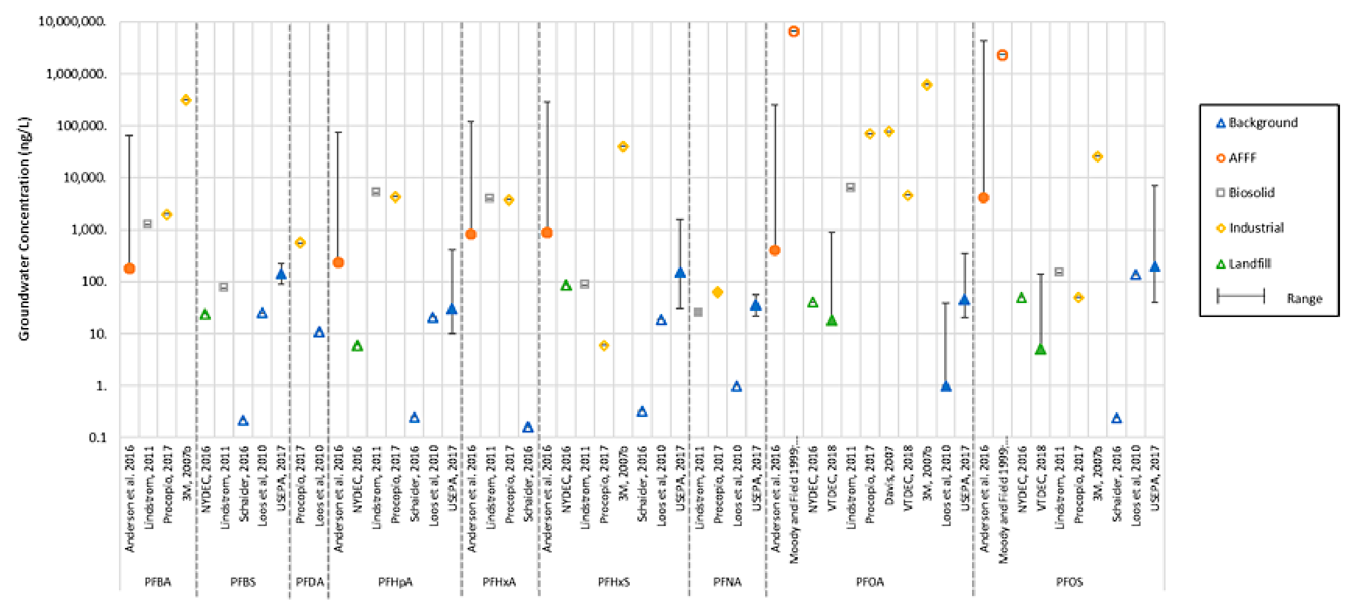


Figure 6-3. Observed PFAS concentrations in groundwater.

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 2018; Post et al. 2013).

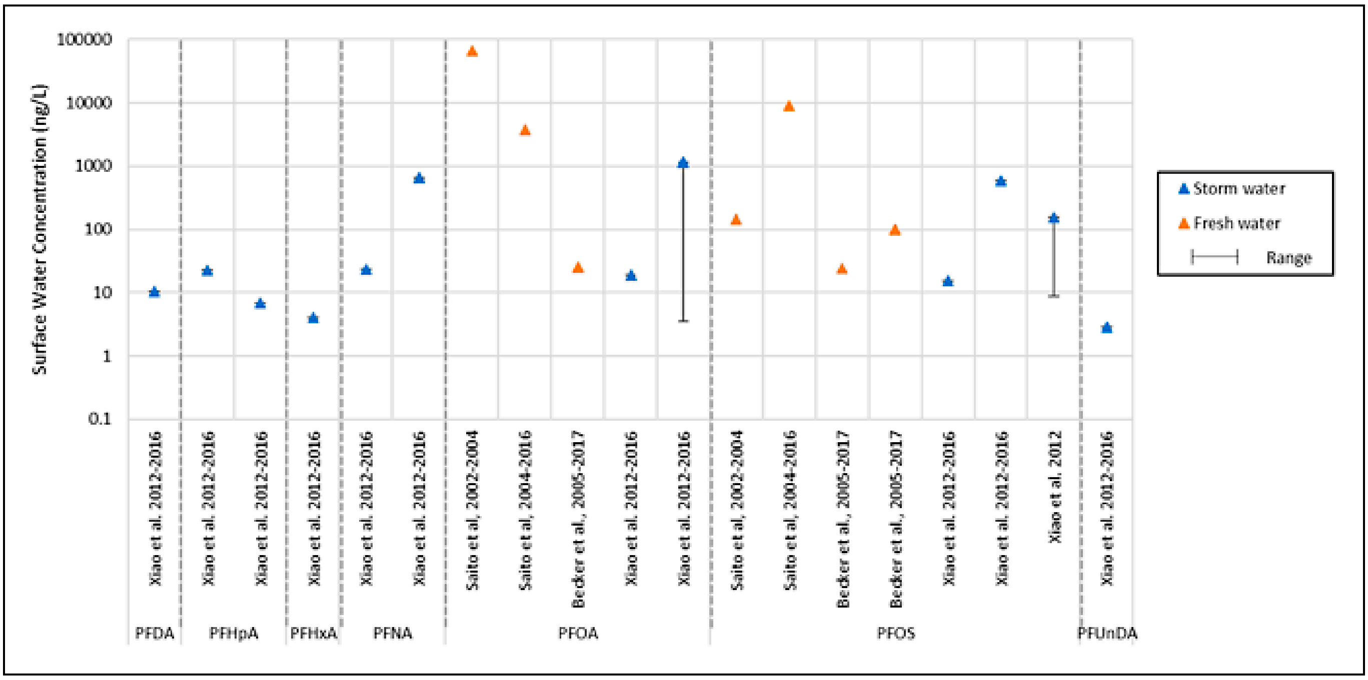


Figure 6-4. Observed PFAS concentrations in surface water.

6.5 Biota

Because PFAS are distributed globally and have a propensity to bioconcentrate, they have been found 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 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 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.

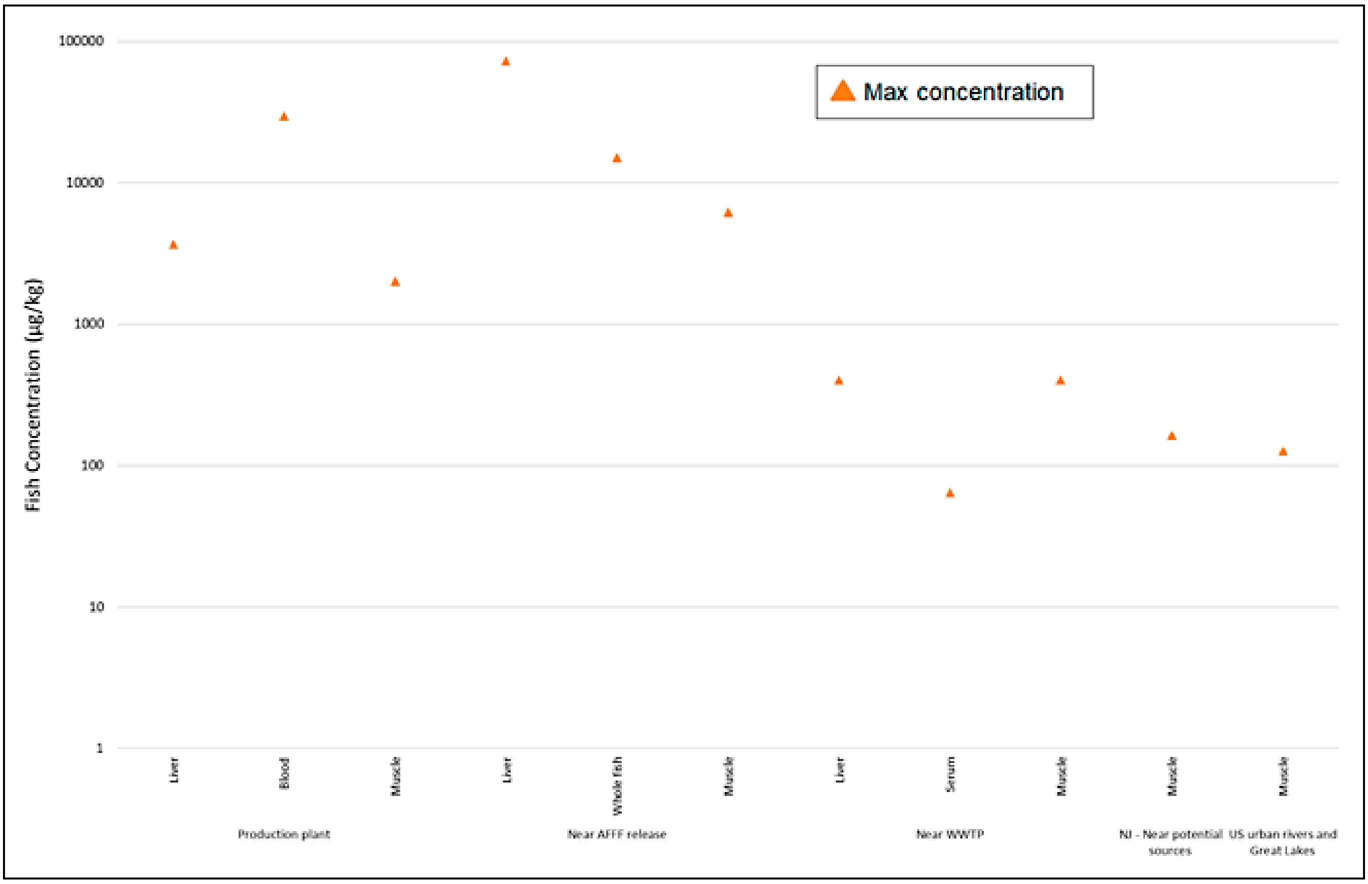


Figure 6-5. Observed PFAS concentrations in fish.

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 Artic 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.

Updated September 2020.

7 Human and Ecological Health Effects of select PFAS

The PFAS Team developed a Human and Ecological Effects training video with content related to this section.

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 per- and polyfluorinated ether carboxylates (PFECAs) commonly known as the GenX chemicals 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.

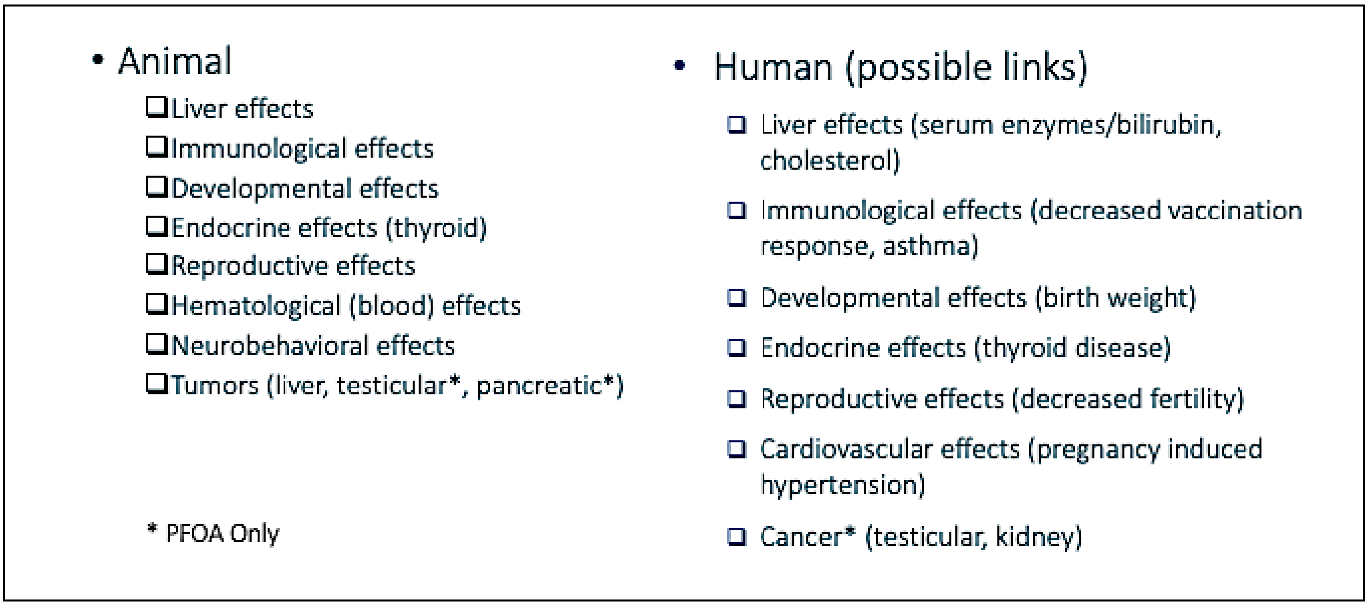
For further information on the scientific names and carbon chain length of PFAAs addressed in these sections, see Section 2.2 of this document. Use of the human health effects information in guidance values is discussed in Section 8.3 and in site risk assessment in Section 9.1.

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 several PFECAs including the GenX chemicals, hexafluoropropylene oxide dimer acid (HFPO-DA) and its ammonium salt, (also known as perfluoro-2-propoxypropanoic acid [PFPrOPrA] and ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoate, respectively) and 4,8-dioxa-3H-perfluorononanoate, commonly known as ADONA. These PFECAs 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.



- Animal
  - ☐ Liver effects
  - ☐ Immunological effects
  - ☐ Developmental effects
  - ☐ Endocrine effects (thyroid)
  - ☐ Reproductive effects
  - ☐ Hematological (blood) effects
  - ☐ Neurobehavioral effects
  - ☐ Tumors (liver, testicular*, pancreatic*)

* PFOA Only

- Human (possible links)
  - ☐ Liver effects (serum enzymes/bilirubin, cholesterol)
  - ☐ Immunological effects (decreased vaccination response, asthma)
  - ☐ Developmental effects (birth weight)
  - ☐ Endocrine effects (thyroid disease)
  - ☐ Reproductive effects (decreased fertility)
  - ☐ Cardiovascular effects (pregnancy induced hypertension)
  - ☐ Cancer* (testicular, kidney)

Figure 7-1. Some health effects of PFOA and/or PFOS identified from published studies (not exhaustive).

USEPA has finalized its toxicity assessments for the GenX chemicals (USEPA 2021) and PFBS (USEPA 2021). The USEPA announced in October 2021 that the draft toxicity assessment for four additional PFAAs (PFNA, PFHXA, PFHXs, PFDA) will be released by the Integrated Risk Information System (IRIS) in spring to fall 2022 and the final PFBA assessment will be completed by the fall of 2022 (USEPA 2021). The USEPA (2021) also made a final regulatory determination to establish drinking water standards (maximum contaminant levels, MCLs) for PFOA and PFOS. As part of this effort, the current USEPA toxicity evaluation for PFOA and PFOS will be updated. USEPA has requested review from the Science Advisory Board of the USEPA's draft documents to support the National Primary Drinking Water Rulemaking for PFAS (USEPA 2021).

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 et al. (2018) and Lau (2012), and in several chapters of the Agency for Toxic Substances and Disease Registry (ATSDR) toxicological profile (ATDSR 2021); DeWitt (2015), and NICNAS (2018) for PFAS in general. Some references for specific PFAS are included in this list:

- PFOA: Australia Government DOH (2018); USEPA (2016); USEPA (2016) and NJDWQI (2017) NJDWQI (2017)
- PFOS: USEPA (2016); USEPA (2016); MDH (2019); and NJDWQI (2018)
- PFNA: NJDWQI (2015)
- PFBS: MDH (2017) and USEPA (2021)
- PFBA and PFHxS: MDH (2018); MDH (2019)
- GenX chemicals: RIVM (2016), Chemours (posted online by NC DEQ (2018)); and USEPA (2021)
- Short-chain PFAAs: Buck (2015) and Danish EPA (2015)
- PFECAs: 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 most 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, PFDoA) 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).

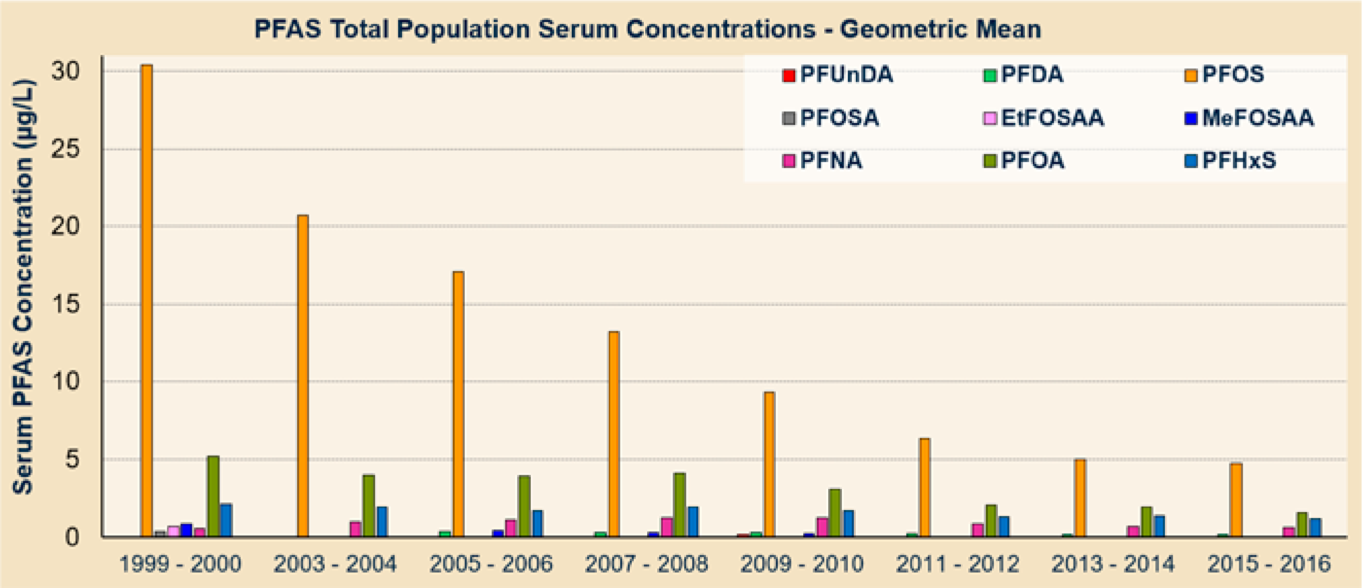


Figure 7-2. Geometric mean serum concentrations (ng/ml) of selected PFAAs (NHANES, 1999-2016).

In the general population, where this 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 2021), 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 (for example, in fluoropolymer manufacturing facilities) 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 (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, Ye, and Calafat 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 et al. 2005; White et al. 2009; Kato, Ye, and Calafat 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 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 2011).

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 2011), 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 2017; Post, Gleason, and Cooper 2017).

Finally, toxicokinetics in rodents (Loveless et al. 2006; De Silva et al. 2009) and humans (Zhang 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 2018). 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 Figure 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 (TWI) 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. The 2018 EFSA TWI's for PFOA and PFOS were replaced with EFSA's revised recommendations released Sept. 17, 2020. These recommendations, also based on human data, set a TWI of 4.4 ng/kg body weight for the sum of four PFAS (PFOA, PFOS, PFNA, and PFHxS) in food (EFSA 2020).

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 PFECAs. 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
- PFECAs including ADONA and the GenX chemical HFPO-DA.

Section 17.2.5.1 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, PFTrDA, PFTeDA, 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 2019; NTP 2019) 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 17.2.5.1 for additional discussion of studies in animals that have evaluated the effects of these PFAS on noncancer and cancer endpoints.

There is increasing awareness and interest in potential human exposure to PFAS other than the PFAAs and the PFECAs, GenX and ADONA, that are discussed in Section 17.2.5.1. These include ether and polyether PFAS, dicarboxylic acid polyether PFAS, fluorotelomer alcohols, and fluorotelomer sulfonic acids. Information relevant to health effects of these additional PFAS is discussed in Section 17.2.6.1.

7.1.5 PFAS Mixtures

This section provides a summary of current toxicity-based approaches for addressing mixtures of PFAS and currently available information on toxicity of PFAS mixtures. This is an active area of research. Additional information is presented in Section 17.2.

7.1.5.1 Approaches for Assessing Toxicity of PFAS Mixtures

Multiple PFAS are present in the blood serum of almost all U.S. residents (Section 7.1.1), and PFAS often occur as mixtures of individual chemicals in the environment (for example, drinking water, fish, soil, and air). Therefore, approaches to assess the toxicity of PFAS mixtures are needed. Development of approaches for consideration of the health effects of mixtures of PFAS is a priority for USEPA, ATSDR, and other U.S. federal agencies, as discussed at a recent National Academy of Sciences (NAS) workshop on federal research on human health effects of PFAS (NAS 2021). Approaches to assessing the toxicity of PFAS mixtures have also been the subject of several peer-reviewed publications (discussed below), including Peters and Gonzalez (2011), Bil et al. (2021), Cousins et al. (2020), and Goodrum et al. (2021). However, as discussed at the NAS workshop, relevant data on several aspects of this topic are limited. For example, there is a lack of information on in vivo and in vitro toxicity of PFAS mixtures, as well as on health effects in human populations when exposure to multiple PFAS has occurred (NAS 2021).

As is the case for mixtures of environmental contaminants in general, the toxicity of PFAS mixtures can be evaluated through studies of defined or undefined mixtures (mixtures of known concentrations of individual PFAS or complex mixtures that may include both known and unidentified PFAS, respectively). The small database of currently available toxicity studies of PFAS mixtures is summarized in Section 17.2. These include a few studies of the undefined PFAS mixtures found in AFFF and a limited number of studies of defined PFAS mixtures, including in vitro studies of nuclear receptor activation in transfected cultured cells, and toxicity studies in cultured cells and zebrafish. Notably, no rodent or primate studies of defined mixtures of PFAS were located. When evaluating exposure and health effects for PFAS mixtures in drinking water or other media, it must be emphasized that identification of the PFAS that are present is dependent both on the composition of the mixture and the suite of PFAS detected by the analytical method that was used (McDonough et al. 2019). Methods currently used for routine analysis are described in Section 11.2. Additional analytical methods (for example, nontarget analysis) that are primarily used in research studies can identify numerous additional PFAS not currently included in standard methods.

As discussed in USEPA and ATSDR guidance for risk assessment of mixtures (USEPA 1986; USEPA 2000; ATSDR 2018), toxicological interactions among components of a mixture may include dose additivity, response additivity, synergism, and antagonism. Dose additivity is based on the assumption that the chemicals in the mixture have the same mode of action (MOA) and cause the same effects, and differ only in potency. The components are assumed to have similarly shaped dose-response curves, and the effect caused by the mixture is assumed to be the sum of the effects caused by each of the individual chemicals present. Response additivity is based on the assumption that the toxic effect of a mixture can be predicted by summing the doses of each chemical in the mixture (relative to each chemical's critical effect dose) such that the contribution from each chemical to the overall effect of the mixture is not influenced by the other chemicals. For example, when assuming additivity, the sum of the incremental cancer risks of multiple individual co-occurring carcinogens can be used to estimate the total cancer risk of the mixture. Toxicological interactions of components of mixtures may also be synergistic (greater than additive) or antagonistic (less than additive), resulting in larger or smaller effects than would occur with dose additivity or response additivity.

As discussed in this section, currently available toxicological information for PFAS does not clearly support a specific approach for conducting risk assessments of PFAS mixtures. While the toxicological effects of many PFAS are generally similar, the most sensitive toxicological endpoints may vary among PFAS. Additionally, multiple MOAs for PFAS toxicity are likely; these MOAs appear to be complex, and currently are not well understood. Furthermore, the MOA for a specific PFAS may not be the same for all effects (for example, hepatic toxicity, developmental toxicity), and a specific effect may not occur through the same MOA for all PFAS (for example, different MOAs for liver toxicity of PFOA and PFOS; Peters and Gonzalez 2011; NAS 2021). In the limited number of studies of PFAS mixtures, additive, synergistic, and antagonistic interactions among PFAS have been observed. As noted by Wolf et al. (2014), toxicological interactions of PFAS are dependent on the identities and concentrations of the PFAS in the mixture, the biological model, and the endpoint being evaluated (see Section 17.2).

Some regulatory agencies consider the cumulative toxicity of PFAS that co-occur in environmental media, while other agencies consider PFAS individually as required by their regulatory process and/or the scientific uncertainty as to whether co-occurring PFAS are sufficiently similar to consider them as a group. Several approaches that have been proposed to address the toxicity of PFAS mixtures are discussed in Section 17.2.7.1. The goal of these approaches is to facilitate the risk assessment of PFAS mixtures detected at contaminated sites and to develop health-protective guidelines that potentially account for the combined effects of multiple PFAS. Some general approaches for assessing the cumulative effects of exposure to PFAS, as related to site risk assessment, are discussed in Section 9.1.3.1. Examples of the application of such approaches to PFAS are reviewed by Cousins et al. (2020), who also provided a "summary of existing or proposed grouping approaches based on the sum of various PFAS in drinking water." Most of the approaches that have been proposed assume dose additivity, although scientific uncertainties are associated with this assumption, as discussed above and in Section 17.2.7.1.

7.1.5.2 Toxicology studies of PFAS mixtures

Only a few studies of the toxicity of defined mixtures of PFAS were located and are summarized in Section 17.2.7.2. These include in vitro studies of nuclear receptor activation in cultured cells transfected with the receptor of interest, and toxicity in cultured cells and zebrafish (a model species for human toxicity). Notably, no mammalian (rodent or primate) studies of defined mixtures of PFAS were located.

7.1.6 Evaluating PFAS using New Approach Methodologies

Traditional toxicity testing methods using in vivo mammalian models are time-, cost-, and labor-intensive. As noted in Section 17.2.8, including Table 17.8, mammalian (most commonly rodent) toxicity information is available for only a relatively small group of PFAS, including a number of long- and short-chain PFCAs and PFSAs, certain fluorotelomer alcohols and fluorotelomer sulfonates, and several of the per- and polyfluoroether replacements, with PFOS and PFOA having the most extensive data sets. Under current USEPA risk assessment guidelines used by most states, in vivo mammalian laboratory animal or human data are required for development of chemical-specific toxicity factors (for example, reference doses) used as the basis for standards and guidance values for PFAS in drinking water and other environmental media. It is therefore important that in vivo mammalian data continue to be made available for those PFAS with a high level of public health concern, such as those detected at elevated concentrations in drinking water. However, in vivo mammalian studies are not feasible for all of the individual PFAS, of which there are thousands (USEPA 2020). Additionally, USEPA aims to refine and reduce the use of mammalian species in toxicology testing and to use non-animal testing methods when appropriate. With the goal of rapidly generating toxicity, MOA, toxicokinetic, and exposure information on PFAS compounds and reducing the use of mammalian species in testing, the USEPA is collaborating with the National Toxicology Program (NTP) of the National Institutes of Environmental Health Sciences through the REACT (Responsive Evaluation and Assessment of Chemical Toxicity) Program. New Approach Methodologies, such as rapid toxicity assays in cultured cells and zebrafish, in silico (computational) approaches, and high throughput exposure modeling are being developed and used with the goal of generating data that will inform toxicology and risk assessment of PFAS compounds (Patlewicz et al., 2019; USEPA 2019, 2019). More information on this effort is provided in Section 17.2.8.

7.1.7 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 PFECAs 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 17.2.9) 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 2019). 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**).

It is important to note that neither these spreadsheets nor this section are 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. Application of these data in ecological risk assessment is discussed in Section 9.2

7.2.1 Introduction

Biomonitoring studies across a variety of organisms, habitats, and geographies show that certain PFAS 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 certain PFAS, 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, 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 (**the Excel spreadsheet has three tabs for the following tables**):

- **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. 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 by 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. There are a handful of avian studies on multiple species that investigate egg hatching outcomes and potential correlations to PFAS exposures (Custer et al. 2014; Groffen et al. 2019; Tartu 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

Toxicity	Very High	High	Moderate	Low	Very Low
USEPA: Aquatic Toxicity (Chronic)	<0.1	0.1–1	>1–10	>10	NA

7.2.2 Invertebrates

7.2.2.1 Aquatic

There are more toxicity data available for PFOS than for other PFAS. A summary of the range of acute toxicity surface water concentrations 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 to invertebrates. One exception with this generalization is that of mussel exposures to PFOS and PFOA in the marine environment, where no effect was seen at 0.00001 mg/L but LOEC was reported at 0.0001 mg/L (Fabbri et al. 2014); this would result in classification as a high hazard using the USEPA Hazard Criteria. With the current body of literature, the sensitivity of marine invertebrates to PFOS and PFOA appears equivocal.

Compared to acute studies, there are relatively few chronic studies in aquatic invertebrates. Most chronic effects data are for PFOS and PFOA. 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, with reduced total emergence reported at 0.0023 mg PFOS/L (MacDonald et al. 2004). More recent studies, including McCarthy et al. (2021), show impairment on survival in the chironomid (*C. dilutus*) at even lower concentrations, with EC10 and EC20 values in 20-day tests for PFOS at 1.4 and 1.7 ug/L, respectively. 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 2000).

Some PFAS may potentially cause adverse effects in aquatic invertebrates that span across multiple generations. Marziali et al. (2019) evaluated generational effects in chironomids (*C. riparius*); each generation was exposed to a nominal concentration of 0.01 mg/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. However, potential effects at the population level were not demonstrated in this study based on similar population growth rates between treatments and controls, suggesting that toxicity risk to an ecosystem is unlikely (Marziali et al. 2019).

Table 7-5. Typical range of acute toxicity values for aquatic invertebrates for select PFAS.

PFAS	Range of Toxicity Values (mg/L)	Reference(s)
PFBA	182–5251	Ding et al. 2012; Barmentlo et al. 2015
PFBS	2,183	Ding et al. 2012
PFHxA	1,048	Barmentlo et al. 2015
PFOS	57.9–169	3M Company 2003; Boudreau et al. 2003
PFOS-Marine	1.1 (EC50)–9.4 (EC50)	Drottar and Krueger 2000; Robertson 1986; Hayman et al. 2021
PFOA	131–477	Ji et al. 2008; Ding et al. 2012
PFOA-Marine	9.98–24	Hayman et al. 2021
PFNA	31–151	Zheng et al. 2011
PFDA	26–163	Ding et al. 2012
PFUnA	19–133	Ding et al. 2012
PFDoDA	28–66.3	Ding et al. 2012

PFAS	Range of Toxicity Values (mg/L)	Reference(s)
PFBS	NOEC 13–42.7 LOEC 4.8– >42.7	Sant et al. 2018 McCarthy et al. 2021
PFOS	NOEC 0.0004–94.9	MacDonald et al. 2004; Boudreau et al. 2003; McCarthy et al. 2021; Stefani et al. 2014; Marziali et al. 2019
	LOEC 0.00209-42.9	
PFOA	NOEC 3.125– >227	Li 2010; Ji et al. 2008; McCarthy et al. 2021
	LOEC 6.25– >227	
PFNA	NOEC 0.008–1.36 LOEC 0.04– >1.36	Lu et al. 2015; McCarthy et al. 2021
Note: Refer to the PFAS ecotoxicology data summary Table 7-1 in the separate Excel spreadsheet for toxicological endpoints and values. EC50 = median effective concentration. The concentration of test substance that results in a 50% reduction in growth or growth rate LC50 = concentration of test substance lethal to 50% of test population LOEC = lowest observed effect concentration NOEC = no observed effect concentration		

Benthic Organisms and Sediment Toxicity

Toxicity to benthic organisms is generally the result of exposure to the chemical in overlying water, sediment, and porewater, including trophic transfer and sediment particle ingestion (Zareitalabad et al. 2013). There are relatively few published sediment toxicity studies on PFAS exposure to benthic invertebrates. 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, was reported as 0.22 mg/kg. This value, however, is based on an aquatic probable no effect concentration (PNEC) of 72 µg/L derived from a limited data set and an unspecified K_d value, and thus is not a reliable concentration with which to predict toxic effects. The UK Environment Agency (2004) provided a sediment screening value of 0.0067 mg/kg (wet weight), based upon a PNEC of 2.5 µg/L and a river sediment K_d of 8.7 L/kg. Note, however, that sediment screening values based on K_d may not be applicable across all sites. Section 9.2 (Ecological Risk Assessment) discusses application of K_d in deriving sediment screening values.

More recently, Simpson et al. (2021) conducted a multimedia acute and chronic study on a variety of marine/estuarine invertebrates (including an amphipod, a copepod, a crab, and two species of bivalve) that included PFOS-spiked sediment toxicity tests. Simpson et al. (2021) found that PFOS significantly decreased survival and/or reproduction for the amphipod (*Melita plumulosa*) at sediment concentrations of 29 mg/kg or greater. Although they did not identify a relationship between toxicity and PFOS concentrations in sediment, they observed a strong relationship among toxicity, organic carbon content of sediments, and dissolved PFOS concentrations in the overlying water of the test vessel. These results suggested that the dissolved fraction of PFOS in water is likely a key contributor to sediment toxicity. Based on sediment concentrations normalized to 1% organic carbon (1%OC), the authors derived an LC10 of 132 mg/kg (1%OC) and LC50 of 150 mg/kg (1%OC) for PFOS, and EC10, EC20, and EC50 of 21, 35, and 89 mg/kg (1%OC), respectively, for reproductive effects (Simpson et al. 2021). The focus of Simpson et al. (2021) was on the amphipod, but this publication also provided data for additional marine species. The authors also developed sediment thresholds using K_d and species sensitivity distributions from water exposures (see Section 9.2 for more information).

Table 7-6 summarizes toxicity ranges for PFOS, PFOA, and PFBS in benthic invertebrates from the limited available information. Laboratory-controlled freshwater sediment toxicity tests for PFAS have not yet been published or broadly reported. 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. However, benthic organism toxicity thresholds do not need to be limited to just invertebrates, as shown by the Simpson et al. (2021) paper, which developed PFOS thresholds from a species sensitivity distribution (SSD) generated from published data on other types of species using a K_d approach.

Table 7-6. Typical range of benthic invertebrate toxicity values for select PFAS.

PFAS	Range of Toxicity Values (mg/kg or mg/L)	Reference(s)
PFOS	132 (LC10)–150 (LC50) mg/kg, at 1% organic carbon in sediment	Simpson et al. 2021
PFOS	21 (EC10), 35 (EC20), and 89 (EC50) mg/kg at 1% organic carbon in sediment	Simpson et al. 2021
PFOS (acid)	0.00001 (NOEC)–59 (LC50), in mg/L	Drottar and Krueger 2000; Fabbri et al. 2014; OECD 2002; MPCA 2007
PFOA (acid)	0.00001 (NOEC)–0.0001 (LOEC), in mg/L	Fabbri et al. 2014
PFOS (salt)	<0.0023 (NOEC)– >0.150 (EC50), in mg/L	MacDonald et al. 2004
PFOA (acid)	0.0089, 100 (NOEC, chronic), in mg/L	MacDonald et al. 2004; Stefani et al. 2014
PFBS (acid)	0.0077 (NOEC, chronic), in mg/L	Stefani et al. 2014

Note: Refer to the PFAS ecotoxicology data summary Table 7-1 in the separate Excel spreadsheet for toxicological endpoints and values.
EC10 = concentration of test substance at which 10% of the test organisms exhibit a statistically significant effect
EC20 = concentration of test substance at which 20% of the test organisms exhibit a statistically significant effect
EC50 = median effective concentration. The concentration of test substance that results in a 50% reduction in growth or growth rate
LC10 = concentration of test substance lethal to 10% of test population
LC50 = concentration of test substance lethal to 50% of test population
LOEC = lowest observed effect concentration
NOEC = no observed effect concentration

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 melifera*), 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 have been shown to carry down through multiple generations in the roundworm (*Caenorhabditis elegans*). 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 et al. 2014; Zareitalabad 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 in comparison with the controls. Importantly, the authors report tissue concentrations following exposures to PFBS, PFHxS, PFNA and PFHpA thus indicating potential for trophic transfer from soil to higher level organisms (Karnjanapiboonwong et al. 2018).

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. Typical range of terrestrial invertebrate toxicity values for select PFAS.

PFAS	Range of Toxicity Values (mg/kg)	Reference(s)
Acute Studies		
PFOS	77 (NOEC)–373 (LC50)	Sindermann et al. 2002
Chronic Studies		
PFOS	1 (NOEC)–233 (LOEC)	Mayilswami 2014; Xu et al. 2013; Sindermann et al. 2002 Princz et al. 2018; Zhao et al. 2014; Zareitalabad, Siemens, Wichern, et al. 2013
PFOA	1 (NOEC)–84 (LC50)	He, Megharaj, and Naidu 2016; Zareitalabad, Siemens, Wichern, et al. 2013
6:2 FTS	30 (EC10)–566 (EC50)	NPCA 2006
PFBS	100 (NOEC)	Karnjanapiboonwong et al. 2018
PFHxS, PFHpA	100 (LOEC)	Karnjanapiboonwong et al. 2018
PFNA	100 (LOEC)	Karnjanapiboonwong et al. 2018

Note: Refer to Table 7-2 in the separate Excel spreadsheet for toxicological endpoints and values.
EC10 = concentration of test substance at which 10% of the test organisms exhibit a statistically significant effect
EC50 = median effective concentration. The concentration of test substance that results in a 50% reduction in growth or growth rate
LC50 = Concentration of test substance lethal to 50% of test population
LOEC = lowest observed effect concentration
NOEC = no observed effect concentration

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, but (Drottar and Krueger 2000) calculated a chronic NOAEL based on early life stage mortality to be 0.29 mg/L. Palmer, Van Hoven and Krueger (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' PFAS. 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. Typical range of fish toxicity values for select PFAS.

PFAS	Range of Toxicity Values: EC or LC50 (mg/L)	Reference(s)
PFBA	2,200 (EC50; developmental); >3,000 (LC50; survival)	Ulhaq et al. 2013
PFBS	450 (EC50; developmental); 1,500 (LC50; survival)	Ulhaq et al. 2013
PFOS	7.8 (EC50)–22 (EC50; survival)	Robertson 1986; Palmer, Van Hoven and Krueger 2002
PFOA	430 (LC50)	Ulhaq et al. 2013
PFNA	84 (LC50)	Zhang et al. 2012
PFDA	5 (EC50; developmental); 8.4 (LC50)	Ulhaq et al. 2013
PFOS	NOEC 0.29; EC50 7.2	Drottar and Krueger 2000; Oakes et al. 2005
PFNA	LOEC 0.01 (growth)	Zhang et al. 2012
Note: Refer to Table 7-1 in the separate Excel spreadsheet for toxicological endpoints and values. EC50 = median effective concentration. The concentration of test substance that results in a 50% reduction in growth or growth rate LC50 = concentration of test substance lethal to 50% of test population LOEC = lowest observed effect concentration NOEC = no observed effect concentration		

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 acute and chronic toxicity data for amphibians.

More amphibian data are available for PFOS in comparison to other PFAS, and indicate mortality generally tends to occur at levels of 10 mg/L or higher, whereas nonlethal effects may occur at approximately 1–2 mg/L (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 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.

Amphibian studies suggest that, while PFOS is more toxic than PFOA, it may be less toxic relative to certain other PFAS, for example, Yang et al. (2014) and Abercrombie et al.(2021). Brown, Flynn, and Hoverman (2021) found increased trematode infection in the northern leopard frog resulting from exposure to 0.01 mg/L PFHxS, whereas no effect was observed for PFOS (however, no such effect was noted in the higher PFHxS treatment dose of 0.1 mg/L; the authors postulated that this could potentially be due to adverse effects of PFHxS to the trematode itself).

Many of the older amphibian studies focused on early life aquatic exposures. More recent studies suggest that amphibians may be even more sensitive to PFAS if one looks at later life stages; nonlethal effects other than survival; growth and reproduction; terrestrial exposure routes; or multiple exposure media. Abercrombie et al. (2021) indicated LOECs ranging from 0.05-0.12 mg/L for a toad, frog, and salamander exposed to PFOS, PFOA, or PFHxS in a soil substrate. Flynn et al. (2021) found enhanced PFOS and PFOA toxicity in a spiked sediment outdoor mesocosm study, suggesting that evaluating only aquatic exposures may underestimate toxicity from exposure to PFAS in multiple media, which is more representative of actual field conditions.

Table 7-9. Typical range of amphibian toxicity values for select PFAS.

PFAS	Range of Toxicity Values-NOEC/LOEC (mg/L)	Reference(s)
Acute Studies		
PFOS	3.6 (NOEC)–81 (EC50)	Yang et al. 2014; Stevens and Coryell 2007; Ankley et al. 2004; OECD 2002
PFOA	115 (LC50)	Yang et al. 2014
Chronic Studies (EC10)		
PFOS	1 (LOEC; metamorphosis)–2 (EC10; longevity)	Fort et al. 2019; Yang et al. 2014
PFOA	5.89 (EC10; longevity)	Yang et al. 2014

Note: Refer to Table 7-1 in the separate Excel spreadsheet for toxicological endpoints and values.
EC10 = concentration of test substance at which 10% of the test organisms exhibit a statistically significant effect
EC50 = median effective concentration. The concentration of test substance that results in a 50% reduction in growth or growth rate
LC50 = concentration of test substance lethal to 50% of test population
LOEC = lowest observed effect concentration
NOEC = no observed effect concentration

7.2.3.3 Birds

There are currently a limited number of published laboratory studies available that address PFAS toxicity in avian wildlife species (Newsted et al. 2006; Newsted et al. 2005; Newsted et al. 2007; Newsted et al. 2008; Dennis et al. 2020; Bursian et al. 2021). The northern bobwhite quail (*Colinus virginianus*) and the mallard duck (*Anas platyrhynchos*) were exposed to PFOS (Newsted et al. 2005; Newsted et al. 2006; Newsted et al. 2007) or PFBS (Newsted et al. 2008) via the diet. -The LD50s reported following acute exposure to PFOS are 61 mg/kg-bw/d and 150 mg/kg-bw/d for the northern bobwhite quail and the mallard duck, respectively (Newsted et al. 2006). In a separate chronic dietary study, Newsted et al. (2007) found that a feed concentration of 10 mg PFOS/kg resulted in an average daily intake (ADI) LOAEL of 0.77 mg/kg-bw/d based on increased liver weight in female quail. A feed concentration rate of 50 mg/kg resulted in an ADI LOAEL of 6.4 mg/kg-bw/d based on lethality in mallards (Newsted et al. 2007).

More recent avian studies on the northern bobwhite (Dennis et al. 2020) and Japanese quail (Bursian et al. 2021) evaluated dietary effects of PFOS, PFOA, PFHxS, and the AFFF formulations from 3M and Ansul. Bursian et al. (2021) estimated average daily doses causing 50% mortality (ADD50) at 5 days' exposure ranging from 38 mg/kg-d for PFOS (≥98% chemical grade) to 130 mg/kg-d for PFOS in feed spiked with 3M AFFF, which is a product formulation (see Section 3) that is a mixture of fluorinated and other compounds (LC50 of 351–467 mg/kg of feed, respectively). More information about AFFF is included in Section 3. This subacute study also evaluated effects resulting from a mixture of PFOS and PFOA; the authors suggested that these results showed potential additive effects, and a relative potency of PFOA approximately half that of PFOS (Bursian et al. 2021). Dennis et al. (2020) evaluated chronic toxicity associated with PFOS and a mixture of PFOS and PFHxS in drinking water on the northern bobwhite quail. Reduced body weight in females and impaired hatching success were observed at doses lower than those used in the Newsted study (Newsted et al. 2007), deriving a chronic toxic dose of 0.0031 mg PFOS+ PFHxS/kg-bw/d and 0.00245 mg PFOS/kg-bw/d, respective to the previously mentioned endpoints.

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 relative to PFOS. Acute dietary exposure to PFBS resulted in NOAELs of 3,160 and 5,620 mg PFBS/kg-feed for the northern bobwhite quail and mallard duck, respectively, for the lethal endpoint; these feed concentrations are equivalent to an ADI of 774 mg/kg-bw/d in quail and 2,190 mg/kg-bw/d in mallard ducks (Newsted et al. 2008). A NOAEC for northern bobwhite quail reproduction following dietary exposure to PFBS was reported at 900 mg/kg-feed, equivalent to an ADI of 87.8 mg/kg-bw/d.

Although there are few PFAS laboratory toxicity studies for birds, there are even fewer effect-based field studies. Custer et al. (2012) and Custer et al. (2014) evaluated PFOS exposure in tree swallows, identifying a negative association between PFOS concentration in eggs (~150 ng/g-ww) and hatching success. One issue with the findings as suggested by the authors is that the greatest observed effects on hatching were typically found in areas that likely have co-contamination issues (PCBs, PAHs, mercury); however, the influence of these other contaminants is still not clear. This issue of effects from co-contaminants came to light when Custer et al. (2019) conducted a field study evaluating the effects of PFAS on tree swallows in a more isolated area with known PFAS impacts (Clark's Marsh near the former Wurtsmith Air Force Base, MI); other potential contaminants were at or below regional anthropogenic background levels. This study resulted in mean PFOS egg concentrations of 662 ng/g-ww, and overall hatching success was not impacted. Groffen et al. (2019) conducted a field study in great tits (*Parus major*) near a former fluorochemical plant. They reported median egg concentrations of 48,056 ng/g-ww for PFOS, 18 ng/g-ww for PFOA, and 315 ng/g-ww for PFDS. The authors concluded that reduced hatching success in the birds was associated with a mixture of PFAS (PFOS, PFDS, PFDoDA, PFTrDA, and PFTeDA) (Groffen et al. 2019). Taken together, a linear relationship between PFAS exposure and potential effects in avian species remains uncertain; this highlights the importance of considering co-exposure of common environmental contaminants and PFAS mixtures when reviewing field studies.

Lastly, indirect effects, such as reduction in a local food source resulting from a PFAS release, may potentially affect bird populations. de Vries et al. (2017), for example, found a decline in abundance of flamingos following a release of fire-fighting foams containing PFOS and other PFAS to a salt lake; the authors postulated that this decline was potentially related to a reduction in prey item abundance due to PFOS toxicity. Table 7-10 summarizes the avian studies.

Table 7-10 Typical range of avian toxicity values for select PFAS

PFAS	Range of Toxicity Values	Reference(s)
Acute Studies–Dietary (mg/kg-bw/d)		
PFOS	LD50s: 38–150	Newsted et al. 2006; Bursian et al. 2021
PFOA	ADD50: 68	Bursian et al. 2021
PFBS	NOAEL: 774-2,190	Newsted et al. 2008
Chronic Studies – Dietary/ Drinking Water (mg/kg-bw/d)		
PFOS	LOAEL: 0.00245-0.77	Dennis et al. 2020; Newsted et al. 2007
PFOS + PFHxS	LOAEL: 0.0031	Dennis et al. 2020
PFBS	NOAEL: 87.8	Newsted et al. 2008
Note: Refer to Table 7-2 in the separate Excel spreadsheet for toxicological endpoints and values. ADD50 = average daily dose resulting in 50% mortality LD50 = dose that is lethal to 50% of test population LOAEL = lowest observed adverse effect level NOAEL = no observed adverse effect level		

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 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 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 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 possible immune effects (Kannan, Perotta and Thomas 2006).

Table 7-11 summarizes these studies.

Table 7-11. Summary of PFAS toxicity studies in mammalian wildlife

Species	Summary of Findings	Reference
Sea otter *Enhydra lutris*	Higher PFOS/PFOA concentrations in liver samples found in diseased otters versus nondiseased group	Kannan, Perrotta and Thomas 2006
Bottlenose dolphin *Tursiops truncatus*	Significant positive associations between serum total PFAS concentrations and multiple immunological, hematopoietic, renal, and hepatic function endpoints	Fair et al. 2013
Wood mouse *Apodemus sylvaticus*	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 et al. 2004
Wild pig *Sus scrofa*	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, 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 2000). 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. 2001, Desjardins et al. 2001; Desjardins et al. 2001).

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 7-12 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 7-12. Typical range of terrestrial plant toxicity values for select PFAS.

PFAS	Range of Toxicity Values (mg/kg)	Reference(s)
Acute Studies		

PFAS	Range of Toxicity Values (mg/kg)	Reference(s)
PFOS	<3.9 (NOEC; growth)– >1,000 (EC50; survival)	Qu et al. 2010; Zhao et al. 2014; Li 2009; Brignole et al. 2003
PFOA	107 (EC50; growth)–170 (EC50; growth)	Li 2009; Zhao et al. 2011
Chronic Studies		
PFOS	1 (NOEC; growth)	Zhao et al. 2014
PFOA	30 (NOEC; growth)	Zhao et al. 2014
Note: Refer to Table 7-2 in the separate Excel spreadsheet for toxicological endpoints and values. EC50 = median effective concentration. The concentration of test substance that results in a 50% reduction in growth or growth rate NOEC = no observed effect concentration		

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 in the current literature (as of 2021). 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 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 (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 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.

Updated August 2021.

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8 Basis of Regulations

The PFAS Team developed a Risk Assessment and Regulations training video with content related to this section.

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 on the fact sheets page). 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 also posted on the fact sheets page 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 on the fact sheets page 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 2017). Additionally, the Organisation for Economic Co-operation and Development OECD (2015) 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. The USEPA (2021) website on PFAS laws and regulations includes information about some of these programs.

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.

8.2.2.1 National Defense Authorization Act (NDAA)

Through the NDAA, which is enacted early each year, Congress mandates a number of actions that the Department of Defense (DOD) must comply with, some of them concerning PFAS. At times, separate PFAS-related requirements for the USEPA or other federal entities are also made. Although these activities are not regulatory or guidance in nature, they are important in advancing human health exposure studies of PFAS in drinking water, remediation of PFAS-contaminated water, development of new technologies to reduce PFAS exposure, and inter-agency collaboration on PFAS.

The NDAA for fiscal year 2018 (https://www.congress.gov/bill/115th-congress/house-bill/2810/text) mandated the Centers for Disease Control and Prevention (CDC) and the Agency for Toxic Substances and Disease Registry (ATSDR) to study PFAS exposure and health implications in communities near current or former military bases and known to have had PFAS in their drinking water, groundwater, or other sources of water. The study is required to be completed within 5 years of the enactment of the 2018 NDAA (or 7 years if an extension is requested and justified).

The NDAA for fiscal year 2019 (https://www.congress.gov/bill/115th-congress/house-bill/5515/text) included the following requirements for the DOD:

- Assessing PFAS contamination at DOD installations and the surrounding community and identifying remediation actions, if needed, within 180 days after the USEPA establishes maximum contaminant levels (MCLs) for PFAS in drinking water
- Conducting an assessment of health implications of PFAS exposure to members of the armed forces and veterans who may have been exposed while serving in the armed forces

The NDAA for fiscal year 2020 (https://www.congress.gov/bill/116th-congress/senate-bill/1790/text) included the following requirements for the DOD:

- 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
- Disposing of PFAS-containing materials by incineration to limit or eliminate PFAS air emissions, comply with Clean Air Act requirements, store waste in accordance with hazardous waste storage requirements (40 CFR Part 264). These activities are to be conducted only at Subtitle C (of Solid Waste Disposal Act) permitted facilities.

For the USEPA, some of the requirements of the 2020 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. These are discussed in Sections 8.2.2.4 and 8.2.2.9, respectively.

The NDAA for fiscal year 2021 (https://www.congress.gov/bill/116th-congress/house-bill/6395/text) contains the following PFAS-related components:

- Allowing DOD to award cash and/or nonmonetary prizes for the development of non-PFAS-containing firefighting agent to replace aqueous film-forming foam (AFFF)
- Mandating a survey of technologies other than firefighting agent solutions to replace AFFF
- Researching alternatives to AFFF, especially using green or sustainable chemistry
- Establishing an interagency working group to coordinate federal PFAS research and development
- Prohibiting DOD from purchasing certain items (e.g., nonstick cookware, stain-resistant floor coverings, etc.) containing PFOS or PFOA
- Notifying agricultural operations within 1 mile downgradient of a DOD installation or National Guard facility where PFOA, PFOS, or PFBS have been detected in groundwater above certain levels

Other than requiring an interagency PFAS work group to be formed, the 2021 NDAA did not have specific requirements for other federal entities.

The NDAA for fiscal year 2022 (https://www.congress.gov/bill/117th-congress/senate-bill/1605) contains several additional PFAS-related components, including a temporary moratorium on incineration of AFFF generated by DOD.

8.2.2.2 USEPA PFAS Action Plan

USEPA issued a PFAS Action Plan (USEPA 2019) in February 2019 and an update a year later (USEPA 2020). The plan included a discussion about the process for moving forward to establish PFOA and PFOS MCLs for drinking water, and it included a number of main actions that encompassed more than just safe drinking water issues. More information about USEPA’s previous actions to address PFAS are available on their website (USEPA 2021).

8.2.2.3 USEPA Strategic Roadmap

In October 2021, the EPA published the *PFAS Strategic Roadmap: EPA’s Commitments to Action 2021–2024* (USEPA 2021). The USEPA’s stated goals for addressing PFAS are focusing on research, restriction, and remediation. The strategic roadmap includes actions across the different divisions of USEPA. More information about USEPA’s actions in 2021 to address PFAS are available on their website (USEPA 2021).

8.2.2.4 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 MCLs for specific chemicals and to 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 or to water not being used for drinking.

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 2016, USEPA 2016). 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 2009). 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 2016, USEPA 2016). 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 2016, pg. 2).

Much of the current occurrence data available regarding PFAS in public drinking water was generated by USEPA under the SDWA UCMR program (USEPA 2017). 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 was 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).

The USEPA and some states use 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), 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 2017).

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

Chemical	**Reporting Limit (ppt)**	**Number of PWSs**[1]	**PWS (%)**[1]
PFOS	40	46	0.9
PFOA	20	13	0.3
∑ PFOA + PFOS2		63	1.3

[1] Number and percent of PWSs that exceeded the health advisory by chemical

[2] PWSs that exceeded the combined PFOA and PFOS health advisory (USEPA 2016; 2017)

The USEPA has not established regulations for any PFAS under the SDWA; however, in its 2019 PFAS Action Plan (USEPA 2019), the agency indicated that it would take steps to evaluate the need for MCLs for PFOA and PFOS, and proceeded to develop a preliminary Regulatory Determination for these two PFAS. In February 2021, the EPA made a Final Regulatory Determination for PFOA and PFOS—a key step in the development of national primary drinking water regulations (that is, MCLs). The agency must now propose MCL(s) within 2 years of this date, and finalize them within 18 months of the proposed regulation.

For PFAS and other unregulated drinking water contaminants with limited occurrence data, the USEPA begins the process of making regulatory decisions under the SDWA by evaluating the nationwide extent of drinking water contamination. This evaluation begins with including contaminants in the Contaminant Candidate List (CCL) under the UCMR, which requires public water systems to collect drinking water data on listed contaminants. On July 19, 2021, the USEPA published the draft fifth CCL5 (USEPA 2021).

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 2009, 2014, 2015).

8.2.2.5 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 2017). 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 perfluoroalkyl carboxylic acids (PFCAs) and their salts and precursors that were used in carpets or to treat carpets (USEPA 2015). 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 2017). 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. 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 2018).

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 perfluoroalkyl carboxylate (LCPFAC) substances 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. In October 2021, USEPA published the National PFAS Testing Strategy. "This Strategy will help EPA identify and select PFAS for which the Agency will require testing using TSCA authorities" (USEPA 2021).

8.2.2.6 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 2019), 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 2017). 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 1997). The ARAR process can be complex and can result in impacts on scope, budget, and public acceptance components of a project (USEPA 2019).

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 2021) and the RSL online calculator (USEPA 2017) 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 2003). 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. USEPA issued a final toxicity value for PFBS in April 2021 (USEPA 2021). In October 2021, USEPA issued a final toxicity assessment for GenX chemicals (USEPA 2021). 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 2016).

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 2016) 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 4.1and 5.1), site-specific values will need to be derived.

8.2.2.7 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 2015). 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.

On June 23, 2021, New Mexico Governor Michelle Lujan Grisham petitioned USEPA Administrator Michael Regan to designate PFAS as “hazardous waste” under the Resource Conservation and Recovery Act, citing imminent and substantial endangerment. On October 26, 2021, EPA administrator Regan responded to the governor’s petition (USEPA 2021). In this response it was announced that USEPA will be initiating the process to add four PFAS (PFOA, PFOS, PFBS, and GenX) as RCRA Hazardous Constituents. In addition, there will be a rulemaking effort to clarify that RCRA has the authority to require the cleanup of wastes that meet the definition of hazardous waste. This will mean that “emerging contaminants such as PFAS can be cleaned up through the RCRA corrective action process.” (USEPA 2021).

8.2.2.8 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 (2021) 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.

8.2.2.9 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 2018). 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.

8.2.2.10 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 2020). 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 2020).

8.2.2.11 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).

8.2.2.12 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 description of ATSDR's actions regarding PFAS is on their web page (ATSDR, 2018). In May 2021, ATSDR released a final *Toxicological Profile for Perfluoroalkyls* (ATSDR 2021). 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 entities posted as an Excel file on the fact sheets page 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, to supplement that survey with the most up-to-date information on state PFAS actions, ITRC has developed a table that summarizes the regulations and programs in each state that target PFAS (provided as an Excel file on the fact sheets page). The focus of this table is on PFAS regulations that have been enacted by any of the states or territories of the United States. The table also includes state programs that may not be mandated by a specific regulation, but which state agencies are pursuing on a discretionary basis. This table does not include any numeric criteria, but instead includes a description of the type of regulation or program, and a link to the applicable website. For specific regulatory values, refer to the PFAS water and soil values tables.

The following subsections describe several different categories of state-adopted laws and regulations along with examples of each. The examples below may become outdated with time, so please refer to the table for the most up-to-date information.

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 2018, PFOS and PFOA were listed as potential developmental (reproductive) 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 of consumer products, and also prohibits 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 2021 by the state. The state is currently evaluating whether to also regulate PFOA and PFOS as carcinogens under Proposition 65.

The California Department of Toxic Substances Control (DTSC) Safer Consumer Products (SCP) program is also addressing PFAS. If a product-chemical combination is designated as a "Priority Product" under the SCP regulations, the responsible entities must conduct a formal alternatives analysis to document whether the chemical is essential in the product and whether safer alternatives exist. Based on the results of the alternatives analysis, the state can take a variety of regulatory responses, including banning the sale of the product or requiring investment in the development of green chemistry solutions. The SCP program of DTSC finalized the priority product designation for carpets and rugs with PFAS that considers PFAS as a class (CA DTSC 2021), and is also evaluating treatments for converted textiles and leathers containing PFAS (CA DTSC 2021) and plant fiber-based food containers that contain PFAS as Priority Products and food packaging (CA DTSC 2021).

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 2018)) and food contact materials (Washington State Legislature 2018). 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 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 $\geq$ 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 Corrective Action Plan (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 2016, 2016).

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 2017). 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 2017).

8.2.3.3 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 PFAS water and soil values table, on the fact sheets page). 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, 2003, 2013)) can be used to derive screening levels for groundwater and soil. As of August 2021, 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 2017). 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 PFAS water and soil values table on the fact sheets page and USEPA (2021) Certain states (for example, Alaska, Connecticut) have developed values for the protection of groundwater (see the ITRC PFAS water and soil values table on the fact sheets page).

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 polices 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.

8.2.3.4 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 for PFAS would be established in the same manner as other pollutants. Michigan is currently the only state with PFOA and PFOS discharge standards. The Michigan Department of Environmental Quality Rule 57 Water Quality Values can be found on their web page (MI EGLE 2019).

8.2.3.5 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. Currently, Alaska, Delaware, Illinois, Maryland, Michigan, Minnesota Montana, New York, Vermont, and Wisconsin are 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). In March 2021, Michigan Environment, Great Lakes, and Energy (EGLE) issued an interim strategy for the application of biosolids containing PFAS (MI EGLE 2021). It focuses on reducing PFAS inputs into wastewater treatment plants while further assessing the impacts associated with land application of biosolids containing PFAS.

New Hampshire has an ambient air limit for ammonium perfluorooctanoate of 0.05 ug/m^3 (24-hour) (NH DES 2016).

In 2019, California's Water Resources Control Board held a public meeting where it unveiled its PFAS Investigation Plan (CA Water Boards 2019). Since that initial meeting, California has issued a series of PFAS investigation orders to airports, landfills, chrome plating facilities, publicly owned treatment works, and bulk oil terminals. PFAS sampling orders have also been issued to public water systems (CA Water Boards 2021). PFAS sampling results are available on the CA Water Boards (2021) 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. California has banned the manufacture, sale, and use of PFAS-containing AFFF in most applications, effective January 2022 (see Regulatory Programs table)

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 on the fact sheets page 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	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 2018) Importantly, the MRL is a daily dose, applicable for any oral exposure; it is not a threshold concentration in water or other environmental media.	https://www.atsdr.cdc.gov/mrls/index.asp

Term	Acronym	Agency	Definition	Link
Regional Screening Level	RSL	USEPA Regions	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 2019)	https://www.epa.gov/risk/regional-screening-levels-rsls-users-guide#intro

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 2019)	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 2018)	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, posted on the fact sheets page, of PFAS water and soil values from state, federal, and some international countries and the table 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 2019).

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 2009; 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 on the fact sheets page 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 2016). USEPA (2016) 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 (2018) 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 (2018) 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 2017). 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 2017). 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 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 2009) 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 2017). In 2019, MDH selected a different key study in mice with immunotoxicity as the critical effect (MDH 2019).

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 2016). The USEPA derived an RfD for PFOS based on decreased neonatal rat BW from the two-generation study by Luebker et al. (2005) because this key study and critical effect combination yielded the lowest RfD of the remaining studies (USEPA 2016).

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 et al. (2005), (2005) and this immune effect is supported by other studies in mice and humans (NJDWQI 2018). NJDWQI (2018) discussed some concerns and issues related to USEPA's rationale and selection of the to Luebker 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 again 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 (2018) 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 2016).

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 2011). 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 2011). 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 on the fact sheets page 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 2016, 2016). 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 animal$^{1/4}$ divided by BW human$^{1/4}$) or the ratios of elimination half-lives. The USEPA (2014) 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 (2018) 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 2018, 2017). 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 on the fact sheets page 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 on the fact sheets page 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 (2011).

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/kg BW-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 2011) 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 2018, 2019).

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 (USEPA 2014). 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 2000), 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 2017, 2018), 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 2017, MDH 2017).

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9 Site Risk Assessment

The PFAS Team developed a Risk Assessment and Regulations training video with content related to this section.

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 2015) 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 (2016) USEPA (2016)	20	Delayed bone development and accelerated male puberty in mice (following developmental exposure)	20	Reduced growth rate of offspring (following developmental exposure)
ATSDR (2018) **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 2015). 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 2003, 2013); (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, 2003) 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 (2003), 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 2015). 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 2019), 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 2015) 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, see Section 3 of the RISK-3 guidance (ITRC 2015). 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.

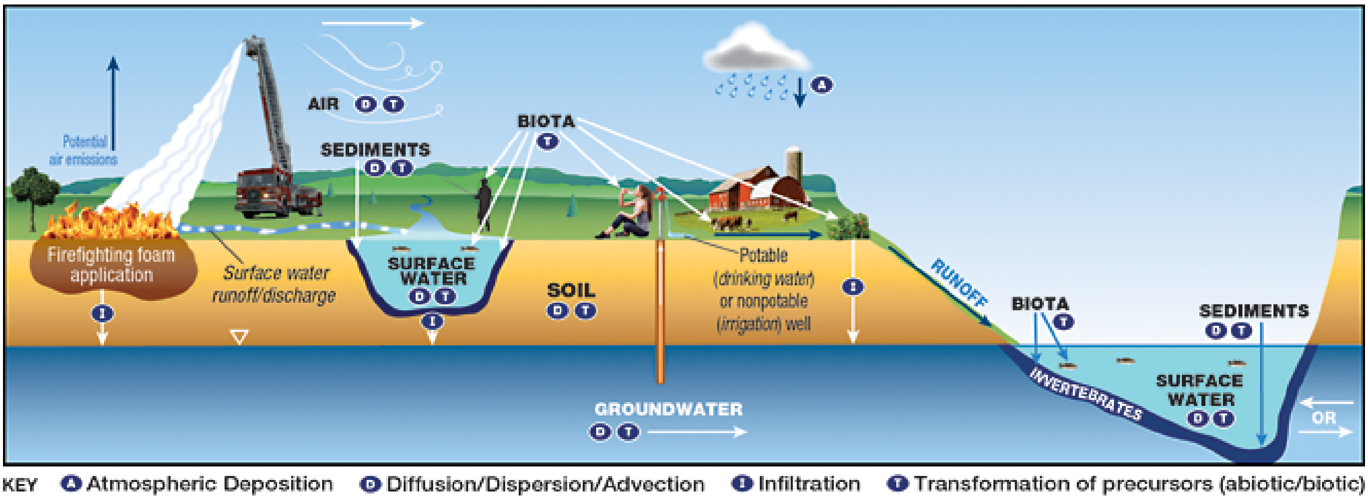


Figure 9-1. CSM for fire training area.

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

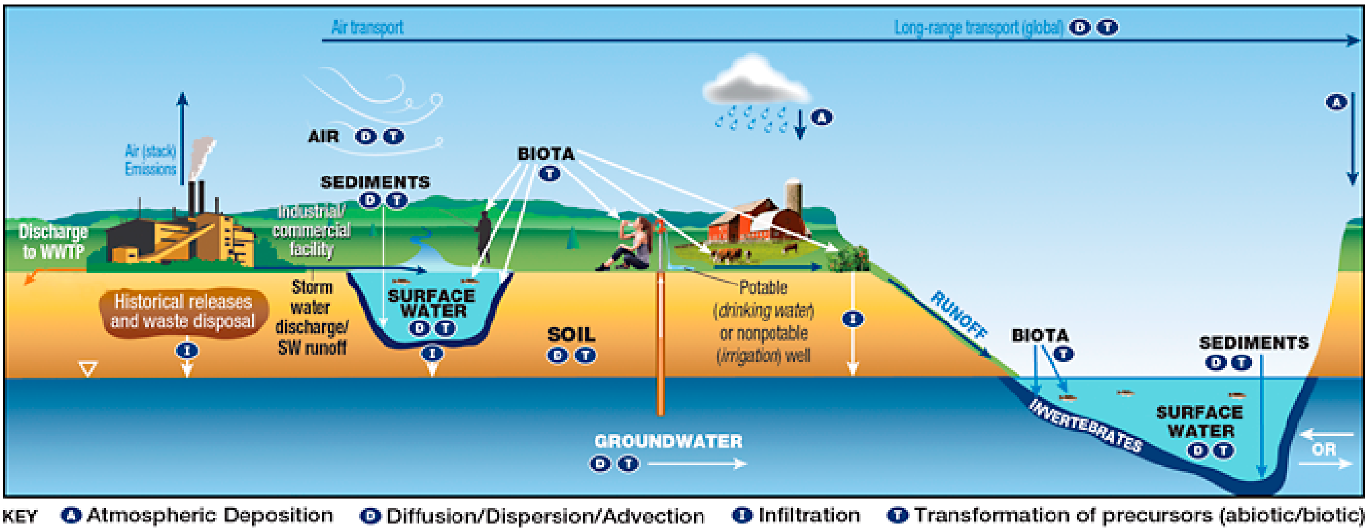
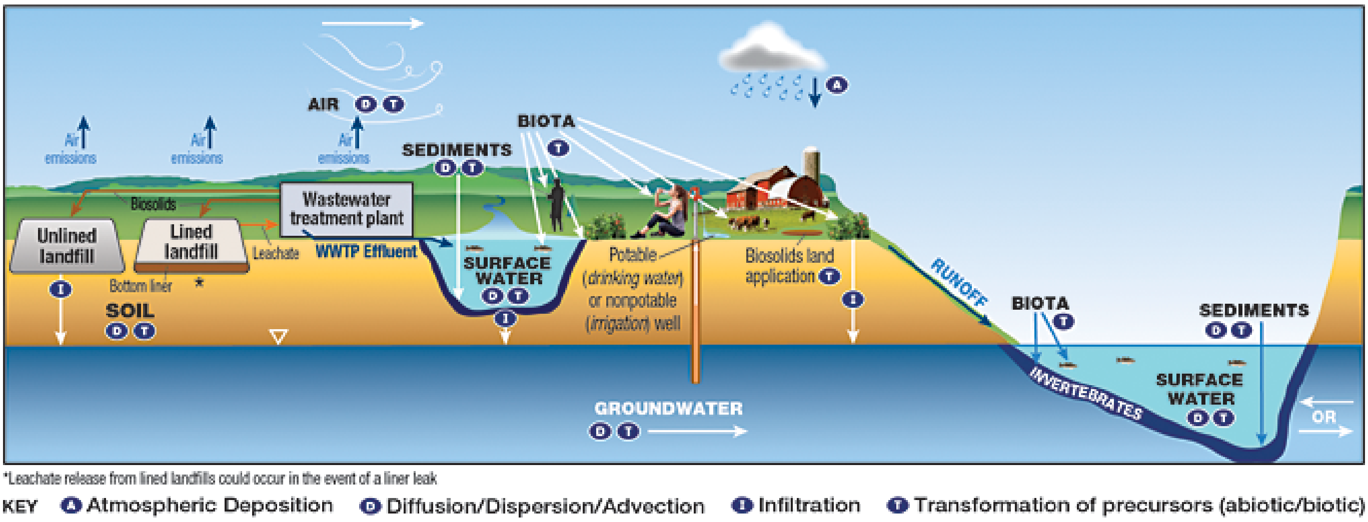


Figure 9-2. CSM for industrial sites.

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



*Leachate release from lined landfills could occur in the event of a liner leak

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. 2016, Verner et al. 2016; 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 2016, USEPA 2016), 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.

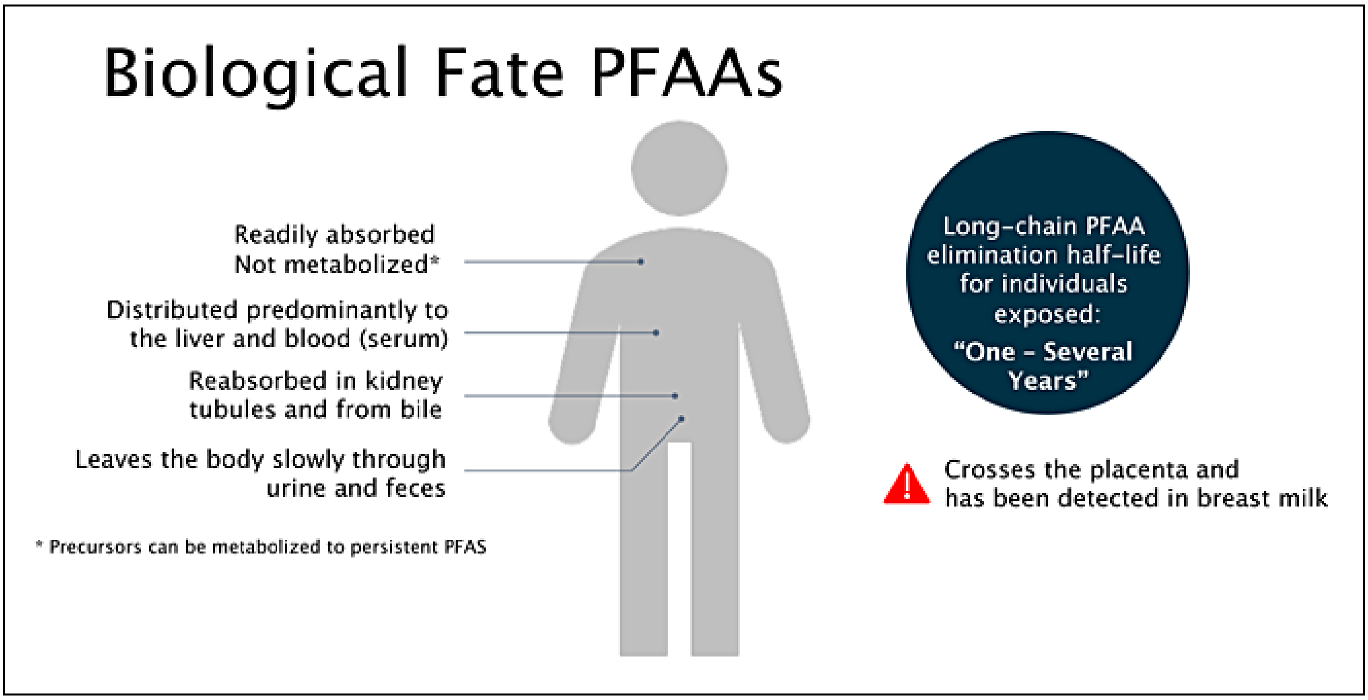


Figure 9-4. Biological fate of long-chain PFAAs.

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.

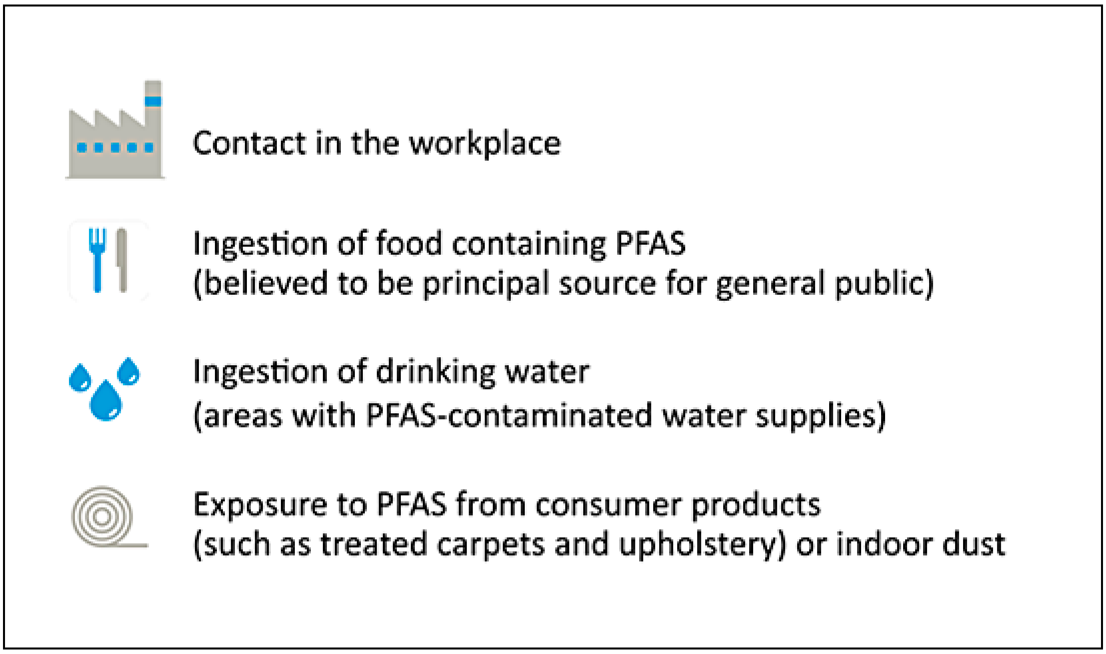


Figure 9-5. Predominant human exposure pathways.

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 2003; ATSDR 2020; NTP 2016; CONCAWE 2016). USEPA has compiled an online resource for PFAS information that includes guidance on environmental behavior and site characterization (USEPA 2017). 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 2020). 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 2015). 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 2015) 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.

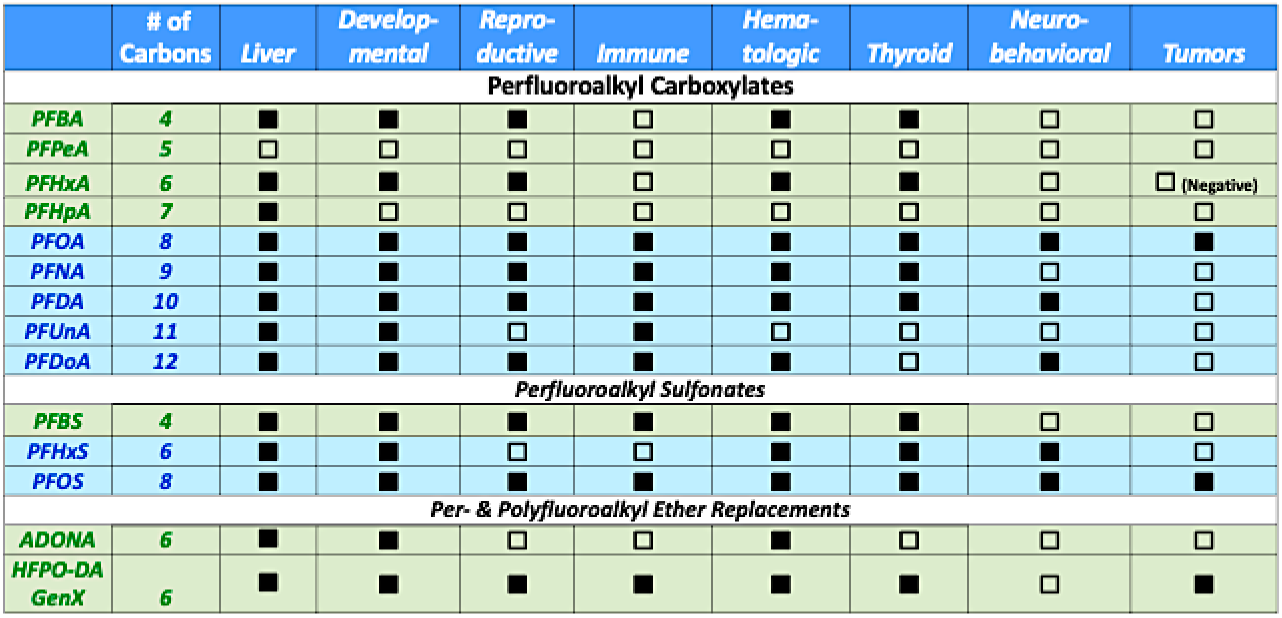
9.1.3.1 Assessing the Cumulative Effects of Exposure to PFAS

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 2019) Health Consultation PFAS HC-508.



	# of Carbons	Liver	Develop-mental	Repro-ductive	Immune	Hema-tologic	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 (2016), USEPA (2016), and USEPA (2018) 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 2005) carcinogen risk assessment guidance provides for development of a slope factor for chemicals with "suggestive evidence" when supported by available data. USEPA (2016) 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 (2018) developed a slope factor for PFOS of 9 x 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 suseptibility 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

This section summarizes information that is currently available to conduct ecological risk assessment (ERA) of PFAS. The information presented is based on a review of current regulatory guidelines from within the United States and other jurisdictions, peer-reviewed publications, and other sources as noted. Sufficient information needed for performing ERAs exists only for some PFAS. When possible, discussions in this section indicate to which PFAS the discussions apply. Two recent publications funded by the US DOD, Conder et al. (2020) and Divine et al. (2020), discuss PFAS ERA in detail and provide a summary of much of the available data needed for conducting PFAS ERA within the U.S. These are the most comprehensive reports to date for completing PFAS ERAs within the U.S. The European Union (EU) also has a substantial amount of data available within their Environmental Quality Standards (EQS) for performing PFAS ERA, but the EQS use different guidelines and approaches than those in the U.S. Use of these data will likely result in conflicting values and differing conclusions on data usability and adequacy for performing an ERA.

This section discusses challenges within three key components of ERA: ecological effects assessment, exposure assessment, and risk characterization. Conder et al. (2020) and Divine et al. (2020) are referenced throughout those discussions as applicable. In addition, a workshop sponsored by the Society of Environmental Toxicology and Chemistry (SETAC) was held in August 2019 and focused on the state-of-the-science supporting risk assessment of PFAS. A breakout group within that workshop focused specifically on ecotoxicology and ecological risks of PFAS. The expert panel in that breakout group produced a detailed manuscript describing the currently available information, data gaps, and uncertainties, and approaches to address these needs (Ankley et al. 2020). Like the Conder et al. (2020) and Divine et al. (2020) reports, the recommendations of Ankley et al. (2020) are also directly related to conducting PFAS ERAs and are mentioned here to provide readers an understanding of subjects that are relevant but that still have uncertainty so they can assess the importance of those subjects for their specific needs. Ankley et al. (2020) is referenced throughout this section as applicable. Additional recommendations from Ankley et al. (2020) not included later in this section are listed below:

- a need for prioritizing which PFAS to study and evaluate relative to ecological risk and toxicity
- environmental monitoring beyond PFOS and PFOA
- advancing the understanding of PFAS uptake, elimination, and bioaccumulation
- broader understanding of toxicity across taxa
- the use of new approach methods (often referred to as NAMs) and
- studying and assessing PFAS as mixtures.

The remaining text for this section is organized into three main components of ERA: ecological effects assessment, exposure assessment, and risk characterization.

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. Some major considerations for ecological effects assessment are identifying ecological screening thresholds, understanding ecological receptor variability, and evaluating ecological toxicity of mixtures. These are discussed in the following sections.

9.2.1.1 Ecological Screening Thresholds

The recently published manuscript by Ankley et al. (2020) includes a discussion of media-specific ecological screening thresholds that are available for certain PFAS around the world: PFOS, PFOA, PFBA, PFPeA, PFHxA, PFBS, and PFHxS. Ankley et al. (2020) did not claim the list of thresholds to be comprehensive of all ecological thresholds for PFAS around the world. The discussion here in this section presents thresholds that are included within that document with discussion relevant to ITRC’s intended audience. Ankley et al. (2020) can be referenced for a more detailed discussion and complete table of available thresholds from around the world.

U.S.—Federal Thresholds

Currently, there are no ecological risk-based PFAS guidelines or media screening thresholds available that are recommended by the USEPA. In support of the Air Force Civil Engineer Center, Argonne National Laboratory is currently developing draft ecological screening thresholds for surface water and soil. Values will be developed for 4-, 6-, 8-, 9-, and 10-carbon linear PFCAs and the 4-, 6-, and 8-carbon linear PFSAs (see Section 2 for detailed naming conventions). Work is being completed in consultation with Tri-Services Environmental Risk Assessment Working Group, and USEPA’s Ecological Risk Assessment Forum (Ankley et al. 2020). However, these values are draft and are not yet publicly available. The USEPA is also in the process of reviewing available PFAS aquatic toxicity data to evaluate the ability to develop criteria for the protection of aquatic life and is conducting some of their own laboratory research to support this effort. However, at the time of publication, USEPA has not announced a schedule for developing PFAS ambient water quality criteria (AWQC) protective of aquatic life or a schedule for a final decision on whether AWQC will be developed.

There have been a number of published studies and reports that follow U.S. federal guidelines (USEPA 1995) for developing aquatic life criteria. Giesy et al. (2010), Salice et al. (2018); Conder et al. (2020), and Divine et al. (2020) all calculated thresholds protective of aquatic organisms exposed to PFOS in freshwater environments. Giesy et al. (2010) also reported a Tier II freshwater value for PFBS, while Conder et al. (2020) derived Tier I values for PFOS in both freshwater and marine environments and for PFOA for freshwater. Divine et al. (2020) developed Tier I freshwater values for PFOS and PFOA and Tier II values for 23 other PFAS. Tier I values meet the data required described in USEPA (1995) guidelines while Tier II values are developed with methods that incorporate uncertainty factors when the availability of required data is insufficient. Section 16.3 provides greater detailed discussion on the methods for developing thresholds protective of aquatic life.

U.S.—Thresholds for Specific States

Several states have established some criteria that are intended to protect aquatic organisms in their respective surface waters. The text below is not intended to be exhaustive and only summarizes some of the values that were available at the time this text was developed (Spring 2021).

In Michigan, AWQC 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 procedures 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, and given their 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 surface water criteria for the protection of aquatic biota. These values are based on guidelines in Minnesota Rules chapter 7050 (MR7050). Continuous chronic criteria for the protection of aquatic biota in surface water are available for PFOA (1,700 µg/L) and PFOS (19 µg/L) (Stevens and Coryell 2007; Stevens and Coryell 2007). Florida has established Provisional Surface Water Screening Levels that are in the same range as those for Minnesota: 1,300 µg/L PFOA in freshwater, 37 µg/L PFOS in freshwater, and 13 µg/L PFOS in salt water (FL DEP 2020).

In California, the San Francisco Bay Regional Water Quality Control Board (SFB RWQCB) has released Interim Final Environmental Screening Levels (ESLs) for PFOS and PFOA (SFB RWQCB 2020). These values were specifically developed for use within the jurisdiction of the specific water board, not the state of California, not the California Department of Toxic Substances Control, and not the entirety of the United States. Other jurisdictions may use these values, as is often the case with many published thresholds. However, with the number of different water boards in California, it is important to understand the applicability of these ESLs. These values include groundwater protection levels that are protective for direct exposure to freshwater and marine organisms, including rare, threatened, and endangered species. The values are based on a 99% protection level (lower 1st percentile of a species sensitivity distribution [SSD]) compared to a 95% protection level (lower 5th percentile of an SSD) used for a typical AWQC. There are also groundwater ESLs that are protective of adverse effects to birds and mammals from the consumption of aquatic prey (Table 9-3). These wildlife protection values (listed by the SFB RWQCB and in Table 9-3 as secondary poisoning ecotoxicity) are based on values published in Divine et al. (2020). Separate soil ESLs are included in the SFB RWQCB document that are protective of (1) plants and invertebrates or (2) birds and mammals. There are two soil ESLs for each chemical for both significantly vegetated and minimally vegetated areas for a total of four distinct values each for PFOS and PFOA as shown in Table 9-4.

Table 9-3. SFB RWQCB groundwater ESLs: Aquatic habitat ecotoxicity levels for PFOS and PFOA (SFB RWQCB 2020)

Protected Organisms	PFOS (µg/L)	PFOA (µg/L)
Direct exposure ecotoxicity: Freshwater	0.56	540
Direct exposure ecotoxicity: Saltwater	2.6	540
Secondary poisoning ecotoxicity: Freshwater and saltwater	0.075	4.4

Table 9-4. Soil ESLs: Terrestrial habitat levels (SFB RWQCB 2020)

Protected Organisms	PFOS (mg/kg)	PFOA (mg/kg)
Significantly vegetated areas		

Protected Organisms	**PFOS (mg/kg)**	**PFOA (mg/kg)**
Plants and invertebrates	7.7	0.084
Mammals and birds (NOAEL-based)	0.013	0.57
Minimally vegetated areas		
Plants and invertebrates	33	0.84
Mammals and birds (LOAEL-based)	0.05	1.1

International Thresholds

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 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 whole-body 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 whole-body fish. 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 PFOA 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 9-5, 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 for Australia and New Zealand (HEPA 2020). The protocol for developing guideline values in Australia (Warne et al. 2018) includes some specifications for full lifecycle and multigenerational testing that were not sufficiently represented in the limited available marine studies. 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. It should be noted that the freshwater SSD and subsequent protection values are influenced by a multigenerational study (Keiter et al. 2012) with zebra fish (*Danio rerio)* that produced data that are noticeably lower than other data. Efforts to validate the data by repeating the study and its methods are ongoing at the US Army Corps of Engineers Environmental Research and Development Center (Gust et al. 2021). The ongoing work includes an expanded and more carefully determined dosing range, greatly increased replication base on statistical power analysis, expanded analytical chemistry with external validation, and an expanded suite of endpoints to improve overall toxicological context (Gust et al. 2021). 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 for marine water were 14,000 and 8,500 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 9-5. 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 9-6.

Table 9-6. Environmental quality standards (EQS) for PFOS (European Union 2011, 2013)

Category/Description	Units	Value
MAC-EQS (freshwater) (European Commission 2011, 2013)	µg/L	36
MAC-EQS (marine) (European Commission 2011, 2013)	µg/L	7.2
Pelagic Community EQS (freshwater) (European Commission 2011)	µg/L	0.23
Pelagic Community EQS (marine) (European Commission 2011)	µg/L	0.023
$QS_{biota, sec pois}$ (European Commission 2011)	mg/kg (ww)	0.033
$QS_{biota, sec pois}$ (freshwater) (European Commission 2011)	µg/L	0.002
$QS_{biota, sec pois}$ (marine) (European Commission 2011)	µg/L	0.00047
EQS (biota) (European Commission 2011, 2013)	µg/L	9.1
AA-EQS (freshwater) (European Commission 2011, 2013)	µg/L	0.00065
AA-EQS (marine) (European Commission 2011, 2013)	µg/L	0.00013

Category/Description	Units	Value
MAC-EQS = maximum acceptable environmental quality standard AA-EQS = annual average environmental quality standard QS biota, sec pois = secondary poison standard for concentration in fish tissue QS = quality standard EQS (biota) – environmental quality standard		

Other Considerations for Thresholds

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 with PFOS and PFOA that have been conducted to date are in two species, the bobwhite quail (*Colinus virginianus*) and mallard duck (*Anas platyrhynchos*). 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 and other benthic aquatic life with 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. The Norwegian Pollution Control Agency (NPCA) established 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 (NPCA 2008; Bakke et al. 2010) for benthic invertebrates. The technical basis for the NPCA values relied on the principles of equilibrium partitioning (EqP) between sediment and surface water using a partitioning coefficient (Kd). The no-effect sediment value is based on a PNEC of 72 µg/L from a limited data set and an unspecified Kd. A sediment screening value of 6.7 µg/kg (wet weight) from the United Kingdom’s Environment Agency (2004) was also developed using EqP with a PNEC of 2.5 µg/L and a river sediment Kd of 8.7 L/kg. Simpson et al. (2021) have estimated sediment thresholds of 60 µg/kg PFOS and 250 µg/kg PFOS (both normalized to 1% organic carbon) protective of 99% and 95% of species, respectively, based on EqP using a Kd of 10 L/kg with an HC1 of 6 µg/L and HC5 of 25 µg/L. HC5 and HC1 are commonly established for contaminants from SSDs developed for the contaminant. These HCx (for example a HC5) represent the concentration above which the lower x proportion of species in the distribution may see adverse effects.

All of 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

Another 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 *Toxicological Profile for Perfluoroalkyls* (ATSDR 2021), 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. Recommendations for selecting TRVs from available data for conducting ERAs are included in Divine et al. (2020), Conder et al. (2020), and Johnson et al. (2021). 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 and bobwhite quail were the first published work relevant to ERA. Divine et al. (2020) and Conder et al. (2020) presented the data from their studies as well as data from other studies and for other PFAS that can be used for selecting avian TRVs. More recent publications relevant to ERA include that of Bursian et al. (2021), who looked at oral exposure of Japanese quail (*Cortunix japonica*) to PFOS, PFOA, and AFFF (both 3M and Ansul products), and (Dennis et al. 2020; Dennis et al. 2021) who looked at northern bobwhite quail exposed to PFOS and PFHxS. 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). A recent study (Furst, Weible, and Salice 2019) exposing brown anoles (*Anolis sagrei*) to PFOS and PFHxS provides data relevant to ERA. Measures of apical endpoints included decreased growth of juveniles exposed to PFOS, while exposure to PFHxS resulted in decreased egg viability in female anoles. To date, there are no other 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 limited, though more are available than are reptile data. Toxicity tests are available for eight different PFAS in the USEPA ECOTOX database and address exposure to four different species: the African clawed frog (*Xenopus laevis*), western clawed frog (*X. tropicalis*), Asiatic toad (*Bufo gargarizans*), and northern leopard frog (*Rana pipiens*)(USEPA 2019). A recent study (Flynn et al. 2019) is also available that looked at effects in American bullfrogs (*Rana catesbeiana*) exposed to a mixture of PFOS and PFOA. A laboratory bioaccumulation study (Abercrombie et al. 2019) of PFOS and PFOA in the eastern tiger salamander (*Ambystoma tigrinum*) and the American toad (*Anaxyrus americanus*) also provides some useful data for ERA.

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 ECCC (2018), CRC CARE (2017), Conder et al. (2020), and Divine et al. (2020). SSDs produced by CRC CARE (2017) showed lettuce to be more sensitive to PFOS than earthworms, but found the opposite occurred for PFOA. Divine et al. (2020) calculated Tier I water quality values for PFOS and PFOA, Tier II water quality values for another 21 PFAS, and soil screening values for plants and soil invertebrates for 6 PFAS each. 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), C*hironamous 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 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 2017), but they are more sensitive by just an order of magnitude or less. Additional studies by Simpson et al. (2021) and Hayman et al. (2021) have expanded the understanding of potential toxic effects in aquatic organisms in marine waters but an SSD that includes data from both of these studies has not been published.

SSDs have not been published for avian, mammalian, reptilian, or amphibian species. Although SSDs could possibly be generated for laboratory mammalian species exposed to some PFAS, data are insufficient to generate robust SSDs that are applicable 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. Existing data would be more conducive to an effects distribution because the number of species within the class of organisms would be so limited. A limited amount of published data is available for avian, reptilian, or amphibian animals, but these data are insufficient to determine a robust SSD or even an effects distribution.

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 do 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

An additional major challenge in effects assessment for PFAS is considering the toxicity of mixtures. PFAS nearly always occur as complex mixtures in natural environments with multiple PFAS present at concentrations that vary by site and source of PFAS. At this time there are only limited data available to understand the toxicity of more than just a few chemicals based on single chemical exposure experiments such as direct toxicity to lower trophic level organisms or dietary exposures to upper trophic level wildlife. Thus, the ability to understand the toxicity of mixtures is limited by the scarcity of available toxicity data. However, in the absence of such data, several strategies using structural and physical properties and toxicity information from PFAS with available data may be helpful to infer potential mixtures effects, including mixtures with PFAS of unknown toxicity. These strategies include the use of in silico predictive techniques (for example, quantitative structure-activity relationships (QSARs)), using read-across from data-rich PFAS to inform data-poor PFAS, and estimating potential mixture risk using dose-addition risk assessment methods (for example, hazard index or relative potency factor approaches). Examples of published studies using QSAR for estimating PFAS toxicity include Hoover et al. (2019), Kovarich et al. (2012), and Cheng and Ng (2019) and additional citations within each of those publications. These studies typically evaluate an in vitro endpoint (such as cell death (Hoover et al. 2019)) or in silico measurements (such as the binding ability of known PFAS to specific cellular proteins (Cheng and Ng 2019; Kovarich et al. 2012)) and then use QSAR to estimate how other PFAS would respond to that same endpoint or target. Similarly, Droge (2019) derived phospholipid membrane−water partition coefficients (K_{MW}) that were used within a model to predict induction of narcosis ($LC_{50,narc}$) and which could be used in the future with K_{MW}-QSARs.

Most of these studies aim to fill data gaps for individual PFAS. Since it is not yet clear how PFAS may cause toxicity to various ecological receptors, the applicability of these data to ecological risk assessment of mixtures is unknown. However, with additional chemical-specific data, methods for estimated combined toxicity, such as hazard index or relative potency factors, could then be applied. Caution should be used when applying any of these approaches; some of these methods are novel and others may be well established but are predicated on specific data-supported assumptions that have not been universally accepted. Standardized toxicity tests, such as those performed with terrestrial and aquatic invertebrates and plants, are available for performing controlled dosing experiments and for exposure tests with field samples containing natural mixtures. Laboratory dosing experiments with whole mixtures, mixtures of prioritized PFAS, or with specific formulations, and with exposure concentrations that bracket environmental relevance, are all needed to inform ecological toxicity of mixtures.

There are a number of ongoing research projects investigating simultaneous exposure of ecological receptors to multiple PFAS (primarily the UCMR3 chemicals) and their precursors, with these studies mostly using binary mixtures (Lee et al. 2017; Flynn et al. 2019; Bursian et al. 2021; Dennis et al. 2020; McCarthy et al. 2021). However, the relative toxicity, additivity, or synergistic effects of PFAS remain incompletely understood and still uncertain. McCarthy, Roark, and Middleton (2021) discussed some of the challenges with designing, conducting, and interpreting toxicity tests with mixtures of PFAS. The understanding of PFAS mixtures is still developing and there is little consensus in the scientific community regarding how to assess the potential adverse impacts of PFAS mixtures. Complicating a limited understanding of PFAS mixture toxicity is that both absolute and relative concentrations of PFAS mixtures will vary across sites and across time. Reliance on empirical data such as site-specific toxicity sampling or community structure studies ultimately may be needed to fully understand the potential impacts of mixtures.

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. As noted by Divine et al. (2020), there are differences between the numeric value of BSAFs developed from field data versus laboratory methods, and also between values from laboratory studies using the same methods.

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 range from 7 to 49 kg sediment/kg tissue wet weight (as reported by authors). Divine et al. (2020) and Conder et al. (2020) summarized BSAFs for aquatic invertebrates and bivalves and for aquatic crustaceans for 15 PFAS. Both reports also discussed a variety of PFAS BAFs for amphibians, aquatic plants, benthic invertebrates, crustaceans, and fish. There is overlap, as well as difference, in the studies discussed and presented by Conder et al. (2020) and Divine et al. (2020). Much of this data is also described in Section 5.5. The Conder et al. (2020) report leans toward describing available data while the Divine et al. (2020) report goes a step further and attempts to apply the data to develop screening values from wildlife food web models, similar to the secondary poisoning values available in the EU (Table 9-6).

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. The ability to combine effects thresholds (Section 7.2) and exposures to characterize risk to environmental receptors is outlined in a few publicly available sources. McCarthy, Kappleman, and DiGuiseppi (2017), Conder et al. (2020), and Divine et al. (2020) have identified exposure factors and effects thresholds that can be used for completing quantitative ERA within current regulatory frameworks. The risk characterization of any chemical has uncertainty associated with it, and ecological effects characterization for PFAS is no exception. However, at this time based on the data presented in this section, meaningful PFAS risk management decisions can be supported in some situations using the current state of ecological risk assessment science. Broad risk management decisions regarding the ecological risk of PFAS should not be made for most risk assessments. In some cases, with consideration of the knowledge gaps and uncertainties for the site-specific scenarios being evaluated, stakeholders can work together to reach defendable scientific management decisions. Such risk characterizations using non-site-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 2012) 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 Production, Uses, Sources, and Site Characterization training video with content related to this section.

The intent of this section is not to present general site characterization principles, but to highlight unique considerations or examples 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 2021), 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 3.3, 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.

Further, because of the widespread use of PFAS-containing products, there may be multiple locations that act as a source of PFAS at a site. In addition, PFAS are often detected at low levels in samples from locations without any apparent or nearby sources. In those instances, there may be a need to evaluate the site-specific anthropogenic background concentrations and determine their contribution to PFAS concentrations in environmental media at a site. See, for example, Strynar et al. (2012).

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.

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).

Partitioning: Because of their physical and chemical properties and the variability of those properties, certain PFAS may partition from water through different mechanisms (including hydrophobic effects, electrostatic interactions, and interfacial behaviors) to other media or forms, including air, micelles, foam, solids, NAPL, and interfaces between these phases. Phase partitioning is discussed in more detail in Section 5.2 and as appropriate in several subsections in this section.

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.

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 2014). 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 2015). 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 (Ju et al. 2008). A study assessing PFAS concentrations in river and groundwater from several locations found that concentrations and trends in groundwater were generally similar to those observed in surface water, suggesting the aquifer was contaminated with the same source as the surface water (Sharma et al. 2016). Areas with high hydraulic conductivity allow for the rapid spreading of PFAS over large areas. However, even in lower permeability geologic deposits, PFAS contamination is a problem because the combination of long groundwater residence times and persistence of most PFAS results in a long-time presence of these compounds in water resources (Banzhaf et al. 2017). 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

This section highlights some important considerations for site investigation that are relevant for PFAS. The general principles of site investigation are similar for PFAS as for any chemicals.

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 2017). The amount of information to be collected to complete an adequate assessment is a site-specific determination based on many factors such as complexity of stratigraphic and lithologic variability, project objectives, and available budget. High resolution site characterization (HRSC) techniques are normally appropriate to obtain adequate subsurface information (for example, grain size and permeability) to complete stratigraphic assessments (see https://clu-in.org/characterization/technologies/hrsc/index.cfm for more information on HRSC). ITRC has guidance on implementing advanced site characterization tools (see https://asct-1.itrcweb.org/).

Geochemical parameters that may be pertinent to potential PFAS migration and possible remedies also require consideration during the investigation. The understanding of soil type (possibly including f_{oc} surface charge, exchange capacity, grain size, minerology, and water content) and groundwater chemistry (possibly including cation concentrations or the ionic strength of aqueous solutions, oxidation-reduction conditions, and pH) at the site is needed to assess transformation, partitioning (including desorption), and migration in groundwater or 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 more 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 PFOA, 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). Batelle, through the Pacific Northwest National Laboratory, has patented a version of this electrochemical sensor and is licensing its use (Battelle 2021). Rodriguez et al. (2020) provided a review of PFAS-detecting sensors and expected future direction for sensors.

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; Guo, Zeng, and Brusseau 2020).
- 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 PFSAs and PFCAs will help the investigator understand sources and potential long-term concentrations.

10.3.3 Extent of PFAS

As with other chemicals, 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. Some 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.

Another factor in the extent of PFAS at mature sites is prior remediation intended to address other contaminants. For example, groundwater pump and treat systems designed and operating to address other contaminants may have partially captured PFAS or their discharge may have spread PFAS. Other remediation methods such as oxidation may result in a change in the relative concentrations of individual PFAS.

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, see 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 and 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 PFAAs 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; Brusseau 2019; Brusseau et al. 2019, 2019; Costanza, Abriola, and Pennell 2020; Lyu and Brusseau 2020; Schaeffer et al. 2019; Silva, Šimůnek, and McCray 2020; Sima and Jaffe 2021). These enhanced attenuation processes are discussed in Section 5.2.4.1 (partitioning to air/water interfaces) and Section 5.2.5 (NAPL-water interface). 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 some PFAS may have changed 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 Koc 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 Koc, 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. Assuming equilibrium desorption may result in overestimation of PFAS removal during remediation activities (Sima and Jaffe 2021).

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). For example, Guo, Zeng, and Brusseau (2020) conducted a sophisticated modeling study indicating that PFOS in the vadose zone at a hypothetical fire training site is primarily sorbed at the air-water interface and only 1–2% of PFOS is in the aqueous phase under the modeled conditions. This indicates that strong PFOS attenuation may occur in the vadose zone over time, although Guo, Zeng, and Brusseau (2020) showed that eventually there still may be discharge of PFOS to the underlying water table under their modeled conditions. This is consistent with high concentrations of PFOS observed at some fire training sites. 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.

For example, models such as USEPA's VLEACH (information and model available at https://www.epa.gov/water-research/vadose-zone-leaching-vleach), and Seview's Seasonal Soil (SESOIL) compartment model (information and model available at http://www.seview.com/aboutsesoil.htm) can simulate one-dimensional vertical transport in the vadose zone via diffusion, adsorption, volatilization, biodegradation, cation exchange, and/or hydrolysis. But these models do not include air-water interface interactions that are 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) [SW-846 Method 1312 (USEPA 2014)] and the Toxicity Characteristic Leaching Procedure (TCLP) [SW-846 Method 1311 (USEPA 2014)] may provide insight into the leachability of PFAS from vadose zone materials. The TCLP is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes for waste characterization purposes (USEPA 2014). The SPLP is designed to determine the mobility of both organic and inorganic analytes present in liquids, soils, and waste to evaluate the potential of contaminants to leach into groundwater (USEPA 2014). Therefore, the SPLP is typically used for soils in site characterization contaminant leaching studies and allows for less acidic extraction fluids (simulating exposure to acid rain) than the TCLP test (simulating exposure in a landfill) so it can better represent environmental conditions expected to be encountered at a site.

USEPA has also developed a Leaching Environmental Assessment Framework (LEAF). LEAF is a leaching evaluation framework consisting of four leaching tests (SW-846 Methods 1313, 1314, 1315, and 1316), a data management tool, and approaches for estimating constituent releases from solid materials (USEPA 2019). The four leaching tests discussed have been validated for inorganic constituents, but the methods and/or framework may be helpful when evaluating leaching of PFAS in the environment.

Optimizing LEAF leaching tests for use with PFAS is one component of an in-progress SERDP-ESTCP sponsored study: Development and Validation of Novel Techniques to Assess Leaching and Mobility of Per- and Polyfluoroalkyl Substances (PFAS) in Impacted Media, ER-1126 (SERDP-ESTCP 2021). The project overview states that the study has the overarching goal of developing a framework for evaluation and prediction of the release of PFAS from AFFF-impacted media. Identified specific objectives include: 1) development of a standard leaching assessment methodology for AFFF-impacted media; 2) utilization of approaches including high resolution mass spectrometry (HRMS), mid-infrared spectroscopy (MIR), and chemometrics to evaluate and develop a predictive model of PFAS sorption and desorption to AFFF-impacted media; and 3) comparison of results of laboratory testing to leaching and mobility under field-relevant conditions to develop an approach for translation of bench-scale test results to site-scale implications.

Stahl et al. (2013) completed a study evaluating the behavior of PFOA and PFOS in soil and the carryover from soil to plants. Plant samples and percolated water collected by a lysimeter were analyzed for PFOA and PFOS throughout a period of 5 years. PFOA was found to pass through the soil much more quickly than PFOS, and of the original mass applied, 96.88% of the PFOA and 99.98% of the PFOS were still present in the soil after a period of 5 years. Plants were found to have accumulated 0.001% of the PFOA and 0.004% of the PFOS. Loss through the soil through leachate was reported to be 3.12% for PFOA and 0.013% for PFOS.

A follow-up to this leaching study was completed by Gassmann, Weidemann, and Stahl (2021). The study used 8 years of data from a lysimeter and MACRO—a one-dimensional, process-oriented, dual-permeability model for water flow and reactive solute transport in soil (information and model available at https://www.slu.se/en/Collaborative-Centres-and-Projects/SLU-centre-for-pesticides-in-the-environment/models/macro-52/). The study evaluated the ability of MACRO to simulate leaching and plant uptake of PFOA and PFOS using two adsorption concepts: a kinetic two-side sorption concept usually applied for pesticide leaching (scenario I) and the formation of what Gassmann, Weidemann, and Stahl (2021) called non-extractable residues (NER) (scenario II). NER are adsorbed PFAS that either do not leach or leach very slowly from soil. Leaching of PFOA and PFOS could be adequately simulated for scenario II, but scenario I was not able to reproduce sampled leaching concentrations (Gassmann, Weidemann, and Stahl 2021). Plant uptake was simulated well in the first year after contamination but was not simulated well in the following years (Gassmann, Weidemann, and Stahl 2021). The model results suggest that more than 90% of the original mass of PFOA and PFOS is present as NER after 8 years, which they concluded was a larger percentage of the mass compared with other studies (Gassmann, Weidemann and Stahl 2021). The authors also concluded that even though there are open questions and more research is necessary, the study showed that it is possible to use an existing leaching model for the long-term simulation of PFOA and PFOS leaching in unsaturated soils and the short-term simulation of plant uptake. Furthermore, they concluded that even though not all environmental processes are yet understood, this model may already provide valuable information for groundwater protection and crop safety.

Given the complexity of predicting the mass discharge of PFAS 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. Care should be taken when selecting an approach to assess PFAS leachability to ensure it is appropriate for the physical environmental setting and parameters that are present, and considers the end use of the data.

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).

Schaefer et al. (2019) calculated aqueous diffusivity values for nine PFAAs; however, prediction of the influence that back-diffusion will have on PFAS remediation timeframe remains uncertain because the back-diffusion of PFAS from low permeability materials involves desorption. As discussed above, PFAS desorption may be a rate-limited process and these rates have a high degree of uncertainty (Sima and Jaffe 2021). In addition, the irreversible fraction of PFAS in low permeability materials is uncertain at this time. Therefore, the uncertainty associated with modeling remediation timeframes of PFAS back-diffusion should be noted.

10.4.3.4 Upgradient Site Contributions

Alternate Sources

Sources that may exist within, upgradient of, or near a site under investigation, that are distinct from the PFAS source being investigated.

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.

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 PFSAs.

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.

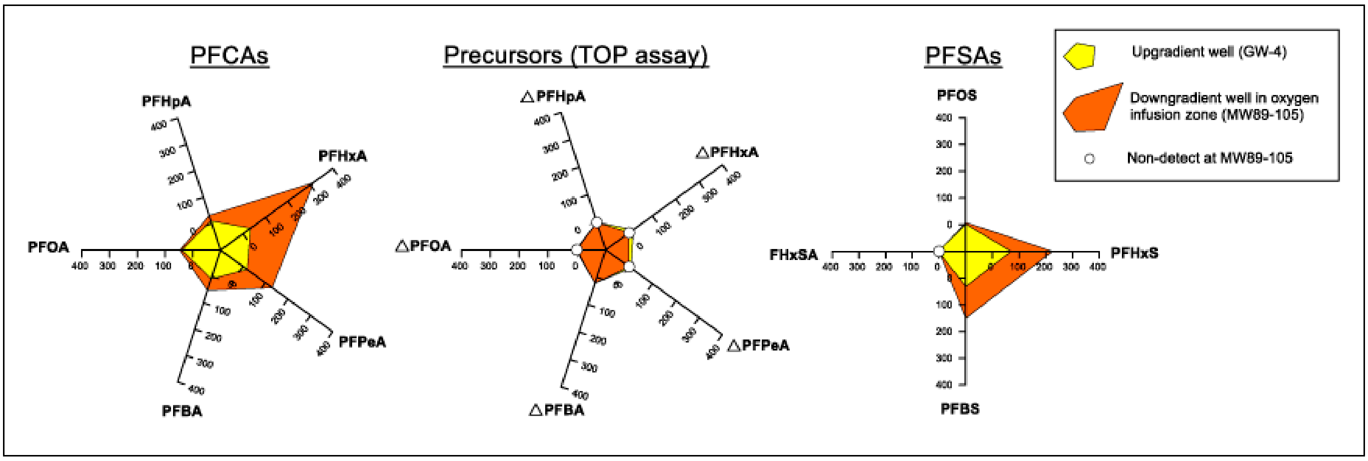

Figure 10-1. Radial diagrams showing the production of various PFAAs in the vicinity of an oxygen infusion zone at an AFFF release site remediated for hydrocarbons in groundwater.
*Source: G. Carey, Porewater Solutions. Used with permission***.**

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 2009).

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 (McGuire et al. 2014; Barr 2017; Carey et al. 2019; Guo, Zeng, and Brusseau 2020; Persson and Andersson 2016; Gassmann, Weidemann, and Stahl 2021). Sima and Jaffe (2021) provide a critical review of applicable transport processes, modeling approaches, and potential limitations and uncertainty associated with modeling PFAS transport. 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 (Sima and Jaffe 2021). 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 PFSAs 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. The field of PFAS forensics is in its nascent stages. Researchers are still conducting studies to more fully understand the fate and transport of PFAS in the environment, and they continue to evaluate tools to investigate changes in PFAS composition for the purposes of source attribution. Benotti et al. (2020) have suggested a tiered approach for characterizing the PFAS signatures associated with source materials and have suggested that some or all aspects of this approach may be useful when evaluating PFAS contamination in soil or water samples. However, until more details on the chemical composition of source materials is available, and until researchers understand the full scope of forensic information that may help elucidate sources, the best approach for associating or dissociating environmental contamination from one or more sources is to compare PFAS information in a soil or water sample to similar information from the site-specific source area/s. An overview of PFAS source identification analyses can be found in Dorrance, Kellogg, and Love (2017).

To that end, any site-specific investigation begins with a careful review of available records. In a best-case scenario, such records may directly link a source to environmental contamination without significant contribution from any other potential sources. More often than not, source attribution of PFAS contamination is more complicated. Groundwater plumes of PFAS contamination are heterogeneous due to weathering and differential rates of subsurface transport between PFAS. Care must be taken not to attribute changes associated with fate and transport to different sources. If there are two or more likely sources contributing to mixed contaminant plumes, the challenge becomes greater still. In addition, atmospheric transport and deposition of some PFAS could be considered (Ahrens, Rakovic, et al. 2016; Davis et al. 2007; Galloway et al. 2020).

The following sections describe some of the source identification tools that may be used or considered for use in identifying sources 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 to one or more known or suspected sources (see the text box in Section 10.4.3.4). The data from available analytical methods 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. The following sections describe some of the forensic information that may be useful to evaluate sources, as well as some tools for comparing samples within a data set.

10.5.1.1 Manufacturing Signatures

PFAAs (PFCAs and PFSAs) can be produced as a mixture of homologues of different chain lengths depending on the various manufacturing process(es) used (Section 2.2). PFAAs produced by electrochemical fluorination (ECF) can include both even and odd chain-length homologues. PFAAs produced by fluorotelomerization contain mostly even chain-length homologues. However, transformation of some of the fluorotelomer precursors results in the formation of odd chain length PFCAs (Prevedouros et al. 2006; Dasu, Liu, and Lee 2012; Liu and Mejia Avendano 2013). Most commercial laboratories can report PFCA homologues ranging from C4 to C14 and select PFSA homologues between C4 and C12. USEPA (2009) 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.

Laboratories generally report the concentration of a given PFAA as the total of the branched and linear forms; however, the concentration of the linear form and an estimated concentration for the branched form can be reported independently. The concentration of branched form must be estimated because standards do not yet exist for most branched-chain PFAA (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).

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.

10.5.1.2 Visual Representations of Data

It is common to show representations of measured PFAS in figures or graphs to give the reader a visual sense for relative abundance. Two common graphs for representing PFAS data are bar graphs and radar plots. If one is considering the role of concentration, then it is helpful to plot PFAS concentrations on the axes. However, if one is considering the patterns of data, then it is helpful to plot relative abundance, or the concentration of each PFAS divided by the sum of all measured PFAS, on the axes. It is also suggested to group subclasses of PFAS together and order them by perfluorinated alkyl chain length. For example, PFCAs ordered from the shortest to longest perfluorinated alkyl chain length, followed by PFSAs ordered from the shortest to longest perfluorinated alkyl chain length, followed by fluorotelomer sulfonates ordered from the shortest to longest perfluorinated alkyl chain length allows the viewer to compare changes in compositional patterns both within and between different subclasses of PFAS to assess changes that may occur due to environmental fate and transport. When showing data in this fashion, it is common to report estimated concentrations or J-flagged values and use the value of zero (0) for nondetects. A comparison of PFAS signatures between two samples (Sample A and Sample B) using either bar graphs (Figure 10-2) or radar plots (Figure 10-3) is shown below.

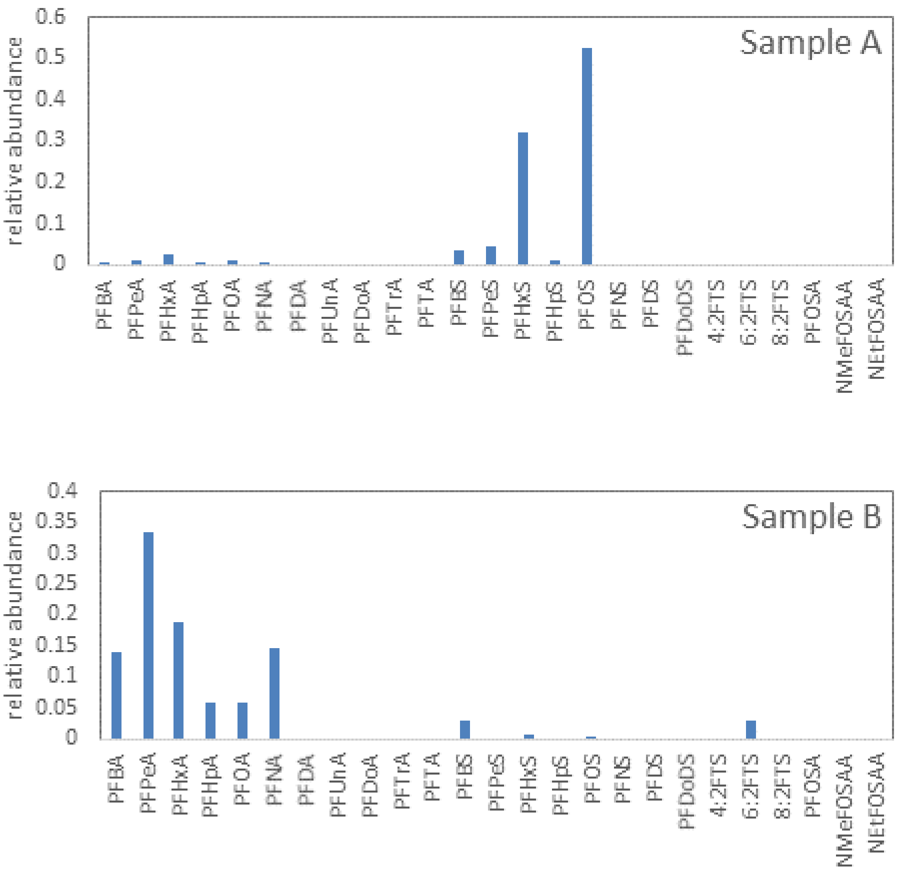

Figure 10-2. Comparison of PFAS signatures in Sample A and B using bar graphs. The concentration of each PFAS has been divided by the sum of all measured PFAS to represent the relative abundance of PFAS in each sample.

Source: M. Benotti, NewFields. Used with permission.

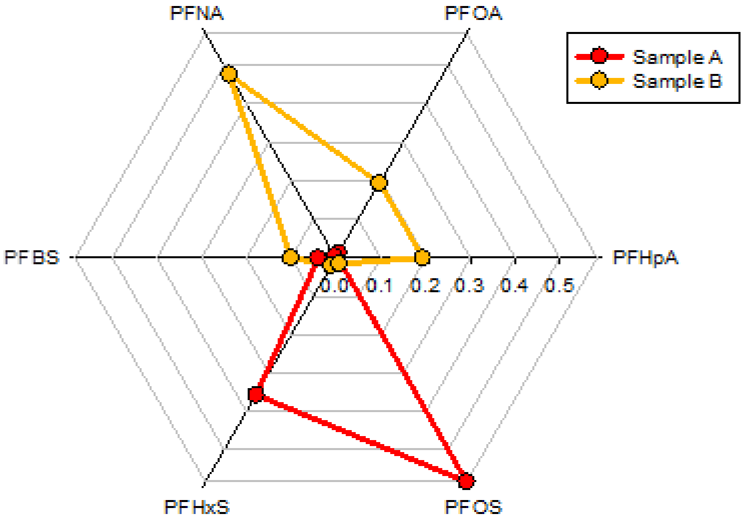

Figure 10-3. Comparison of PFAS signatures in Sample A and B using radar plots. The concentration of each PFAS has been divided by the sum of all measured PFAS to represent the relative abundance of PFAS in each sample.

Source: M. Benotti, NewFields. Used with permission.

10.5.1.3 Diagnostic Ratios

In some applications of PFAS forensics, it may be beneficial to show similarities or differences between sample signatures using relative abundances of one or more PFAS or diagnostic ratios, or double ratio plots. Without a comprehensive library of PFAS source materials, such ratios should be site-specific, and should be selected to query the data for a site-specific question and to show similarity or differences between contamination throughout the site and those in known or purported source area/s. Examples of factors that may help identify suitable diagnostic ratios include the relative abundance of PFCAs, PFSAs, or FTSs, the ratio of PFCAs to PFSAs (or more specifically the ratio of PFOA to PFOS), the ratio of even-numbered to odd-numbered PFCAs, the relative abundance of linear to branched isomers of selected PFAS, and others. Table 10-1 shows some example diagnostic ratios for PFAS in Sample A and Sample B above.

Table 10-1. Example diagnostic ratios to compare PFAS signatures of Sample A and Sample B.

	Sample A	**Sample B**
relative abundance of PFCAs	0.062	0.93
relative abundance of PFSAs	0.94	0.041
relative abundance of FTSs	0	0.029
PFCAs/PFSAs	0.066	22
PFOA/PFOS	0.0217	13

10.5.1.4 Multivariate Statistical Tools Such as Principal Component Analysis (PCA)

PFAS data sets, including TOP assay data, are amenable to a variety of multivariate numerical data analysis techniques that provide a means to categorize PFAS compositional data. The advantages of multivariate numerical methods are that they provide a convenient means to analyze large data sets and reduce the output into relatively straightforward graphical output that describes the most important factors affecting chemical variability throughout the data set. Principal component analysis (PCA) is a multivariate statistical procedure that uses an orthogonal transformation to convert a set of observations of possibly correlated variables into a set of values of linearly uncorrelated variables called principal components. In other words, it identifies and graphically shows the most important features of data that describe similarities and differences between sample chemistries within a data set. The investigator can use this tool to identify samples that have similar or different PFAS signatures and what changes are driving those differences. Changes in PFAS patterns may be attributable to changes associated with fate and transport, or there may be changes that can be explained only by additional sources. Figure 10-4 presents an example PCA scores plot, which demonstrates the similarity or dissimilarly of PFAS signatures between all samples in a data set.

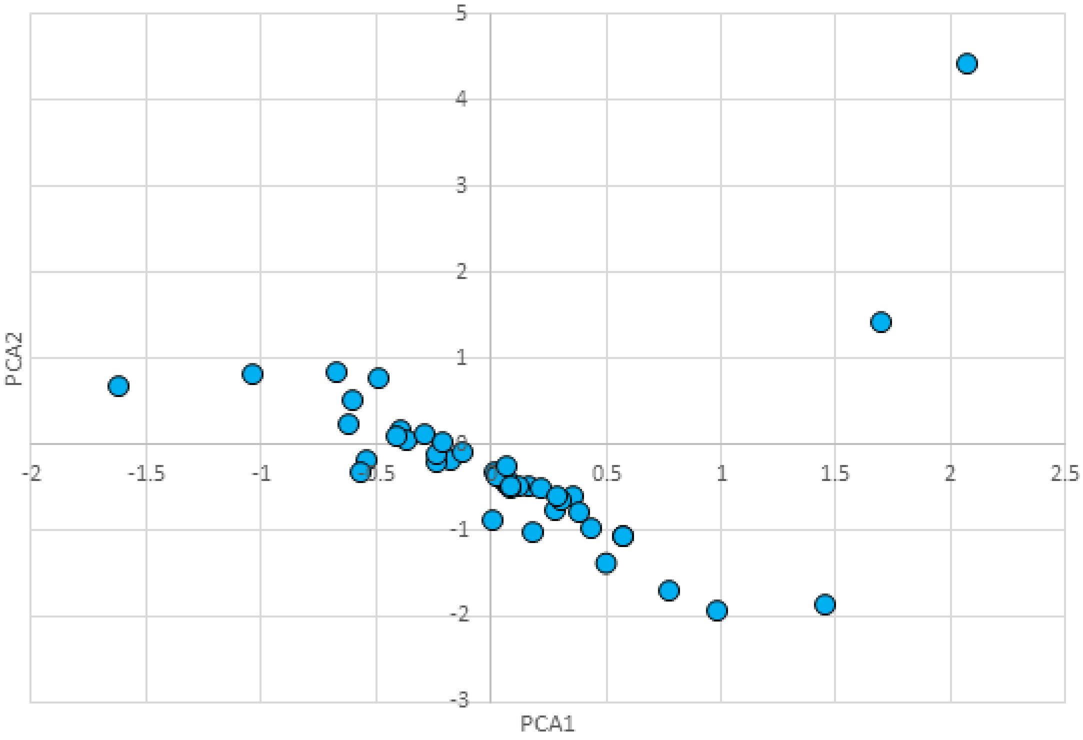

Figure 10-4. PCA scores plot of the analysis of a PFAS data set. Each circle represents the pattern of PFAS contamination of an individual sample. Samples that plot close together have similar PFAS signatures. Samples that plot apart have dissimilar PFAS signatures.

Source: M. Benotti, NewFields. Used with permission.

Examples of chemical fingerprinting for PFAS source identification can be found for wastewater treatment plants (Clara et al. 2008), differentiating AFFF sources (KEMI 2015; Hatton, Holton, and DiGuiseppi 2018; see also Section 3.5), landfills (Lang et al. 2017; Xiao et al. 2012), surface water (Xie et al. 2013), sediment (Qi et al. 2016), and groundwater (Yao et al. 2014). Multivariate statistical analyses (that is, PCA, cluster analysis, and 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 et al. (2014) used PCA in water and sediment samples to distinguish between rural/agricultural and urban/industrial sources.

10.5.1.5 High Resolution Mass Spectrometry (HRMS)

High resolution mass spectroscopic methods using quadrupole time-of-flight mass spectrometry (qTOF/MS) can be used to determine both the chemical formula and structure of unknown PFAS in source materials (see Section 11.2.2.5 for further information on qTOF/MS) (Newton et al. 2017; Moschet et al. 2017; Barzen-Hanson et al. 2017; Battelle 2020; Washington et al. 2020; Getzinger, Higgins, and Ferguson 2021; Guelfo et al. 2021). PFAS suspect screening libraries have been developed to include broader lists of PFAS analytes found across many different PFAS sources (Newton et al. 2017; Moschet et al. 2017; Barzen-Hanson et al. 2017; Getzinger, Higgins, and Ferguson 2021). Because analytical standards are not available for most PFAS included under this extended list of analytes, often these analytical tools are used for qualitative/semiqualitative analysis. These methods have the potential to greatly increase the number of identified PFAS, including precursors and the transformation products, and hence provide more accurate source identification (Washington et al. 2020, Getzinger, Higgins, and Ferguson et al. 2021; Guelfo et al. 2021).

10.5.2 Challenges and Reasonable Expectations

Important factors when considering source identification for PFAS 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.

Updated August 2021.

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11 Sampling and Analytical Methods

The PFAS Team developed a Sampling and Analysis training video with content related to this section.

Due to the extensive use of a wide array of PFAS resulting in trace levels of PFAS, in most environmental media across the globe 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 and representative data support the development of a defensible conceptual site model (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 chemicals, there are several considerations for the practitioner when establishing a sampling program for PFAS. These include 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 control (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 (USEPA 2021). Although some draft methods have been published (PFAS Analytical Methods provided as an Excel spreadsheet), all are not discussed in this document because details included in these methods are subject to change prior to the methods being finalized. In the case of USEPA Draft Method 1633, an exception has been made in this document due to the USEPA Office of Water’s recommendation of its use in Clean Water Act (CWA) compliance testing applications, including National Pollutant Discharge Elimination System (NPDES). The publication of this draft method followed the completion of single-laboratory validation of the method. The method is currently undergoing multilaboratory validation. Once completed, information from this study will be used to update the QC criteria included in the draft method before the final method is proposed at 40 CFR Part 136 for nationwide Clean Water Act monitoring. This method is applicable to wastewater, groundwater, surface water, landfill leachates, soil, sediment, biosolids, and tissue.

The USEPA Office of Land and Emergency Management has validated and published a sample preparation procedure and analysis procedure applicable to groundwater, surface water, and wastewater. USEPA SW-846 Method 3512 is a sample preparation method, and USEPA SW-846 Method 8327 is the associated analytical method.

Currently, there are two USEPA methods that are validated and published for the analysis of PFAS in drinking water sources: USEPA Method 537.1, Version 2.0 (USEPA 2020) (which replaced USEPA Method 537.1, and USEPA Method 537 Version 1.1) and USEPA Method 533 (USEPA 2019). For simplicity in the text, subsequent references to USEPA Method 537.1 assume the most current version. These methods are required for PFAS analyses of drinking water and include performance data for drinking water from surface water and groundwater sources. These methods are prescriptive in that changes to preservation (including sample collection, in the case of USEPA Method 537.1), sample extraction steps, and quality control requirements are prohibited by both methods.

The DOD has also validated and published a method (DoD AFFF01) for the determination of PFOA and PFOS in AFFF concentrates for demonstration of compliance to MIL-PRF-24385 (Willey 2021).

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, 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 modified decontamination measures.

Examples of USEPA region-specific or program-specific PFAS sampling protocols include:

- USEPA (2019) Region 4, Laboratory Services and Applied Science Division, Athens, GA, *Field Equipment Cleaning and Decontamination at the FEC*, ASBPROC-206-R4, 2019
- 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), Contaminated Sites Guidelines*
- DoD AFFF01 *Determination of Perfluorooctanoic acid and Perfluorooctanesulfonic acid in Aqueous Film Forming Foam (AFFF) for Demonstration of Compliance to MIL-PRF-24385* (Willey 2021)
- State guidance:
  - MA DEP (2020) 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 (2017) *Quality Assurance Project Plan; Statewide Survey of Per- and Poly-fluoroalkyl Substances in Washington State Rivers and Lakes.*
  - NH DES (2019) New Hampshire Department of Environmental Services, *Laboratory Testing Guidelines for Per- and Polyfluoroalkyl Substances (PFAS) at Waste Sites, 2019*
  - MI EGLE 2018 to present, PFAS Sampling Guidance Documents, including:
    - MI EGLE (2021) PFAS Sampling Guidance
    - MI EGLE (2019) Surface Water Foam PFAS Sampling Guidance
    - MI DEQ (2018) Wastewater PFAS Sampling Guidance
    - MI DEQ (2018) Surface Water PFAS Sampling Guidance
    - MI DEQ (2019) Fish Tissue Sampling Guidance

A work plan, such as a comprehensive project-specific quality assurance project plan (QAPP), should be created to address PFAS-specific considerations. If a work plan is not created for a project, the sampling and quality assurance and quality control (QA/QC) 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 work plan, 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 holding times) are defined by USEPA Methods 537.1, 533, and 8327, they do not provide all the information that is needed to conduct a sampling event for PFAS. DoD AFFF01 contains all the information needed to conduct sampling of AFFF concentrates. **Tables 11-2** and **11-5**, included in the PFAS Analytical Methods Excel spreadsheet, cover the sample container types, sample size, number of containers required, and holding time and preservation requirements for each of these finalized and draft published PFAS analytical methods, respectively.

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. The chain–of–custody (COC) form 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 QC 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 work plan 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. Laboratories verify the PFAS content of each batch of supplied water through analysis. Documentation of this verification should be maintained for data validation purposes and should be reviewed by the project team to ensure that the project’s definition of “PFAS-free” is met. If the water was not supplied by the laboratory, a sample of the water used in the field should be sent to the laboratory for testing.

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 work plan. 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 used. 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 extensive use of a wide array of PFAS, sampling crews should review all materials and sampling protocols to avoid contamination and possible adsorption issues. Examples of problematic materials that if used and contacted samples could potentially introduce bias include, but are not limited to:

- 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. Program-specific sampling protocols such as those previously listed in this section often 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.

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 work plan. USEPA Method 537.1 requires the use of polypropylene containers and caps/lids for drinking water sampling, and USEPA SW-846 Method 8327 was validated using polypropylene containers for groundwater, surface water, and wastewater sampling. However, USEPA SW-846 Method 8327 states that other types of containers such as high-density polyethylene (HDPE) may be used if the needs of the project can be met with their use. USEPA Method 533 allows for the use of polypropylene or polyethylene containers and polypropylene caps/lids for drinking water sampling. USEPA Draft Method 1633 requires the use of HDPE containers for wastewater, groundwater, surface water, landfill leachate, biosolids, soil, sediment, and tissue sampling. The volume of aqueous sample that is required for analysis varies from method to method and the mass of solid material required for analysis in accordance with USEPA Draft Method 1633 is dependent on the matrix of the sample.

Because the concentration levels of PFAS in aqueous samples, excluding drinking water samples, determine whether the whole sample or an aliquot is used in the laboratory preparation, USEPA Draft Method 1633 requires collection of an additional aliquot of each aqueous sample for screening purposes. The method allows for a smaller aliquot of wastewater, groundwater, or surface water than collected for analysis to be collected for screening and determination of percent suspended solids. This second aliquot allows the laboratory to screen the sample without affecting the integrity of the sample collected for analysis. Coordinating with the laboratory is crucial to determine the appropriate sample numbers and volumes as well as QA/QC samples.

Best practices in sample preparation should be used when selecting the size, volume, and representativeness of samples. To minimize effects from analyte sorption on sample containers, USEPA Methods 537.1 and 533, and USEPA Draft Method 1633 all require the laboratory to prepare the entire sample collected, including sample container rinsate(s). DoD AFFF01 requires the container holding the diluted AFFF concentrate be prepared in its entirety, including a rinse of the container.

11.1.4 Sample Preservation, Shipping, Storage, and Holding Times

Sample preservation, shipping, storage, and holding time requirements are dependent on the method that is intended to be used. Drinking water methods (USEPA Method 537.1 and 533) are the only USEPA methods requiring the addition of a chemical preservative at sample collection. USEPA Method 537.1 required the addition of TRIS (Trizma), while USEPA Method 533 requires the addition of ammonium acetate. According to both of these methods, samples must be chilled during shipment and not exceed 10°C during the first 48 hours after collection. When they are received by the laboratory, samples must be at or below 10°C and stored in the laboratory at or below 6°C until extraction. These two methods differ in their required holding times, as USEPA Method 537.1 requires samples to be extracted within 14 days of collection, while USEPA Method 533 requires samples to be extracted within 28 days of collection.

The shipping, storage, and holding time requirements for wastewater, groundwater, and surface water samples stated in USEPA SW-846 Method 8327 differ than those provided by USEPA Draft Method 1633. USEPA SW-846 Method 8327 requires all samples and sample extracts to be chilled from the time of sample collection to analysis and not exceed 6°C. Since a holding time study was not performed in conjunction with the validation of USEPA SW-846 Method 8327, the method offers a holding time of 14 days from sample collection to sample extraction and a 30-day holding time from sample extraction to sample analysis as a guideline.

The shipping, storage, and holding time requirements contained in USEPA Draft Method 1633 are based on a published holding time study for PFAS in wastewater and surface water (Woudneh et al.2019) and the results of a holding time study conducted in conjunction with the single-laboratory validation study of USEPA Draft Method 1633. The holding time study performed during this validation study assessed what impact, if any, two storage temperatures had on 40 PFAS in wastewater, groundwater, surface water, soil, sediment, and biosolids samples and sample extracts. The recovery of 40 PFAS in samples stored at -20°C and 4°C and extracts stored at 4°C was evaluated at defined intervals over the course of 90 days. While the statistically determined holding time requirements are similar for each matrix, they are not identical (see **Table 11-5**, included in the PFAS Analytical Methods Excel spreadsheet). Observed losses and/or gains in the concentration of some PFAS, most likely caused by transformation of precursors, resulted in shorter holding times for samples and extracts held at 4°C as opposed to -20°C. Due to the observed extreme loss of NFDHA, an additional caveat in the method recommends samples be extracted and analyzed as soon as possible if NFDHA is an important analyte for the project.

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 work plan. 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 laboratory-verified 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 laboratory-verified 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 as investigation-derived waste (IDW), based on plans included in the site-specific QAPP or work plan.

11.1.6 Field QC Samples

Field QC samples are a means of assessing quality beginning at the point of collection. Such field QC samples typically include field reagent blanks, source water blanks, equipment rinse blanks, and field duplicates. Collection and analysis of field QC samples are important for PFAS investigations because of very low detection limits and regulatory criteria (parts per trillion (ppt)), to ensure accuracy and representativeness of the results for the sampled media, and to assess potential cross-contamination due to the extensive use 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 or work plan 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.

Of all the USEPA PFAS methods, only USEPA Methods 537.1 and 533 contain specific requirements for the field QC samples that must accompany 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 Methods 537.1 and 533 specify 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 the other USEPA PFAS methods do not contain any field QC sample requirements, Table 11-1 provides a list of field QC samples typical for the collection of these matrix types 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 or work plan. For laboratory QC considerations, see Section 11.2, Analytical Methods/Techniques.

Table 11-1. Typical field QC samples

QC Sample	Description	Minimum Suggested Frequency
Field reagent blank (FRB)	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 used 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 (ERB)	Final rinse of nondedicated sampling equipment with laboratory-verified PFAS-free water (decontamination blank) or rinse of sampling equipment (dedicated or nondedicated) prior to the sampling event in cases where PFAS content is unknown or suspected	One per day per type of sampling equipment used for each matrix sampled For cases in which PFAS content is unknown or suspected, prior to sampling event
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), as described in USEPA Methods 537.1 and 533 for collection of drinking water samples, consists of a sample bottle filled with reagent water prepared 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 contained in another bottle that was sent to the field and seals and labels the bottle for shipment along with the samples back to the laboratory for analysis. FRBs help to determine if PFAS were introduced into the samples during sample collection/handling and help to account for additional factors, such as introduction of contaminated airborne particles. A laboratory reagent blank is also analyzed in a laboratory setting to ensure the reagent water meets USEPA Methods 537.1 and 533 requirements.

FRBs 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 Methods 537.1 and 533 as “samples collected from the same sample site and at the same time” (USEPA 2020; USEPA 2019).

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). Site groundwater or surface water should not be used as source water at sites that are under investigation for PFAS, as they have potential to contain PFAS. PFAS test results of publicly supplied water at a site should be evaluated when considering it for use as source water. Regardless, it is imperative that any water used as source water be sampled and analyzed. 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 in the same manner 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 from PFAS that may be present in these materials.

Frequency of collection of such 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 should be found. A more conservative sampling program may include provisions for additional periodic sampling in cases where the conditions of the source water change.

11.1.6.3 Equipment Rinse Blank (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 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 Methods 537.1 or 533 because drinking water compliance samples are generally collected from the source without the use of other equipment. ERB collection for other programs 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 is 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. The frequency of collection of ERBs can be reduced by using all dedicated or disposable equipment where possible. However, many of these options are limited due to the extensive use of PFAS in many of these equipment materials. ERBs should also be considered for dedicated equipment prior to and during a sampling event if the PFAS contribution from equipment is unknown or suspected.

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 the pump 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 Methods 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 per matrix. FD collection frequency should be discussed with stakeholders as necessary and be evaluated as part of the comprehensive site-specific QAPP or work plan.

11.1.6.5 Performance Evaluation (PE) Sample

A PE sample contains project analytes with known concentrations of PFAS. This sample can be submitted to the laboratory as a blind sample. Analysis from this sample provides a positive control from a second source.

11.1.6.6 Additional QC Samples

In addition to the field quality control samples described above, split samples and matrix spikes can provide project managers additional quality assurance regarding identification of PFAS target analytes and precision and bias in measured sample concentrations. Split samples are defined here as co-located quality control samples, taken at the same time and each sent to a different laboratory. These types of samples do not apply to routine compliance monitoring situations and may not be required in all sampling events. Aqueous QC samples should not be split into two samples from the original container. Analysis of these QC samples provides a measure of interlaboratory variability.

11.1.7 Sampling Procedures

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 PFAS-adsorbing sampling equipment and supplies, as previously discussed. A site-specific QAPP or work plan must 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 used is essential. ERBs are recommended to ensure supplies such as bailers, beakers, and dippers are PFAS-free, and that decontamination is effective.

In addition, the sampling team must document any observations during the sampling event that could be a source of bias (for example, the presence of PTFE tape on a faucet).

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 protocols established in the USEPA Methods 537.1 and 533. These protocols define 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 Methods 537.1 and 533. USEPA Methods 537.1 and 533 may also apply in instances when the water quality of the private drinking water supply source is similar to finished drinking water (for example, has low level of total organic content). The following summarizes the sampling considerations described in these protocols:

- 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 of collection (USEPA Method 537.1) or within 28 days of collection (USEPA Method 533).

Based on a review of industry experience and guidance, additional considerations for collecting drinking water samples for PFAS analysis are as follows.

- The sample should be collected from a tap or spigot located at or near the [glossary_exclude]well-head[/glossary_exclude] 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. If collecting a sample to characterize human or other exposure, the sample should be collected from the tap or spigot at the point of use.

- 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 (2013), 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.

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

The following summarizes considerations for groundwater sampling.

- Non-potable water samples do not require a chemical preservative, unless otherwise required by the cited analytical method(s). Clean laboratory-provided HDPE or polypropylene bottles are recommended; typically, 125-mL to 1-L bottles may be used, but the sample volume may depend on the analytical method used.
- Low-flow sampling is preferred for collection of groundwater samples for PFAS to keep the turbidity of samples to a minimum. See Section 11.2.1.2 for issues associated with elevated levels of suspended solids in aqueous samples.
- Bailers should be used with caution due to the potential for PFAS to accumulate at the air/water interface. If bailers are used, it is important to make sure that at least one well volume is purged to remove static surface conditions.
- High density polyethylene Hydrasleeve no-purge sampling devices can also be used for groundwater sampling, but this may be dependent upon site conditions.
- 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 by 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 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 or work plan.
- In addition to equipment, ensure tubing or bailer twine are PFAS-free.
- Within the context of sample collection objectives outlined in a site-specific work plan, 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. In addition to sample location within the water column, consideration should be given to the well construction, screened interval, and site geology to ensure that the well is representative of site conditions and all relevant COCs. For more information on stratification, see Section 5.2.

Samples should not be filtered, because filters may be either a source for contamination (Ahrens et al. 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. See Preparation of Aqueous Samples with Particulates/Suspended Solids in Section 11.2.1.2 for more details.

In cases where sampling for co-contaminants requires 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 at a 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 or work plan, 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 only 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 2013). 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, sampling points typically installed and used for multiple sampling events, whereas push-point samplers are used as 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. Ensure efficient and consistent homogenization procedures are followed in the field. 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 Section 11.1.2 for equipment and supplies, and Section 11.1.5 for decontamination procedures. Ensure efficient and consistent homogenization procedures are followed in the field. No additional considerations are recommended for PFAS sampling of surface soil.

11.1.7.7 Subsurface Soil

Ensure efficient and consistent homogenization procedures are followed in the field. 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. According to USEPA Draft Method 1633, whole fish or other biota samples should be wrapped in aluminum foil or food-grade polyethylene wrap and homogenized tissue samples should be placed in HDPE containers.

11.1.7.9 Air Emissions to Air and Ambient Air

There is an increasing need for the measurement of PFAS in emissions from stationary sources (for example, chemical manufacturing, industrial use, combustion and thermal treatment), as well as in ambient air. Due to the diverse nature of PFAS, multiple measurement approaches are needed to measure polar and nonpolar, volatile, semivolatile, and nonvolatile (particulate-bound) PFAS.

11.1.7.9.1 Emissions to 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, emissions measurements have been performed using modifications to USEPA SW846 Method 0010 (Modified EPA Method 5 Sampling Train) (USEPA 1986), a method designed for measurement of semivolatile organic compounds. Other methods have been adapted to capture specific individual compounds of interest.

USEPA and European groups (Verein Deutscher Ingenieure [VDI], an association of German engineers) are currently evaluating and investigating which sampling and analytical methods might be, in principle, the most suitable to capture PFAS and resulting byproducts in all fractions of the emissions (particles, moisture, gas phase).

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 PFAS are 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.

In 2021, the USEPA released Other Test Method (OTM) 45 *Measurement of Selected Per- and Polyfluorinated Alkyl Substances from Stationary Sources* (USEPA 2021). This performance-based method was made available by USEPA as a recommended method that can be used to measure 50 specific semivolatile and nonvolatile polar PFAS from a variety of stationary sources. USEPA OTM-45 is largely based on the USEPA SW-846 Method 0010 (Modified EPA Method 5 Sampling

Train) with several modifications. PFAS are collected in four sample fractions: 1) filter; 2) primary XAD-2; 3) impingers (containing water); 4) secondary XAD-2 (for breakthrough determination). Each fraction, with its associated rinses, is extracted and analyzed separately. Analyses are performed by isotope dilution LC/MS/MS. The analytical approach is based largely on EPA Method 533 and includes many of the same analytical qualification criteria. USEPA OTM-45 was released as an "Other Test Method (OTM)" by USEPA's Emission Measurements Center to promote consistency and is considered by USEPA to represent the current best practices to sample and analyze PFAS targets from stationary sources. USEPA OTM-45 is a draft method under evaluation that will be updated as more data from stakeholders become available. 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 QC measures that should be considered include the use of isotopically labeled PFAS field spikes. The latter compounds are typically applied/spiked by the laboratory into the XAD-2 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.

Additional measurement approaches are needed to sample and analyze for other PFAS species, such as volatile and nonpolar PFAS compounds, including PFAS that are specific to chemical manufacturing (for example, hexafluoropropylene oxide or HFPO). For example, some volatile (boiling point < 100°C) polar PFAS can be sampled by modified USEPA Method 18 *Measurement of Gaseous Organic Compound Emissions by Gas Chromatography* (USEPA 2017), in which the analytes are captured in chilled methanol impingers. The methanol reacts with some PFAS compounds to form an ester which enables the capture and subsequent analysis. Other approaches include evacuated passivated canisters and sorbent traps for the more volatile PFAS species.

The ability to identify compounds not targeted for measurement by existing methods is an important need. Nontargeted analyses are critical to being able to identify these compounds. With nontargeted analyses, chromatography (liquid and gas) is combined with high resolution mass spectrometry and multiple ionization techniques to determine atomic molecular weight and associated fragments. These results can be compared to databases for tentative identification. Further spectral interpretation may result in structural identification. This is particularly useful where no chemical standards exist. USEPA Office of Research and Development (ORD) has used nontargeted analysis to support New Hampshire Department of Environmental Services and the Saint Gobain Performance Plastics emission characterization in Merrimack, New Hampshire. (NH DES 2019). It is anticipated that nontargeted analyses will be an important tool to thermal treatment research and the ability to identify potential products of incomplete combustion (PICs).

USEPA ORD is researching and evaluating multiple PFAS measurement approaches for polar and nonpolar, volatile, semivolatile and nonvolatile PFAS, including further development of USEPA OTM-45 for nonpolar PFAS. USEPA ORD is using evacuated passivated canisters for select targeted volatile PFAS. USEPA ORD is also evaluating the use of Fourier Transform Infrared (FTIR) spectroscopy to measure select volatile PFAS in real-time. Several of the PFAS compounds capable of being measured are also being evaluated as potential indicators or surrogates of PFAS destruction performance.

Multiple PFAS emissions tests have been performed at a variety of sources for multiple purposes including source characterization, assessment of control technology performance, and evaluation of treatment technologies. Stationary source, or stack, emissions of PFAS have been measured in North Carolina (NC DEQ 2019) and New Hampshire (NH DES 2019) from industrial facilities that synthesized PFAS (Chemours, NC) or used PFAS in manufacturing processes (Saint Gobain Performance Plastics, NH) (Beahm and Marts 2019). These test programs confirmed that stack emissions from industrial facilities contribute to ground and surface water contamination (NC DEQ 2019). An additional study at Chemours, NC, reported on the commissioning of the recently installed thermal oxidizer control system (Weston Solutions, Inc. 2020).

According to the USEPA's *Per- and Polyfluoroalkyl Substances (PFAS) Action Plan* (2/19) (USEPA 2019), a method for sampling and analyzing PFAS in factory stack air emissions was anticipated in 2020 and is now expected in 2022 (USEPA 2021). USEPA has been participating in the testing at Saint Gobain Performance Plastics (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 2019). One stack test report from the Saint Gobain Performance Plastics facility has been published on the New Hampshire Department of Environmental Services OneStop Navigation website (NH DES 2019).

These test reports detail the sampling and analysis methodologies used thus far in measuring PFAS stack emissions.

11.1.7.9.2 Ambient Air

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 have been performed using modified TO methods, such as TO-13A and TO-9 (USEPA 2020). Both of these methods use 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 m^3. 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 QC measures that should be considered include collection of field duplicate or co-located samples and the use of isotopically labeled PFAS field spikes. 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 (VDI) 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. In addition to concerns over using fluorinated polymers in sampling equipment being a source of contamination, there are also concerns about the potential for adsorption of PFAS to fluorinated polymers, thereby effectively reducing the observed concentration, or affecting any attempt to quantify the phase distributions between condensed and non-condensed phases (for example. PM vs gaseous). This is related, in part, to the concerns about quantification of ambient air concentrations and distributions, as published by Johansson, Berger, and Cousins (2017), showing that the use of GFF (and chemically deactivated glass fiber filters) may irreversibly bind fluoro-carboxylates during collection of samples containing fluoro-acids, which can be in the gas phase depending on their vapor pressure and ambient temperature, and the corresponding carboxylates. This issue for ambient air appears to negatively impact the estimates of phase distributions and so far, may not have a technique that is applicable for quantitative recovery (no answer to this problem has yet been published). A related issue, though separate from the ambient sampling confounding issues, is that quantification of acids/carboxylates via LC/MS does not/cannot distinguish between these two oxidation states, which is important to the phase distribution in ambient air (and emissions to air). There are other techniques (GC/MS or Chemical Ionization Mass Spectrometry (CIMS) (Riedel et al. 2019) that may help address these LC/MS deficiencies, particularly with regard to air measurements.

11.1.7.10 Human Blood, Serum, Tissue

Currently, there are no official or standardized methods for testing human 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 may not be consistent among 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 2020).

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 form.

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. The method DoD AFFF01 contains steps to prepare AFFF concentrate samples. This method requires that a dilution of a subsample of the AFFF concentrate be prepared for extraction. A critical step in this procedure is the amount of time that must elapse, a minimum of 3 hours (Willey 2021) from the time PFAS-free reagent water is added to the aliquot of AFFF concentrate to create the dilution to the time when extracted internal standard can be added to the diluted sample. It was determined during method development and validation that some AFFF concentrates can take up to 3 hours to fully dissolve in the reagent water. In addition, this method requires each AFFF concentrate sample to be prepared and analyzed in duplicate, using another aliquot of the collected sample. It is recommended that these samples be segregated from other samples during sampling and shipping to avoid cross-contamination. AFFF concentrate samples should be segregated during shipping to the laboratory, and clearly identified on the sample chain-of-custody form.

11.2 Analytical Methods/Techniques

11.2.1 Quantitative Techniques

11.2.1.1 General

Analytical methods are still evolving for PFAS analysis. Currently, very few methods are multi-laboratory validated and published. Two multi-laboratory-validated methods, USEPA Methods 537.1 and 533 have been published for analysis of drinking water samples (USEPA 2020; USEPA 2019) and one, USEPA SW-846 Method 8327, has been published for analysis of groundwater, surface water, and wastewater samples. The DoD has published a multi-laboratory validated method, DoD AFFF01 (Willey 2021), for the analysis of AFFF concentrates to demonstrate compliance to the military specification for AFFF (MIL-PRF-24385). The USEPA has also published a single-laboratory validated method, USEPA Draft Method 1633, which they recommend for use for analysis of wastewater, groundwater, surface water, landfill leachates, soils, sediments, biosolids, and tissue. The USEPA released OTM 45 for measurement of PFAS in emissions to air from stationary sources.

- USEPA Method 537.1 tests for 18 PFAS analytes (including 4 PFAS not included in USEPA Method 533)
- USEPA Method 533 tests for 25 PFAS analytes (including 11 not included in USEPA Method 537.1)
- USEPA SW-846 Method 8327 tests for 24 PFAS analytes (does not include all PFAS included in USEPA Method 537.1 or 533)
- USEPA Draft Method 1633 tests for 40 PFAS analytes (includes all PFAS included in USEPA Method 537.1, 533, and 8327 and 8 additional PFAS analytes)
- DoD AFFF01 tests for PFOA and PFOS
- USEPA Other Test Method (OTM) 45 for 50 specific semivolatile and nonvolatile polar PFAS

Other methods have been published by other organizations. Lists of these methods, by various categories, are provided in the PFAS Analytical Methods Excel spreadsheet in the **separate tabs**:

- 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 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).

11.2.1.2 Sample Preparation

USEPA Method 537.1 and 533, USEPA Draft Method 1633, and DoD AFFF01 all require aqueous samples to be prepared using the solid-phase extraction (SPE) technique. USEPA Draft Method 1633 and DoD AFFF01 both require cleanup procedures be used on extracts and all associated batch QC samples to help eliminate matrix interferences (for example, bile salts, gasoline range organics) that could be present. USEPA Method 537.1 and 533, USEPA Draft Method 1633 and DoD AFFF01 all require extraction of the entire sample collected (in the case of DoD AFFF01, the entire prepared dilution), including a rinse of the sample container (in the case of DoD AFFF01, the dilution container).

USEPA SW-846 Method 3512 prepares groundwater, surface water, and wastewater samples by diluting the sample collected with an equal volume of methanol and does not require a rinse of the sample container to be included unless the sample had to be transferred to a larger container in order to allow for the addition of the appropriate volume of methanol. USEPA SW-846 Method 3512 does not use SPE or carbon clean-up steps, which is another significant difference from the other USEPA published methods. USEPA SW-846 Method 8327 states that during method development, some PFAS analytes showed a potential for loss during sample preparation or standard preparation using USEPA SW-846 Method 3512. This method states that a minimum organic cosolvent content must be maintained in standards and samples, and it cautions against aqueous subsampling prior to adding sufficient organic solvent.

USEPA Draft Method 1633 prepares groundwater, wastewater, surface water, and landfill leachates using solid phase extraction (SPE) followed by carbon clean-up steps to eliminate matrix interferences. USEPA Draft Method 1633 uses solvent extraction for soil, sediment, biosolids, and tissue preparation, followed by use of SPE cartridges and carbon clean-up steps to eliminate matrix interferences. Regardless of the method used, 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.

Some PFAS analytical methods, such as USEPA Method 533 and USEPA Draft Method 1633, use isotope dilution and extracted internal standard quantification schemes to calculate sample concentrations. Isotope dilution analysis (IDA) quantitation requires the use of extracted internal standards (EIS) that are the isotopically labeled analogs of the method analytes. Method analytes for which corresponding isotopically labeled analogs are not commercially available are quantitated using the isotopically labeled analogs of a method analyte of similar chemical properties. Since isotopically labeled analogs of PFOA and PFOS are commercially available, DoD AFFF01 uses isotope dilution quantitation. USEPA SW-846 Method 8327 uses an external quantitation scheme to calculate the percent recovery of isotopically labeled analogs that are added to the sample prior to dilution with methanol. This method does not use isotopically labeled analog recoveries to account for sample preparation and matrix interference biases in the sample result. All of the methods discussed above require these isotopically labeled standards be added to the sample at a designated point in sample preparation, depending on the sample matrix:

- aqueous samples–added to field samples while in the original container prior to extraction/dilution
- AFFF concentrates or high concentration aqueous samples – added to dilution of sample prior to extraction
- solid samples and biota–added after homogenization and subsampling, prior to addition of water or extraction solvent prior to extraction

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. Filtration is not recommended for samples with high particulate content because retention of PFAS onto filters has been noted. Centrifugation is often used to reduce or separate out sample particulates. See Preparation of Aqueous Samples with Particulates/Suspended Solids below for more details.

USEPA Draft Method 1633 requires the screening of all aqueous samples using a separate sample container from the one which will be used for sample preparation. Due to limitations in SPE cartridge capacity and potential contamination of sample preparation and/or analytical equipment, the method requires samples containing high concentrations of PFAS (for example, AFFF concentrates) to be diluted prior to SPE and sample clean-up. In these cases, adsorption onto the original sample container is not an issue, depending on the identified project-specific DQOs, because the amount of PFAS adsorbed onto the container walls is negligible compared to the amount of PFAS in the sample.

USEPA Draft Method 1633 requires the entire soil, sediment, and biosolid, sample that is collected be homogenized in the laboratory prior to subsampling. Tissue samples are to be prepared according to project requirements (for example whole fish versus fillet) and homogenized prior to subsampling.

Cleanup procedures can 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. USEPA Draft Method 1633 and DoD AFFF01 require carbon cleanup techniques to be used for all sample matrices. USEPA Draft Method 1633 and DoD AFFF01 require samples to be slowly concentrated to remove methanol from the extract to avoid loss of neutral and other highly volatile method analytes. In addition, USEPA Draft Method 1633 states that if methanol is not sufficiently removed, its presence during SPE can result in poor recovery of long-chain carboxylic acids and sulfonates. Care must be taken to avoid these outcomes.

The preparation batch QC samples that are required by these PFAS methods varies. Common laboratory QC samples included are as follows:

- Method blank – (one per preparation batch of 20 or fewer field samples) 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. Note that method blank is also referred to as Laboratory Reagent Blank in EPA drinking water methods.
- Sample duplicate – (minimum of one per preparation batch of 20 or fewer field samples) An AFFF concentrate sample that undergoes dilution prior to 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 or work plan.
- Laboratory Control Sample (LCS) or Ongoing Precision and Recovery (OPR) – (one per preparation batch of 20 field samples) Must contain all 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.
- Low-Level Laboratory Control Sample (LLLCS) or Low-Level Ongoing Precision and Recovery (LLOPR) – (one per preparation batch of 20 field samples) Must contain all project-specific PFAS at a specified concentration (for example, 0.5 to 2 times the LOQ for USEPA SW-846 Method 8327 or 2 times the LOQ for USEPA Draft Method 1633) 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 preparation batch of 20 or fewer field samples) Unlike LCSs, which contain no matrix interferences, CRMs can be of significant value when dealing with complex matrices such as soil, sediment, and tissue.
- Matrix spike (MS) and MS duplicate (MSD) – (one pair per prep batch of 20 or fewer field samples) An MS/MSD QC pair is not needed if IDA can be used for all PFAS of interest because the EIS recoveries account for the influence of matrix interferences in each sample, not just 1 in 20. If EIS 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.

For samples with high concentrations of PFAS, it is recommended that an LCS duplicate and a sample duplicate are prepared in lieu of an MS and MSD. DoD AFFF01 requires the sample duplicate to be prepared using a different aliquot from the same sample bottle to create the sample duplicate.

Preparation of Aqueous Samples with Particulates/Suspended Solids

USEPA Draft Method 1633 contains a procedure for determining the solids content of aqueous samples. This determination is to be performed using the second container that is required for each sample, not the sample container used to prepare the sample for the analysis for PFAS. The sample preparation procedures for PFAS analysis in USEPA Draft Method 1633 are applicable to aqueous samples containing less than 50 mg of solids. The method provides additional steps to take if particulates clog the SPE cartridge during extraction, including the use of additional SPE cartridges. Solids accumulate high concentrations of PFAS and specifically some of the longer-chain PFAS. Care should be taken to resuspend any solids and to rinse bottles so that measured concentrations consider the entire sample. When these solids settle out in the water samples, concentrations can decrease by an order of magnitude or more.

When samples contain greater than or equal to 50 mg of solid, depending on the laboratory procedure, the resulting concentrations could be different and the reported PFAS compounds (fingerprint) could be different. Ultimately, the data user needs to work with the laboratory to determine the appropriate procedure to be performed, depending on the end use of the data (for example, remedial action, human or ecological risk assessment, permit compliance, etc.). The project objectives may also vary depending on whether the sample matrix is wastewater, surface water, stormwater, or groundwater.

A survey conducted in 2020 by ITRC received responses from 16 laboratories. These responses demonstrated that the laboratory community is *not* consistently preparing aqueous samples in the presence of suspended solids.

- Several laboratories centrifuge the samples and decant off the water portion for subsequent extraction.
- Some laboratories may also extract the remaining particulates and combine the extract with the aqueous extract. However, only one of the surveyed laboratories does this routinely; the others do this only if requested by the client.
- Routine laboratory procedures are not dependent upon whether the matrix is groundwater, surface water, or wastewater.
- Several laboratories filter the samples, if requested by the client. This may result in adsorption of PFAS from the samples and potential cross-contamination, and should be implemented with care.
- After decanting, some laboratories rinse the remaining particulates in the bottle with solvent for the SPE.
- Not all laboratories disclose when samples require special preparation (decanting, centrifuging, or filtering) due to the presence of particulates. Therefore, this would not always be known to the data user.
- Laboratories have different procedures for when particulates clog the SPE cartridge; some labs may re-extract at a dilution, while others may start a new cartridge and attempt to continue with the extraction of the remaining sample.

Laboratories should clearly state whether reported concentrations are dissolved (water only) or “total” PFAS measurements (including sample particulates). Laboratories that are not including the extraction of the particulates (water only) are providing a dissolved PFAS measurement, rather than an overall or “total” PFAS measurement of these aqueous samples that would include the PFAS content of the particulate. Project objectives will determine whether dissolved or total PFAS measurements are appropriate. Sampling procedures should be designed to gather representative samples to meet project objectives. Some issues to consider in the determination of the need for a total or dissolved PFAS measurement are as follows:

Groundwater

- If minimizing presence of particulates is within the project objectives, use of low-flow groundwater sampling or no-purge samplers (for example, HDPE Hydrasleeve) should be considered.
- If turbidity is >10 NTU, consider a “total” measurement if sampling groundwater for compliance, delineation, remedial design, or risk assessment. “Total” can be defined as centrifuge, decant, and extract both phases, to report the dissolved concentration and the suspended/solid concentrations either individually or summed in the report.
- Collect samples for TSS analysis to assist in the evaluation of sample data. In lieu of TSS, turbidity measurements can also be helpful in the evaluation.

Drinking Water

- “Total” PFAS measurements are always required under the SDWA. However, drinking water samples rarely have issues with suspended solids.

Surface Water and Wastewater

- Use a “total” measurement if sampling surface water or wastewater for compliance, permitting, remedial design, or risk assessment.
- A “total” measurement may not be required if sampling for a line of evidence in a source area, rather than for a regulation.
- Collect samples for TSS analysis to assist in the evaluation of sample data. In lieu of TSS, turbidity measurements can also be helpful in the evaluation.

For laboratories performing centrifugation and subsequent decanting, it should be noted that it is important that the extracted internal standards are spiked into the aqueous samples prior to centrifugation. It is important to communicate with your laboratory prior to the collection of samples on the approach that will be used.

11.2.1.3 Sample Analysis

Instrument Type–LC/MS/MS

Currently all methods published by the USEPA and DOD use liquid chromatography-mass spectrometry-mass spectrometry (LC/MS/MS), which is especially suited for analysis of ionic compounds, such as the PFSAs 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. GC/MS may be appropriate for (ambient) atmospheric samples. PFAS are either directly detected using large-volume injection (Scott et al. 2006) or detected as a derivatized compound that is GC/MS amenable (Langlois et al. 2007). At this time, there is no published GC/MS method and very limited commercial availability for the technique for PFAS analysis.

In contrast, LC/MS/MS analysis of PFAS is widely available. 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. Certified standards of the highest purity available, for example, American Chemical Society grade, are quantitative standards that can be used for accurate quantitation. Quantitative standards containing linear and branched isomers are not commercially available for all applicable analytes. Currently, quantitative 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 grade standards, or qualitative standards, that contain branched and linear isomers are available for other PFAS, but these standards do not have the accuracy needed for quantitation purposes. Currently, qualitative standards that contain branched and linear isomers are available for PFOA, PFNA, PFOSA, NMeFOSE, NEtFOSE, NMeFOSA. USEPA Draft Method 1633 and DoD AFFF01 both require the analysis of technical grade standards to verify which peaks represent the branched isomers for method analytes when these standards are available. 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. USEPA Methods 533, 537.1, 8327, Draft Method 1633, OTM-45, and DoD AFFF01 contain storage requirements for both reagents and/or 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 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 PTFE products, solvent lines, and methanol, which could lead to method interferences and elevated baselines in chromatograms if not checked. The evaluation criteria for equipment and standards that is applicable depends on the analytical method used. For instance, USEPA Method 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." (USEPA 2020, pg. 7). USEPA Method 533 further specifies that the isotopically labeled analogs of method analytes and isotope performance standards meet this same requirement (USEPA 2019, 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 Method 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. USEPA SW-846 Method 8327, USEPA Draft Method 1633, and DoD AFFF01 all require two ion transitions from parent to characteristic product ions be monitored and documented for each analyte, with the exception of those analytes without a suitable secondary transition (for example, not detectable or has an inadequate signal-to-noise (S/N) ratio such as PFBA, PFPeA, NMeFOSE, NEtFOSE, PFMPA, and PFMBA). These methods determine ion transition ratio criteria based on information obtained from analysis of standards and use the ratio to detect potential bias in sample results.

Mass Calibration, Calibration Criteria, and Calibration Verification

All LC/MS/MS instruments require mass calibration prior to initial calibration. Mass calibration and mass calibration verification 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, as required by USEPA Draft Method 1633. Mass calibration should be performed according to the manufacturer's instructions. If manufacturer's instructions are not available, USEPA Draft Method 1633 provides an alternative procedure for mass calibration and mass calibration verification. Regardless of the procedures used, this method requires the mass calibration and mass calibration verification ranges to encompass the ion masses monitored by the method.

Following mass calibration and mass calibration verification, an initial calibration should be performed and verified. All of the published USEPA methods and the DoD methods contain requirements for instrument calibration and calibration verification specific to the PFAS concentrations expected in the media for which the method is applicable. USEPA Method 537.1 uses internal standard quantitation, while USEPA Method 533 and USEPA Draft Method 1633 use isotope dilution and extracted internal standard quantitation. USEPA SW-846 Method 8327 uses external calibration quantitation. Isotope dilution quantitation is recommended for complex matrices. The instrument is required to be calibrated at setup and as needed following QC failures such as initial calibration verification (ICV) or continuing calibration verification (CCV) failure. The lowest calibration point should be a concentration at or below the Minimum Reporting Limit (MRL), Minimum Level (ML), or Limit of Quantitation (LOQ), depending on the method. Most methods require the analysis of a standard at the MRL, ML, or LOQ concentration at least daily to document the instrument's ability to accurately quantitate down to that concentration. In addition, some methods also require a reporting limit check QC sample (for example, LLLCS or LLOQ verification sample) to be included with each sample preparation batch to demonstrate adequate quantitation at the lowest concentration is achievable using the sample preparation techniques required by the method.

Some methods, such as USEPA SW-846 Method 8327, require analysis of an ICV, which is a calibration verification standard prepared from a source separate from the calibration standards and analyzed after each initial calibration and before sample analyses are performed. The minimum frequency for ICV is after each initial calibration, prior to sample analyses. CCVs or CVs should be analyzed at the frequency specified in the analytical method. Most USEPA methods require at a minimum CCV/CV to be analyzed prior to sample analysis on days an ICV is not analyzed, after every 10 field samples, and at the end of the analytical sequence. Some methods rotate the concentration of CCVs/CVs to cover the entire calibrated range of the instrument and vary the acceptance criteria depending on the concentration. For example, in USEPA Method 537.1, the calibration acceptance criteria for each analyte are that the lowest calibration point must be within 50–150% of its true value while the other calibration points must be within 70–130% of the true values.

Isotope dilution and extracted internal standard quantitation can correct bias resulting from loss during sample preparation, such as in USEPA Methods 533 and Draft Method 1633. In the case of USEPA SW-846 Method 8327, isotopically labeled analogs are used as surrogates to monitor for loss without being used for recovery-correction of target analyte concentrations. 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 an analyte of interest against the isotopically labeled analog of that analyte, which is added to the sample both prior to and after the onset of sample preparation. EIS quantitation is the comparable technique used when an isotopically labeled analog of an analyte is not commercially available. Addition of EIS prior to sample 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 and EIS quantification schemes can be found USEPA Methods 533 and Draft Method 1633. Methods using isotope dilution should include isotopically labeled analog recovery for each sample and analyte in data reports. Isotopically labeled analog recoveries should be reported, and minimum/maximum isotopically labeled analog recoveries may be required by specific analytical procedures. For instance, USEPA Draft 1633 determines the recovery of these analogs through comparison to the response of analogs typically called non-extracted internal standards (NIS) added to the sample after extraction, prior to analysis.

Depending on project DQOs, low isotope recovery may indicate that quantitation was inadequate; the data are then reported as estimated values or not at all.

Instrument Blanks: When Are They Needed, Criteria, and Corrective Actions to Take

Due to the extensive use of PFAS, instrument blanks are critical in determining if the instrument is potentially affecting PFAS concentrations in samples. Some methods, such as USEPA Draft Method 1633, require instrument blanks to be analyzed following the highest calibration standard analyzed, daily prior to sample analysis, after each CCV/CV, and following samples that exceed the calibration range to ensure carryover does not occur. The acceptance criteria for instrument blanks are dependent on the method. For example, USEPA SW-846 Method 8327 requires the concentration of each analyte to be ≤ ½ the LLOQ or < 10% of the sample concentration. USEPA Draft Method 1633 is the only method which states that if instrument blanks indicate contamination following the highest calibration standard, corrective action, such as calibrating with a lower concentration for the highest standard, must be taken and 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.

Tissue

Interferences related to the matrix can be caused by the co-extraction of bile salts (for example, taurodeoxycholic acid, taurochenodeoxycholic acid, and tauroursodeoxycholic acid) with PFOS from the tissue sample. These bile salts can vary considerably from sample to sample and by species. The use of carbon clean-up steps, such as those required by USEPA Draft Method 1633, helps eliminate these interferences in most extracts; however, when excessive amounts are present in the extract, these steps may only reduce the amount of these bile salts. To address the potential interference, USEPA Draft Method 1633 requires that the chromatographic conditions are adjusted such that these bile salts elute at a retention time beyond 1 minute from the retention time window of PFOS.

11.2.2 Qualitative Techniques

Several techniques employing indirect measurement have been developed that can more comprehensively assess the range of PFAS contamination at a site. These qualitative techniques are not yet 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.

Five primary techniques have been developed to characterize unknown PFAS in a sample. These techniques are not multilaboratory validated or promulgated by USEPA. They are described in more detail in the sections below.

- The total oxidizable precursor (TOP) assay measures PFAA precursors or polyfluorinated compounds that can be converted to PFAAs.
- Particle-induced gamma-ray emission (PIGE) spectroscopy measures elemental fluorine isolated on a thin surface.
- Adsorbable organic fluorine (AOF) or extractable organic fluorine (EOF), paired with combustion ion

chromatography (CIC), measures the 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.
- Chemical Ionization Mass Spectrometry (CIMS) technique detects gas-phase PFAS, particularly fluorotelomer alcohols (FTOHs) and other oxygenated PFAS.

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 oxidation, 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 analyzed using conventional LC/MS/MS to determine the 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, in a water bath or other heating device) to thermolyze persulfate into a sulfate radical. At elevated pH, the sulfate radical is scavenged by hydroxide and forms a hydroxyl radical, which then converts the free PFAA precursor compounds to PFAAs. The predominant products (for example, > 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), cooled to room temperature, and neutralized prior to LC/MS/MS analysis. The increased concentrations of PFAAs generated after the oxidation step provide an estimate of 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 affect 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

The 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 (Ventia 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 Cn (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.

The TOP assay is the most widely commercially available of the qualitative techniques and 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 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.

The TOP assay results in a mixture of PFCA products from 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. Two limitations of the technique arise because of this effect. 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, the TOP assay may under-quantify short-chain PFAA precursors that are telomer-based. Sulfonamido compounds in control experiments did not exhibit a distribution of products; the Cn precursor forms the Cn PFCA in a 1:1 molar ratio.

Some studies have been published on the effectiveness of the oxidative process of the TOP assay on large molecular weight polymer compounds or newer ether-linked PFAS such as ADONA (Zhang et al. 2019). 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), the TOP assay may be similarly ineffective at converting PFAS polymers to free PFAAs. The 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, the 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 is 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 in food packaging (Schaider 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 fluorinated polymeric material, which is a limitation of both the 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 the TOP assay or AOF.

Technique Limitations

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 may not 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 the 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.

The range of operating conditions for PIGE has not been standardized and so far, the technique has been demonstrated with only one commercial laboratory.

11.2.2.4 Adsorbable Organic Fluorine with Combustion Ion Chromatography

AOF (Wagner et al. 2013) or extractable organofluorine (EOF) (Miyake, Yamashita, So, et al. 2007; Miyake, Yamashita, Rostkowski, et al. 2007; Yeung et al. 2008) paired with CIC (AOF/CIC or EOF/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, the extract resuspended into an aqueous solution that could adhere to the activated carbon, and then analyzed with CIC. As with the 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 an aggregate 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 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

Like PIGE, 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” measurements 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. Inorganic 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.

Like PIGE, 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)

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, 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 the molecular formula is 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 CF_2 groups. MS libraries of previously identified PFAS exist for targeted matching, although they will not definitively identify an unknown compound.

Possible Technique Uses

Such high-resolution mass spectrometry analyses 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. Accurate identification of compounds using high-resolution MS is a time-intensive and expensive process. Therefore, 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 the TOP assay, AOF, or PIGE. Compounds may be mistakenly identified as PFAS, and even when correctly identified, their concentrations may be greatly over- or underestimated when other compounds are used for comparative quantitative purposes.

11.2.2.6 Chemical Ionization Mass Spectrometry (CIMS)

Chemical ionization mass spectrometry (CIMS) can be used to detect gas-phase PFAS, particularly fluorotelomer alcohols (FTOHs), and other oxygenated PFAS.

Although GC/MS is not a common or well-established technique used for PFAS analysis, it is particularly applicable to (ambient) atmospheric samples. Currently, there are no published methods for using GC/MS for PFAS analysis, despite the distinct advantages for certain compound classes (for example, fluoro-telomer alcohols) of using GC/MS directly or after derivatization (chemical reaction to convert analyte of interest to a GC/MS-amenable “derivatized compound”) (Langlois et al. 2007), or using large-volume injection (Scott et al. 2006).

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 5.4* (USDOD 2021)*. A summary of key points from these data validation guidance documents, and others as noted in the table, has been compiled as* ***Table 11-6***, *PFAS Analytical Data Usability Table (included as a separate PDF).*

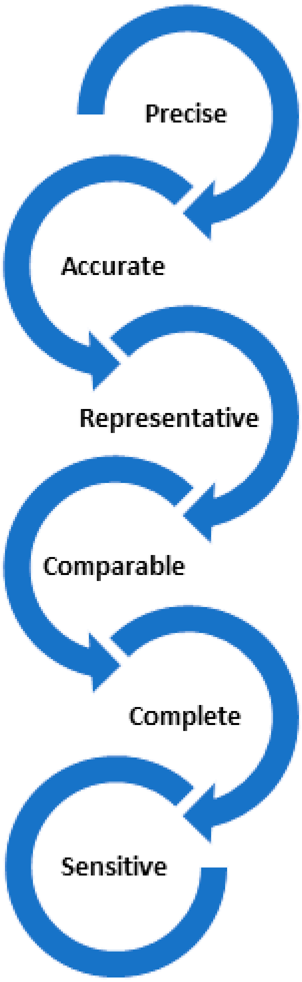
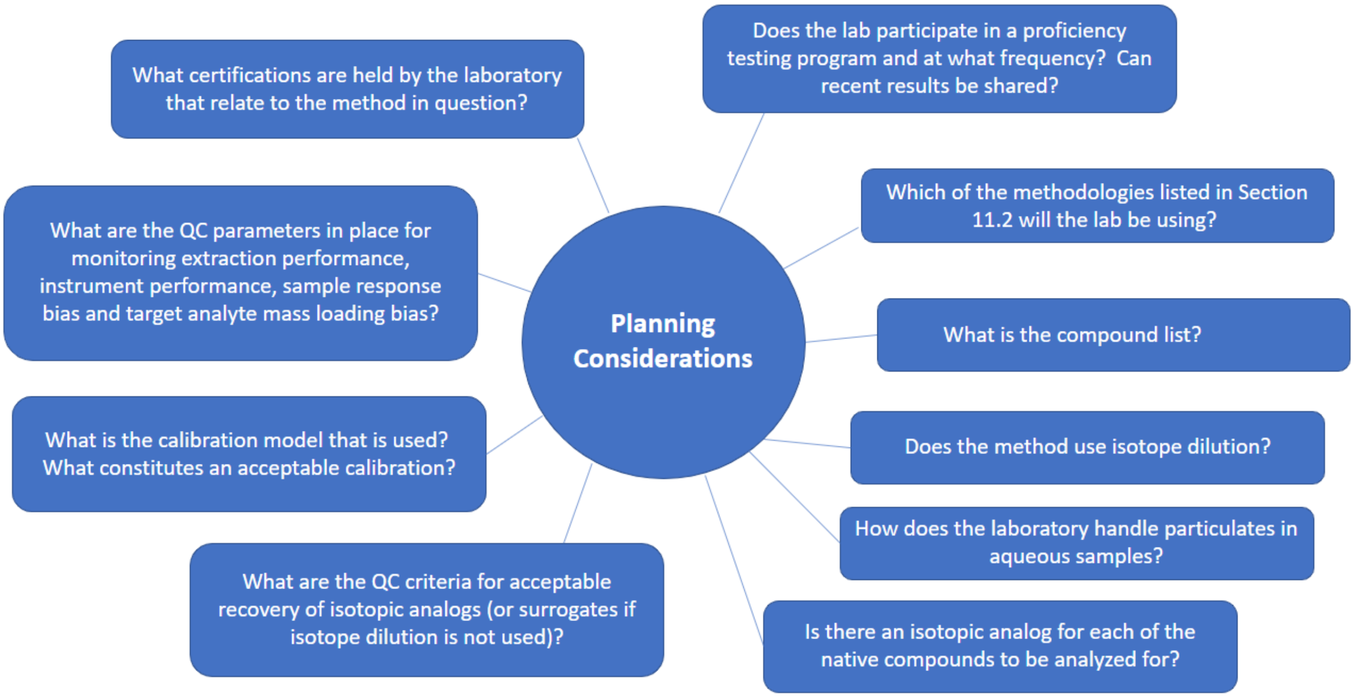


Figure 11-1. Data evaluation factors.

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 laboratory. Figure 11-2 contains laboratory considerations related to data usability in order to plan a sampling program.



Planning Considerations

What certifications are held by the laboratory that relate to the method in question?

Does the lab participate in a proficiency testing program and at what frequency? Can recent results be shared?

Which of the methodologies listed in Section 11.2 will the lab be using?

What is the compound list?

Does the method use isotope dilution?

How does the laboratory handle particulates in aqueous samples?

Is there an isotopic analog for each of the native compounds to be analyzed for?

What are the QC criteria for acceptable recovery of isotopic analogs (or surrogates if isotope dilution is not used)?

What is the calibration model that is used? What constitutes an acceptable calibration?

What are the QC parameters in place for monitoring extraction performance, instrument performance, sample response bias and target analyte mass loading bias?

Figure 11-2. Laboratory planning considerations for data usability.

Source: Modified from figure by 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, laboratory control samples, sample duplicates, matrix 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* (USEPA 2020, USEPA 2020), 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, indicate acceptable precision for the sampling and analysis?
- Do the data from the current sampling event compare well with historical data?
- Do the data make sense from a temporal point of view?
- Do the data make sense from a spatial point of view from one sampling point to the next across the project area?

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.

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.

11.3.3 Sensitivity

A quantitation limit (QL), or Limit of Quantitation (LOQ) 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 QL or LOQ 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 QL can vary from sample to sample and analyte to analyte. The QL should represent the level at which reliable qualitative and quantitative information is routinely reported (**Table 11-3**, included in the PFAS Analytical Methods Excel spreadsheet). When project-specified decision levels or action levels are near the QL, at least one quantitation limit check is recommended in all sample batches to demonstrate adequate quantitation at the lowest concentration.

Sensitivity is related to the QL in that sensitivity refers to the capability of a method or instrument to identify 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 QL (that is, “J” values) can generally be reported as long as all qualitative identification criteria are achieved. Typical QLs 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

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.

Sometimes even though lower QLs were planned for, the laboratory may have to perform dilutions, which causes the QLs 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 QLs may not be an issue if these other target analytes are present at very high levels.

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 QLs 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. If a complex matrix is encountered, the sample sizes may be reduced and/or the injection volumes may be increased, causing the QL 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 (included in the PFAS Analytical Methods Excel spreadsheet) includes the common PFAS reported by existing laboratories. The selected list may be dependent upon project objectives, regulatory requirements, 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; some are qualitative and some are quantitative. 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, PFNA, PFOSA, NMeFOSE, NEtFOSE, NMeFOSA, NEtFOSA, NMeFOSAA, and NEtFOSAA because these are the PFAS for which both linear and branched analytical standards currently 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 should 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 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.

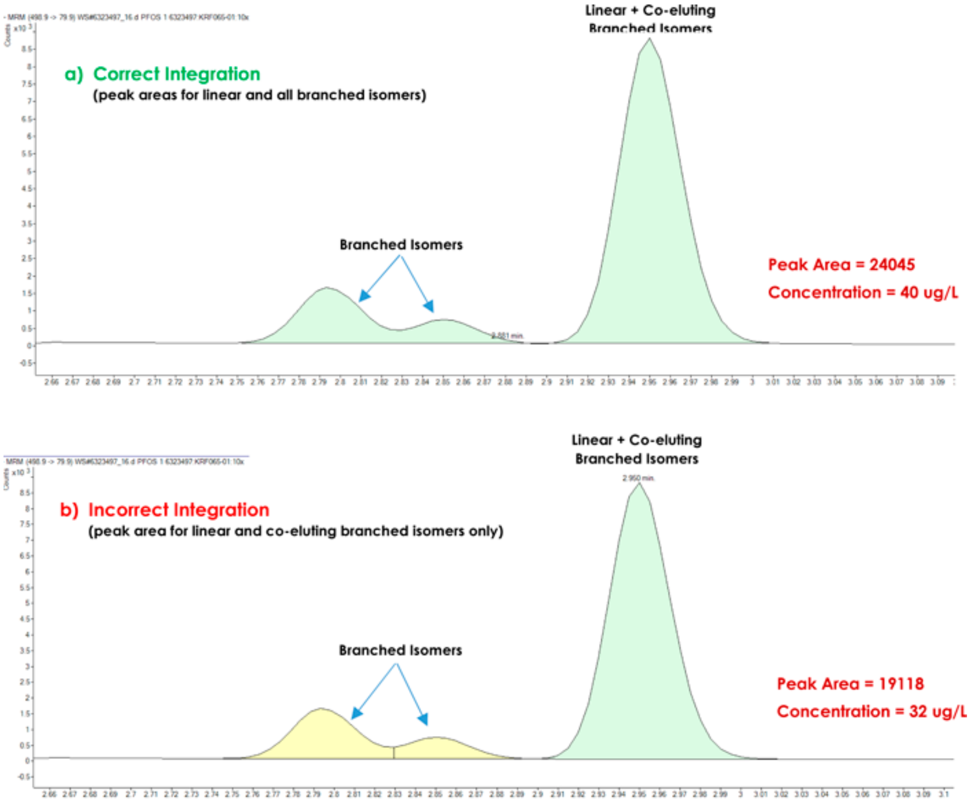


Figure 11-3. LC/MS/MS data illustrating a) complete integration of linear and branched PFOS, and b) partial integration of PFOS. Discrepancies in concentration will depend on the fraction of branched versus linear PFAS present, but in the current example PFOS concentrations in b) were 20% lower than in a).
Source: Bureau Veritas Laboratories, Mississauga, Ontario, Canada. Used with permission.

11.3.6 Isotope Dilution Standard Results and Surrogates

Isotope Dilution Standards

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 analogs 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 extracted internal standards, as defined in the USEPA Draft Method 1633, and function from a data usability standpoint as both an internal standard (used in the calculation of the target compounds) and as a surrogate standard (calculation of the recovery of the standard). Ideally, the number of isotopically labeled analogs used in the isotope dilution technique matches the number of target compounds. For example, USEPA Method 537.1 uses three surrogates for 18 target compounds, while the isotope dilution procedure in USEPA Method 533 attempts to use an isotopically labeled analog for each compound being reported (USEPA 2020). Non-extracted internal standards are also added to the sample or extract immediately preceding analysis.

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 non-labeled 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 isotopically labeled analog recoveries are either developed by the laboratory or dictated by the requirements of the project (for example, work plan or QAPP-specified criteria, regulatory criteria, or method criteria). Poor recovery of EIS 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 EIS recovery is very low (for example, < 10% recovery), nondetects associated with the EIS may be false negatives and should not be used for project decisions. If EIS recovery is low and ≥10%, there may be an indeterminate bias for the affected PFAS. If EIS recovery is high, there will be no effect on non-detects, but positive results for PFAS may have an indeterminate bias.

In the case where an isotope dilution extract is analyzed and requires re-analysis at a high dilution, the sample extract may need to be refortified with labeled isotope compounds or, if possible, a smaller aliquot of sample may need to be extracted to obtain adequate responses of EISs. 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 because these recoveries may be affected by ion suppression or ion enhancement due to the elevated concentrations of target PFAS and therefore may not be reflective of the extraction efficiency or other matrix interferences. 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.

Surrogates in Non-Isotope Dilution Procedures

Method 537.1 uses three surrogates for 18 target compounds, while EPA Method 8327 uses 19 surrogates for 24 target compounds. Injection internal standards are also added to the sample extract immediately preceding analysis. Quantitation of the target compounds and surrogates is performed relative to these injection internal standards. The results from the non-isotope 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 because results are not recovery-corrected.

Acceptance criteria or control limits for surrogate recoveries are either developed by the laboratory or dictated by the requirements of the project (for example, work plan or 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, compounds associated with this surrogate may be biased low. If surrogate recovery is very low (for example, < 10% recovery), nondetects associated with the surrogate may be false negatives and should not be used for project decisions. If surrogate recovery is high, there will be no effect on non-detects but positive results for PFAS may be biased high.

11.3.7 Blank Contamination

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.

As a consequence of the extensive use 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. Laboratory-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 laboratory-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 to determine whether the field sample results are accurate. For example, if the reagent water source used in the field is nondetect for PFAS, but contamination is found in any of the other field-based blanks, this 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 laboratory-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 a sample contains a contaminant within 5x–10x 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 prepared at the laboratory and 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 that are prepared and analyzed in the same manner as the sample. 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.

Review regulatory or method-specific acceptance limits with the laboratory, whether from a QAPP or laboratory-generated.

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. When both results are < 2x the QL, the potential uncertainty increases and therefore the acceptance criteria may need to be adjusted.

- If both results are < 2x the QL, 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 QL or not. If one result is > 2x the QL 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 should 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 perfluorosulfonic acids.

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 should 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, anion, or salt form of the PFAS is reported (Table 11-7).

Table 11-7. 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

11.4 Source Identification

As discussed in Section 10.5 Source Identification, one area of focus for PFAS investigations has been environmental forensics, specifically source identification. With so many industrial processes and transport pathways from which PFAS contamination can originate, attributing the occurrence of one or more PFAS to a particular source is of growing interest.

Source identification relies on the compilation of multiple lines of evidence from analytical data and site information, and the use of uni- and multivariate statistical analyses. Analytical lines of evidence include:

- Extended Target Lists
- Linear/Branched Speciation
- Non-Target Analysis (NTA)

These methods are briefly described in this section.

11.4.1 Extended Target Lists

Many commercial laboratories now analyze for more than 40 individual PFAS and some of these compounds may be indicative of a particular product or industrial process. Analyzing samples taken from or near these possible sources and comparing the profiles of those results to the area of concern, also known as chemical fingerprinting, may provide a demonstration of comparability.

11.4.2 Linear/Branched Speciation

The separate reporting of branched and linear PFAS can provide some indication of the process used to synthesize the PFAS detected. Electrochemical fluorination (ECF) produces a larger number of branched isomers than fluorotelomerization, which may be useful in differentiating sources (Benskin, DeSilva, and Martin 2010). This is not default laboratory reporting and needs to be arranged in advance to confirm availability and method details. However, due to isomer-specific differences in instrument response, and fate, transport and organism uptake/depuration, the use of speciated data for any inference more than presence/absence of a manufacturing source type is challenging.

11.4.3 Nontargeted Analysis (NTA)

The ability to identify compounds not targeted for measurement by existing methods is an important need. Nontargeted analyses are critical to being able to identify these compounds. With nontargeted analyses, chromatography (liquid and gas) is combined with high resolution mass spectrometry and multiple ionization techniques to determine atomic molecular weight and associated fragments. These results can be compared to databases for tentative identification (Liu et al. 2019). Further spectral interpretation may result in structural identification. This is particularly useful where no chemical standards exist.

Nontargeted analysis includes high-resolution mass spectrometry and suspect screening and is discussed in more detail below.

11.4.3.1 High-Resolution Mass Spectrometry

Although not widely commercially available, recent source research has focused on the use of high-resolution mass spectrometry (HRMS) for more comprehensive qualitative determination and fingerprinting for source attribution. As evidenced by SERDP-ESTCP funded projects listed below, the development of mass spectral libraries to match non-targeted analytes to source profiles is part of the ongoing research. NTA uses HRMS such as time-of-flight (TOF), ion-trap, or Fourier transform ion cyclotron resonance (FT-ICR) to generate high resolution accurate mass data. As extensive data sets are generated using HRMS, informed data filtering approaches are used to filter the data specific to PFAS related analytes. The data are first screened against previously generated suspect screening libraries that contain chromatographic/spectrometric information for PFAS characteristic to sources such as AFFF formulation, industrial process, and/or manufactured products. Then, mass spectrometry-specific data analyses, such as Kendrick mass defect plots, and general uni- and multivariate statistical analyses, are used to attempt source identification based on the presence/relative abundance of PFAS identified against the suspect screening libraries and other information (Benotti et al. 2020; Charbonnet et al. 2021).

Secondary Sources

SERDP PFAS Novel Methods for PFAS Source Tracking and Allocations

https://www.serdp-estcp.org/News-and-Events/Blog/Novel-Methods-for-PFAS-Source-Tracking-and-Allocations

ER20–1375 Comprehensive Forensic Approach for Source Allocation of Poly- and Perfluoroalkyl Substances – Chris Higgins, Colorado School of Mines

ER20–1121 Establishing an Approach to PFAS Forensics and a PFAS Source Materials Forensic Library – Mark Benotti, NewFields Government Services

ER20–1205 Machine Learning Pattern Recognition for Forensic Analysis of Detected Per- and Polyfluoroalkyl Substances in Environmental Samples – Tohren Kibbey, University of Oklahoma

ER20–1265 Ultrahigh-Resolution Fourier-Transform Ion Cyclotron Resonance Mass Spectrometry for Fingerprinting, Source Tracking, and Allocation of Per- and Polyfluoroalkyl Substances (PFAS) – Jens Blotevogel, Colorado State University

ER20–1056 Improving Access and Utility of Analytical Data for the Confident Discovery, Identification, and Source-Attribution of PFAS in Environmental Matrices – Benjamin Place, NIST, Department of Commerce

12 Treatment Technologies

The PFAS Team developed a Treatment Technologies training module video with content related to this section.

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 sources 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 technologies such as thermal treatment and chemical oxidation may not be completely effective at treating 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 technologies exists for treatment of either liquids or solids that may be performed either in situ or ex situ. However, field-implemented technologies for treating PFAS in liquids are limited to ex situ technologies.

“Treatment” versus “Remedial Action”

Full-scale treatment of PFAS-impacted liquids or solids is 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 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 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.

The treatment technologies described in this section are organized by degree of development and implementation, as well as 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 13.1.18.
- *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.

Technology Selection

Selecting a technology to meet treatment targets is dependent on:

- available treatment technologies
- an understanding of PFAS fate and transport
- a well-prepared conceptual site model
- defined (and achievable) treatment targets

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.

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 health advisories (USEPA 2016, USEPA 2016), 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 treatment technologies, and the capacity and tools to measure progress and compliance with desired regulatory criteria. A well-prepared conceptual site model (CSM) requires adequate information and is also fundamental to understanding and presenting the rationale and justification for the selected remedy. Additional information on CSMs is provided in Section 2.6, Section 9, and Section 10.

Moreover, proven treatment 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 Strategic Environmental Research and Development (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 12.9.

12.1.2 Tiered Remedial Approach

Along with the factors affecting technology selection (Section 12.1.1), practitioners should also consider the use of a tiered remedial approach to mitigate the risks posed by PFAS. This may include prioritizing protection of known human receptors from exposure to drinking water contaminated by PFAS by using point of entry (POE) or point of use (POU) treatment systems or connecting residents to public water supplies. Based on evaluating potential human and/or ecological receptors, upgrades to wastewater treatment plants may also be needed. Once these initial actions are taken, the source(s) of the PFAS contamination can be addressed using the appropriate remedial technology. A similar approach for the initial steps of site characterization is described in Section 10.2.

12.1.3 Section Organization

The information presented in the following sections reflects the availability of performance results published, presented, or otherwise publicly available. 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 available research is limited.

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 consideration when selecting a treatment technology. Common options for spent media management are off-site disposal by thermal destruction (via commercial incineration or cement kilns), reactivation/regeneration for reuse, and landfilling. Information on specific management considerations for spent media are discussed in the

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

respective sections below.

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.

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
- ER21-1191 Determination of Thermal Degradation Products and Residuals of Per- and Polyfluoroalkyl Substances-Laden Sorbent Materials in Gas and Condensed Phases
- ER21-1238 Sustainable PFAS Treatment Using Layered Double Hydroxide (LDH) Sorbents
- ER20-5182 Validation of Colloidal Activated Carbon for Preventing the Migration of PFAS in Groundwater
- ER18-1026 Rational Design and Implementation of Novel Polymer Adsorbents for Selective Uptake of Per- and Polyfluoroalkyl Substances from Groundwater
- ER20-5252 Anion Exchange Permeable Adsorptive Barriers (PABs) for In Situ PFAS Immobilization and Removal
- ER20-5100 In Situ PFAS Sequestration in AFFF-Impacted Groundwater

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); Woodard, Berry, and Newman (2017); and Zeng et al. (2020). 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; Zeng et al. 2020). 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.

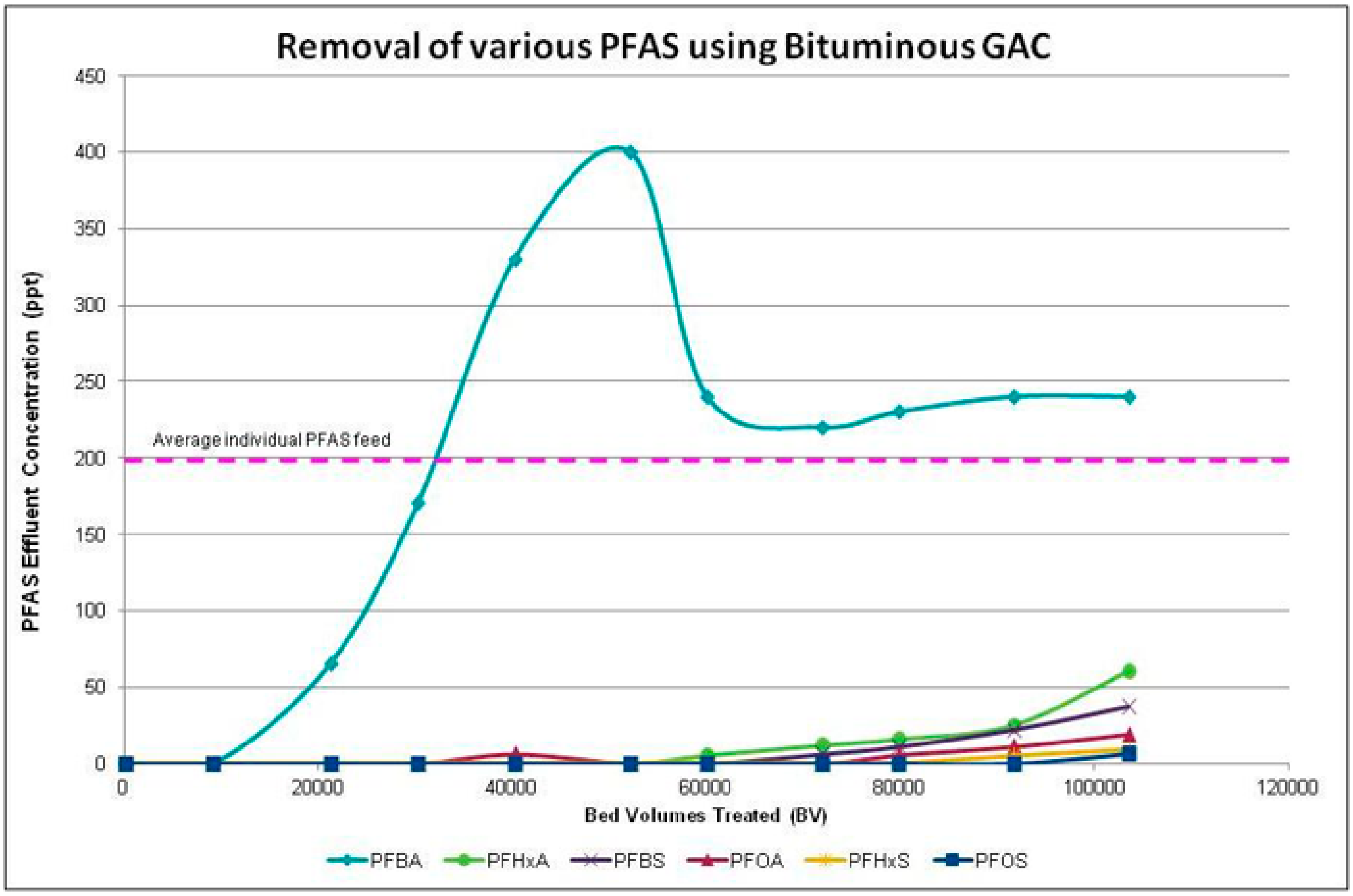


Figure 12-1. Example GAC removal curves at specific influent concentration (15-minute empty bed contact time).

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; Zeng et al. 2020). 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; Zeng et al. 2020). Studies 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 of the case studies on full-scale GAC-based systems used to treat PFAS in the literature are based on treatment of PFOA and PFOS in impacted drinking water sources. As such, limited information is available regarding the treatment of other PFAS, or PFAS in other source waters. 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 10–20 minutes per vessel are typical (AWWA 2019). 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.

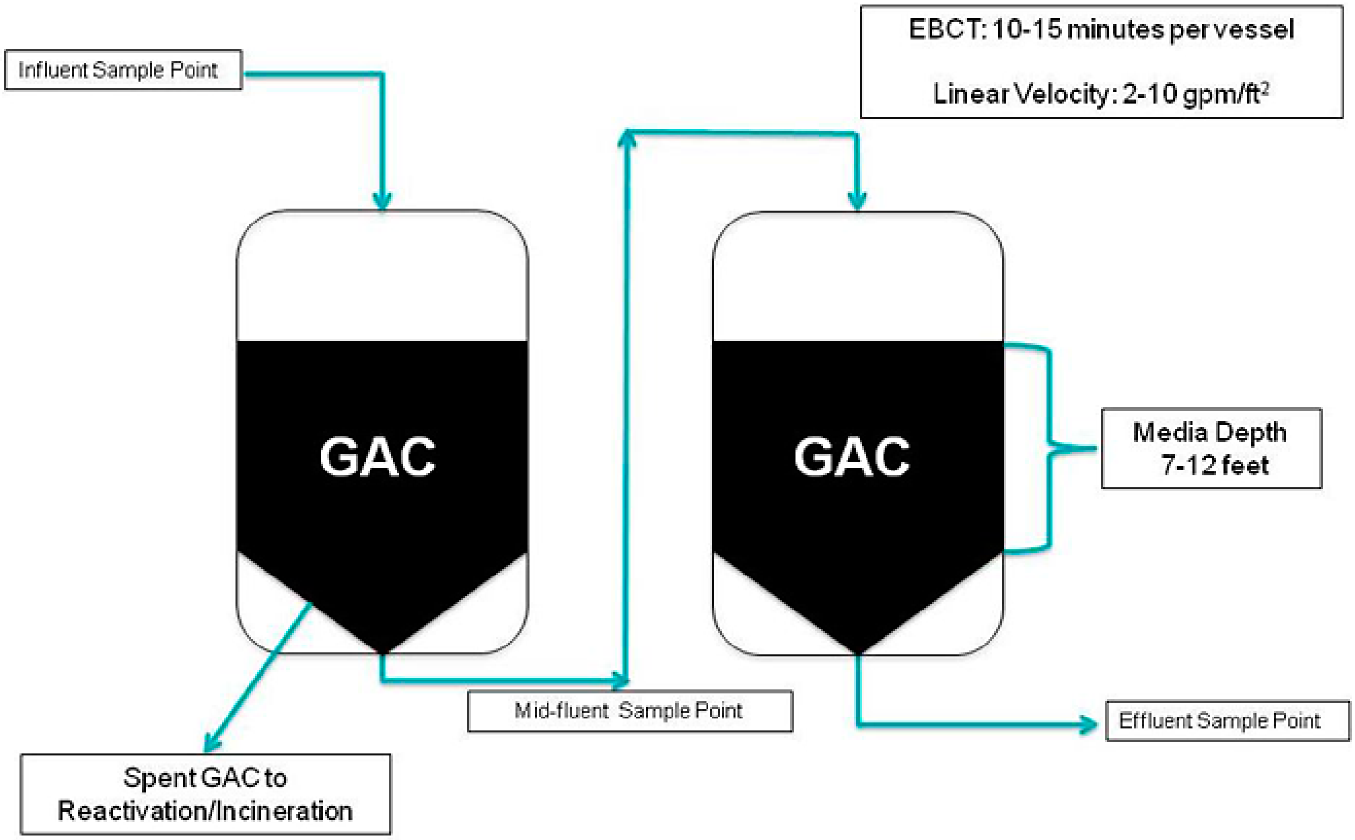


Figure 12-2. Typical GAC treatment system process flow diagram.

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). Additional information is included in Section 12.8.

Related Ongoing Research Funded by SERDP (ER) and Water Research Foundation (WRF)

- ER21-1185 Thermal Decomposition of Per- and Polyfluoroalkyl Substances on Granular Activated Carbon: Kinetics, Mass Balance, and Reuse of Reactivated Carbon
- ER21-1111 An Investigation of Factors Affecting In Situ PFAS Immobilization by Activated Carbon
- ER20-3034 Thermal Reactivation of Spent GAC from PFAS Remediation Sites
- ER19-5181 Improved Longevity and Selectivity of PFAS Groundwater Treatment Using Sub-Micron Powdered Activated Carbon and Ceramic Membrane Filter System

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.

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 1930 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; Zeng et al. 2020). 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 site-specific chemistry and co-contaminants, 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. Breakthrough is calculated as the ratio of the effluent concentration to the influent concentration (C/C_0). It is not uncommon to observe fluctuations in the breakthrough curve in some field pilot studies due to varied influent concentrations over time. For example, after a resin unit is in equilibrium with one PFAS at an initially higher influent concentration, a lower concentration influent can desorb PFAS from the resin, resulting in breakthrough higher than 100%. The typical breakthrough order observed in Figure 12-3 is expected to be similar for various anion exchange resins, as relative anionic bond strengths and carbon chain lengths result in shorter chain PFCAs to longer chain PFCAs desorbing first, followed by shorter chain PFSAs to longer chain PFSAs.

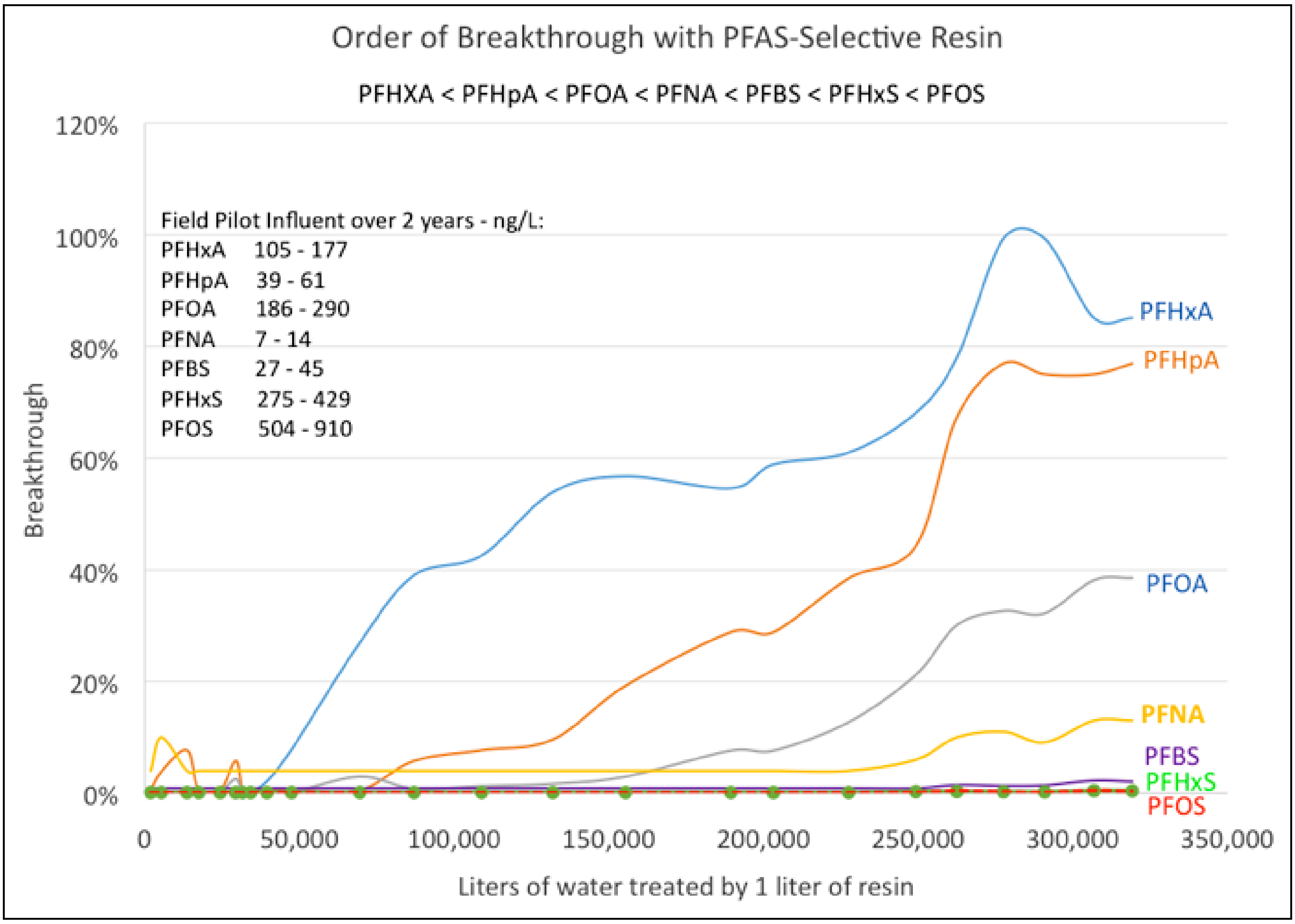


Figure 12-3. Example of IX removal curves from a field pilot study at specific influent concentrations (2.5-minute EBCT). (Note: Initial concentrations in ng/L or ppt.)

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_o), 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 could increase significantly (and thus impact the system's practical implementability) 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.

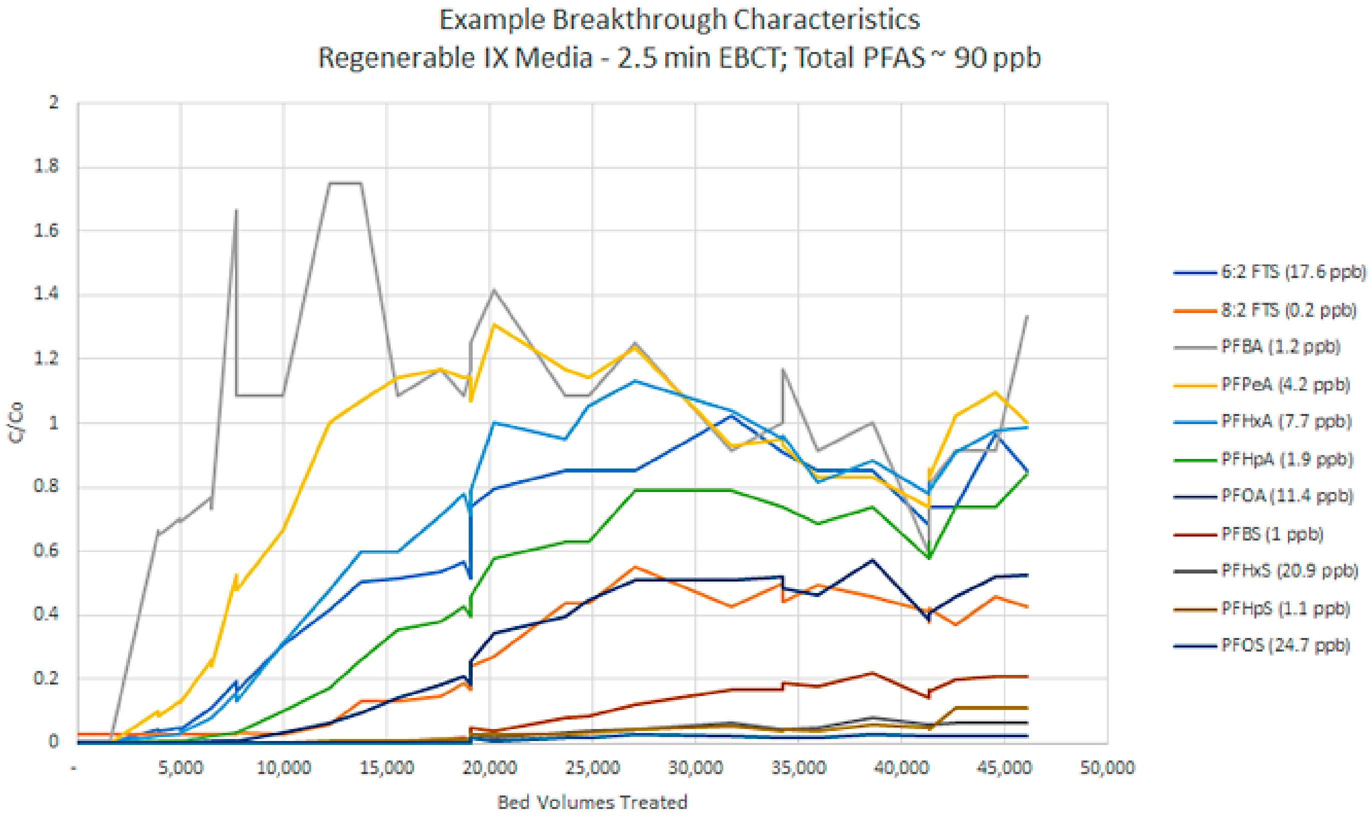


Figure 12-4. Example of regenerable IX removal curves from a field pilot study at specific influent concentrations (2.5-minute EBCT). (Note: Initial concentrations in µg/L or ppb.)

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.

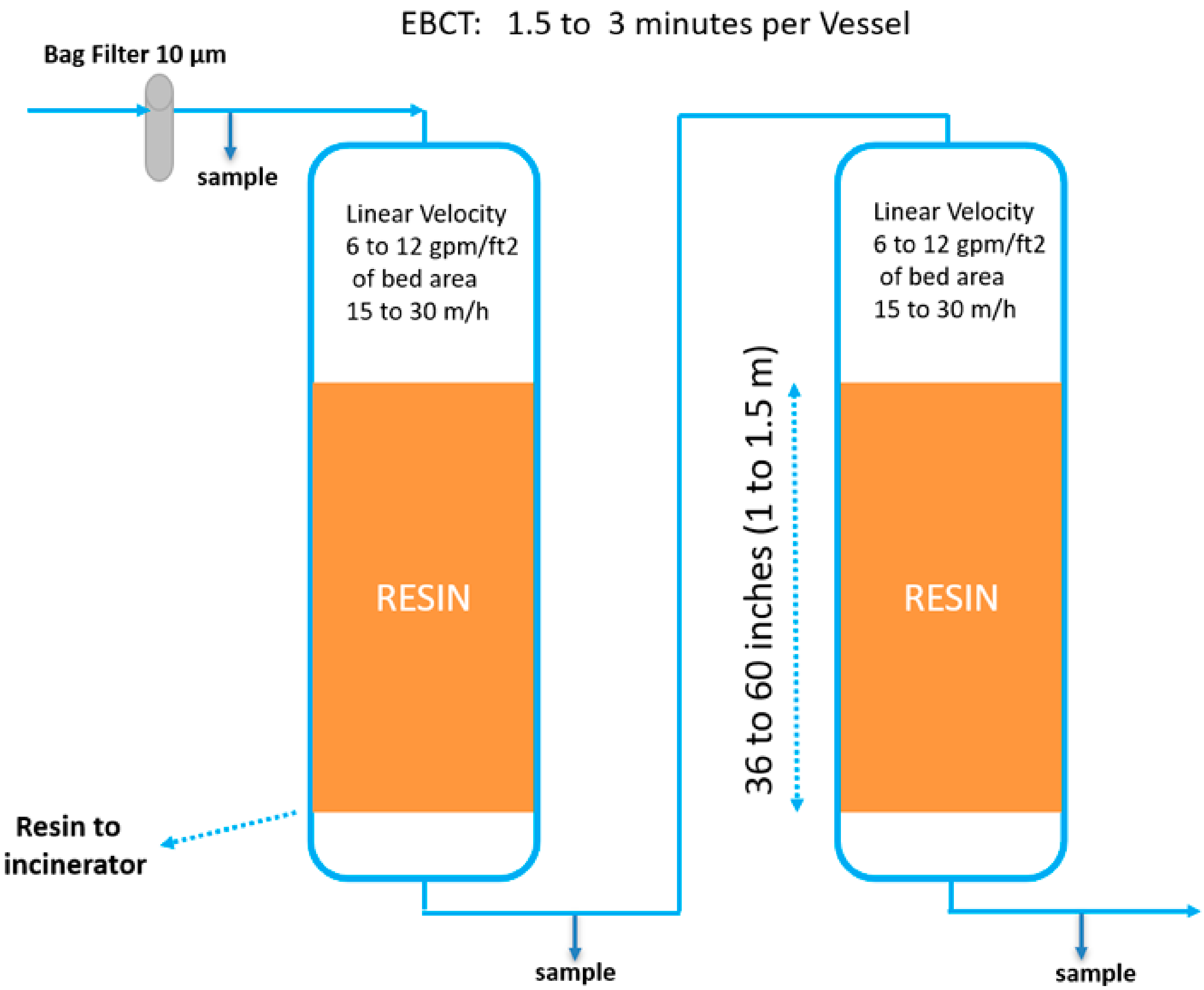


Figure 12-5. Single-use IX process flow diagram.

Source: Used with permission from Purolite 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: Ex situ ion exchange water treatment systems have unique sustainability considerations in addition to those shared with other ex situ sorption media water treatment systems. Major sustainability considerations for ion exchange 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 media transportation followed by destruction or disposal.

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
- ER20-5252 Anion Exchange Permeable Adsorptive Barriers (PABs) for In Situ PFAS Immobilization and Removal
- ER18-1320 Electrochemical Oxidation of Perfluoroalkyl Acids in Still Bottoms from Regeneration of Ion Exchange Resins

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 (high suspended and dissolved solids, co-contaminants) will reduce flux, 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. Because RO is a relatively expensive technology, efforts to improve water quality with pretreatment processes ahead of the RO membranes (filtration, precipitation; see Section 12.7) will result in reduced membrane cost.
- **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. 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

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 such as GAC (Section 12.2.1.1), IX (Section 12.2.1.2), or RO (Section 12.2.2).

Remedial actions for PFAS-impacted drinking water from private wells and other nondistributed sources can include providing alternative drinking water supplies, 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. 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.

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 2017). 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 Containment

The 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, but its impacts on PFAS treatment are less known and is a topic of study.

Effectiveness: Incineration is one of only a few technologies that can potentially destroy PFAS, though the ability to completely destroy PFAS through high-temperature combustion is not well understood (USEPA 2020). In December 2020, USEPA released a draft interim guidance on destruction and disposal of PFAS (USEPA 2020). 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 2020). 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.

Related Ongoing Research Funded by SERDP:

- ER18-1026 Rational Design and Implementation of Novel Polymer Adsorbents for Selective Uptake of Per- and Polyfluoroalkyl Substances from Groundwater
- ER18-1515 Cost-Effective Destruction of Per- and Polyfluoroalkyl Substances from DoD Subsurface Investigation-Derived Wastes using a New Class of Adsorptive Photocatalysts
- ER18-1417 Molecular Design of Effective and Versatile Adsorbents for Ex Situ Treatment of AFFF-Impacted Groundwater
- ER18-1395 Electrically Assisted Sorption and Desorption of Per- and Polyfluoroalkyl Substances
- ER18-1052 Remediation of Per- and Polyfluoroalkyl Impacted Groundwater Using Cationic Hydrophobic Polymers as Ultra-High Affinity Sorbents

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 1970 and 1980. 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.

Related Ongoing Research Funded by SERDP (ER)

- ER20-5100 In Situ PFAS Sequestration in AFFF-Impacted Groundwater
- ER20-5182 Validation of Colloidal Activated Carbon for Preventing the Migration of PFAS in Groundwater

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
- ER18-1300 Removal of Complex Mixtures of Perfluoroalkyl Acids from Water Using Molecularly Engineered Coatings on Sand and Silica

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. Surface-modified clays have been reported to have enhanced adsorption performance for a variety of organic and inorganic constituents (Han et al. 2019, as well as for PFAS (Zhou et al. 2010, 2013).

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 of these materials are lacking in study or field application. Most available literature is limited to academic laboratory experiments (Ochoa-Herrera and Sierra-Alvarez 2008; Punyapalakul 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.

Zeolite and clay minerals use both ion exchange and adsorption mechanisms to remove PFAS from water. These materials exhibit widely varying PFOS and PFOA adsorption capacities (Du et al. 2014), so PFAS adsorption performance should be assessed for each specific zeolite or clay-based media. 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 clays are made by intercalating a modification agent into the clay that has a high affinity for specific classes of contaminants. For PFAS adsorption, the modification agent is attached to the clay via cation exchange sites and includes electrostatic and hydrophobic moieties that are highly specific for PFAS. Mechanistically, PFAS molecules diffuse into the interlayer space of the surface-modified clay and then are bound through ionic and van der Waals forces with the fixed modification agent (Yan et al. 2021).

Two modified clay-based adsorbent products are identified as being used in field pilots or small-scale field trial applications (Arias et al. 2013; Arias Espana, Mallavarapu, and Naidu 2015) to treat PFOA and/or PFOS.

A commercially available surface-modified clay was successful at adsorbing a variety of PFAS from AFFF-impacted groundwater. The media was resistant to fouling by groundwater constituents, such as natural organic matter, and common co-contaminants (diesel, TCE, and 1,4-dioxane) (Yan et al. 2020). Laboratory and pilot-scale column testing of surface-modified clay for PFAS removal from contaminated groundwater that is to be used for drinking water showed PFOS and PFOA removal to the treatment target (2 ng/L). This media demonstrated a shorter empty bed contact time (EBCT) and longer media bed life than 13 other adsorbents (Pannu and Plumlee 2021; Hwang and Grieco 2021). PFAS adsorption (short- and long-chain) by using surface-modified clay with a variety of water types was examined in Grieco et al. (2021) and Najm et al. (2021).

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.

Related Ongoing Research Funded by SERDP:

- ER18-1526 Complete Reductive Defluorination of Poly- and Perfluoroalkyl Substances (PFASs) by Hydrated Electrons Generated from 3-Indole-acetic-acid in Chitosan-Modified Montmorillonite
- ER22-7482 Demonstration-scale Evaluation of a Novel Surface-Modified Clay Adsorbent: Comparison of Fluoro-Sorb, GAC, and IX Resin for the Removal of PFAS and Co-Contaminants in Groundwater

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).

12.5.1.5 Hydrogels and Fluorogels

Efficient removal of short-chain PFAS from water can be achieved using hydrogels and fluorogels because of their high selectivity and affinity for these compounds (Ateia et al. 2019; Kumarasamy et al. 2020). For example, Ateia et al. (2019) demonstrated selective, rapid removal of 16 PFAS using cationic polymer (hydrogel) poly (N-[3-(dimethylamino)propyl] acrylamide, methyl chloride quaternary (DMAPPAA-Q). While adsorption was not reversed in a standard environmental matrix, regeneration was possible using a simple solvent/salt matrix. Performance was maintained in six consecutive sorption/regeneration cycles.

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.

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). New research has focused on functionalizing membrane surfaces to improve PFAS selectivity (for example, Johnson et al. 2019). 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 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 et al. 2012; Kerfoot 2014; Huang et al. 2016; Eberle, Ball, and Boving 2017). Lin 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%n 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 published 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.

Related Ongoing Research Funded by SERDP: (text box)

- ER18-1545 Enhanced Oxidative Destruction of PFAS in Investigation-Derived Waste Soil and Water

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) and 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 (Cao et al. 2020).

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 micro/nano bubbles 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 (SO_4^{2-}) and carbon dioxide (CO_2). Vecitis et al. (2008) reported a complete recovery of SO_4^{2-} 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 SO_4^{2-}, CO_2, 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. Lei et al. (2020) showed a synergistic treatment effect of a combined persulfate/ultrasound approach.

Related Ongoing Research Funded by SERDP:

- ER21-5045 Sonolysis-Based In Situ PFAS Treatment Within an HRX Well

12.5.4.5 Photolysis/Photochemical Oxidation

A thorough review of photolysis/photochemical oxidation technology for PFAS decomposition is reported in Wang 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 Fe^{3+}, $S_2O_8^{2-}$, TiO_2, heteropolyacid photocatalyst ($H_3PW_{12}O_{40}$), CO_3^{2-}, and IO_4^- 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; Gomez-Ruiz et al. 2018). This is due to generation of strong and reactive oxidative species such as $OH^•$, $H^•$, $CO_3^{•-}$ 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 et al. 2012; Giri et al. 2012; Lyu et al. 2015, 2015; 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
- ER19-1403 Validation of UV/TiO2 Activated Alkaline Media (CFM) for Destruction of PFAS in Concentrated Liquid Waste Streams

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 (Liu et al. 2017). These then undergo hydrolysis to form subsequent shorter PFAS (losing CF_2 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 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; Schaefer et al. 2019; Wang et al. 2019). Some other electrodes, such as lead dioxide (PbO_2), titanium oxide (TiO_2), titanium suboxide ($Ti4O_7$), and tin oxide (SnO_2), 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 et al. 2012; Zhou et al. 2012), current density, electrolyte type (Song et al. 2010; Zhuo et al. 2012), electrode distance (Lin 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.

Electrochemical treatment 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 and foam fractionation (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 ($H^{\bullet}$) 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. Cui et al. (2020) offered a detailed critical review focused on mechanisms of reductive PFAS destruction by solvated electrons.

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. Tenorio et al. (2020) showed that PFAS treatment by solvated electrons varies widely among compounds.

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

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; Singh et al. 2019).

Determination of plasma treatment mechanisms and degradation pathways for PFAS is 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
- ER18-1624 Plasma Based Treatment Processes for PFAS Investigation Derived Waste

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.

Related Ongoing Research Funded by SERDP or Air Force AFWERX:

- ER-2426 Quantification of In Situ Chemical Reductive Defluorination (ISCRD) of Perfluoroalkyl Acids in Groundwater Impacted by AFFFs
- Contract Number FA864921P0368: Reactive Bimetallic-Carbon Media for Destruction of PFAS-Containing Aqueous Fire Fighting Foam Stockpile

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 B_{12} 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 B_{12} 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 (C_5-C_8) are the final products (Park, de Perre, and Lee 2017).

Bimetallic $nNiFe_0$ particles supported on activated carbon have demonstrated transformation of both linear- and branched-PFOS isomers, achieving 94% PFOS transformation at 50°C (Zenobio et al. 2020). Transformation byproducts detected in the particle extracts indicate defluorination and desulfonation pathways.

12.5.4.11 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 1997). 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 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). Kim et al. (2019) demonstrated eBeam defluorination of PFOS when used in combination with chemical oxidants.

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.

Related Ongoing Research Sponsored by SERDP:

- ER18-1620 Ex Situ Remediation of Investigation-Derived Wastes containing PFAS by Electron Beam Technology

12.5.4.12 Supercritical Water Oxidation

Supercritical water oxidation (SCWO) is a destructive technology that uses unique properties of water above its critical point at 374°C and 3200 psi. Thus, it is a high temperature and pressure technology. At these conditions an aggressively oxidative environment is created when air is injected.

SCWO is not a new technology and has been evaluated and applied to various organic compounds in liquid streams for decades (Tester et al. 1993). More recently, with the focus on PFAS, bench and pilot-scale systems have been evaluated (Jama et al. 2020; Hori et al. 2008; USEPA 2021).

Related Ongoing Research Funded by SERDP

- ER20-5350 Supercritical Water Oxidation (SCWO) for Complete PFAS Destruction

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 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.

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.

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
- ER20-1023 Microbially-Mediated Defluorination of High-Priority Per- and Polyfluoroalkyl Substances: Microorganisms, Genetics, and Biochemistry
- ER20-1219 Biotransformation and Potential Mineralization of PFOS, PFHxS, and PFOA by Acidimicrobiaceae sp. A6 under Iron Reducing Conditions
- ER20-1430 Biodegradation of Per- and Polyfluoroalkyl Substances (PFASs) via Superoxide-Hyper-Producing Bacteria

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 et al. 2010), 6:2 FTS (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).

12.5.6 Alkaline Hydrothermal Reaction

Applying elevated temperatures and pressures to water in a sealed environment creates a unique reactive environment that has been shown to degrade organic compounds, including PFAS. Wu et al. (2019) demonstrate rapid destruction of particularly recalcitrant PFOS during hydrothermal treatment of a solution amended with NaOH. They propose an initial cleavage of the functional group catalyzed by OH-, followed by sequential carboxylation.

Related Ongoing Research Funded by SERDP:

- ER18-1501 Hydrothermal Technologies for On-Site Destruction of Site Investigation Wastes Impacted by Per- and Polyfluoroalkyl Substances (PFAS)

12.5.7 Foam Fractionation

Due to the surface-active nature of many PFAS compounds, foam fractionation can separate PFAS from bulk liquid solutions. In this approach, air or other gases (including reactive gases such as ozone) are passed through the aqueous phase to create bubbles that form into foam. PFAS partition to the air-water interface of the bubble surfaces and accumulate as foam. The foam, containing concentrated PFAS, is then readily physically separated from the bulk liquid. Buckley et al. (2021) presented a detailed review, including description of key separation mechanisms, of foam fractionation for water treatment.

Surface activation foam fractionation (SAFF) is a process that uses air to generate fine 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. This 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 plant was commissioned on May 13, 2019 and treats 66,000 gpd.

A small one-day field trial in Williamtown, 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; Burns, Stevenson, and Murphy 2021). 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.

Coupling separation of PFAS with destructive approaches can enhance treatment efficiency and effectiveness. For example, ozofractionation uses ozone instead of air to create foam. Use of reactive ozone is an advantage as destruction of some PFAS and other present in the system can occur, as described in Section 12.5.4.1 and by Dai et al. (2019). Lyu et al. (2020) found enhanced treatment by coupling foam fractionation with photodegradation for treatment of PFAS.

Related Ongoing Research Funded by SERDP:

- ER19-5075 In Situ Treatment of PFAS Using D-FAS Technology

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 2019). 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 2019). 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 batch experiments, a reduction of 95-99% of leachable anionic PFAS, including PFOS and PFOA, was achieved with amending contaminated soil with 0.5% to 5% by weight of a commercially-available surface-modified clay (Wang et al. 2021). Other laboratory (Willett and Geary 2021) and in situ field studies (McDonough et al. 2021) on soils mixed with up to 10% by weight of this surface-modified clay showed reduction in leaching of a number of PFAS. In situ solidification is intended to yield a high-compressive-strength monolith that has low permeability. A bench-scale study (Sörengård, 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 (Crownover et al. 2019; DiGuiseppi, 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 volatilized PFAS and air emissions (Lassen et al. 2013; USEPA 2020). 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 treatment 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
- ER19-1408 Analysis of Fate of PFAS During Incineration
- ER20-5250 In Situ Thermal Treatment of PFAS in the Vadose Zone
- ER20-5198 Ex Situ Thermal Treatment of Perfluoroalkyl and Polyfluoroalkyl Substances
- ER20-5350 Supercritical Water Oxidation (SCWO) for Complete PFAS Destruction
- ER21-1288 Multi-Scale Evaluation of PFAS Thermal Destruction Requirements
- ER21-1107 Improved Understanding of Thermal Destruction Technologies for Materials Laden with Per- and Polyfluoroalkyl Substances
- ER21-1234 Experimental and Theoretical Validation of the Chemical Kinetics for the Thermal Destruction of Perfluoroalkyl Alkyl Substances
- ER21-1135 Improving Low Temperature Thermal Treatment of Per- and Polyfluoroalkyl Substances (PFAS) and Infrared (IR) Spectroscopy Methods to Monitor Treatment Efficacy
- ER20-5250 In Situ Thermal Treatment of PFAS in the Vadose Zone
- ER20-5198 Ex Situ Thermal Treatment of Perfluoroalkyl and Polyfluoroalkyl Substances

12.7 Integrated Water Treatment Solutions

This section provides guidance on the development and selection of treatment solutions for water containing PFAS in combination with other constituents. It is often necessary to combine treatment technologies into integrated solutions to achieve project objectives for co-contaminants. While PFAS can affect multiple media, the focus of this section is on treatment of water and the water treatment processes. The water matrix may contain constituents such as TOC, TSS, and TDS at levels that may require pretreatment because they could interfere with and reduce the effectiveness of the PFAS treatment technologies. Regulated organic and inorganic co-contaminants require treatment to meet their respective remedial objectives. An integrated solution can include a combination of treatment mechanisms (separation, sorption, and destruction) and development stages (for example, field-implemented, limited application, and developing).

12.7.1 Development of Alternative Water Treatment Trains

Many factors play into the development and selection of integrated treatment solutions and the considerations and examples provided here are intended to assist in the selection process. The remedial action or treatment objectives are key drivers in selecting treatment technologies and waste disposal methods. Liquid and solid waste stream generation is another critical factor in the selection process as waste may be subject to PFAS regulations. While the focus of this section is on water treatment, the treatment technologies applicable to solid wastes are discussed in Sections 12.3, 12.4, and 12.6. Factors affecting pre-treatment, primary treatment, and post-treatment selection are presented in Section 12.1.1. Selection of an integrated treatment solution may be an iterative process to select a primary treatment technology that best meets project objectives while minimizing the associated pre-treatment, post-treatment, and generated waste streams.

Figure 12-6 (provided as a separate PDF) shows a sample flow chart that includes a variety of options for integrated treatment solutions based on different water and process waste matrices. The water matrix column in the flow chart, which represents the composition of the water to be treated, includes examples of naturally occurring substances and inorganic and organic co-contaminants. The pre-treatment stage provides examples of technologies that can be used as standalone or in combination for treating different co-contaminants. The PFAS treatment system can also include multiple treatment technologies (treatment train) that each generate waste that must be subsequently treated or disposed of. The sample flow chart provides examples of wastes generated by different treatment technologies and corresponding potential disposition options. Factors in selecting PFAS treatment methods are presented in Sections 12.2, 12.3, 12.4, 12.5, and 12.6.

Every water source is different, so proper characterization is important for developing and selecting the proper integrated solution. The following questions may help guide the selection process:

1. What are the remedial action objectives and discharge criteria for all contaminants?
2. What information is available on geochemistry, natural organic matter, and potential inorganic constituents, and what are the remaining data needs for adequate characterization?
    1. What are the pre-treatment options for the identified matrix?
    2. What wastes are generated through pretreatment?
3. What other non-PFAS organic constituents (e.g. volatile and semi-volatile organic co-contaminants) are present at levels that require treatment?
    1. What types of treatment technologies or combinations of technologies apply?
    2. What wastes are generated by application of each treatment technology?
    3. Can the co-contaminants be effectively treated by the same technology as PFAS, and, if so, could this adversely affect PFAS removal? Do the technologies compete with each other, and does this reduce effectiveness and efficiency of PFAS removal?
4. Are field-implemented treatment technologies available for the treatment or destruction of waste streams; if not, consider limited application and developing technologies and possibly pilot testing?

Lu et al. (2020) provided a critical review of PFAS treatment train approaches. Additional recent work is focusing on simultaneous coupling of technologies, where PFAS are sorbed onto reactive particles, which are then destroyed in the presence of catalyst (for example, Zhang, Zhang, and Liang 2019; Xu et al. 2020). Pica et al. (2019); Soriano, Gorri, and Urtiaga (2017); and Soriano, Schaefer, and Urtiaga (2020) described and evaluated combined filtration followed by electrochemical oxidation approaches.

Related Ongoing Research Funded by SERDP:

- ER18-1230 Development, Evaluation, and Technology Transfer of BMPs for Optimizing Removal of PAHs, PCBs, PFASs, and Metals from Stormwater at DoD Sites
- ER18-1278 An Electrocoagulation and Electrooxidation Treatment Train to Degrade Perfluoroalkyl Substances and Other Persistent Organic Contaminants in Groundwater
- ER-2714 Development of Coupled Physiochemical and Biological Systems for In Situ Remediation of Perfluorinated Chemical and Chlorinated Solvents Groundwater Plumes
- ER-2718 Synergistic Treatment of Mixed 1,4-Dioxane and Polyfluorinated Chemical Contaminations by Combining Electrolytic Degradation with Electrobiostimulation
- 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
- ER21-5136 Nanofiltration Followed by Electrical Discharge Plasma for Destruction of PFAS Co-occurring Chemicals in Groundwater: A Treatment Train Approach
- ER20-1286 A Synergistic Platform for Defluorination of Perfluoroalkyl Acids (PFAAs) through Catalytic Reduction Followed by Microbial Oxidation
- ER19-1410 Treatment Train for In Situ Mineralization of PFOS Using Heat-activated Persulfate Oxidation (HAPO)
- ER18-5015 Removal and Destruction of PFAS and Co-Occurring Chemicals from Groundwater via Extraction and Treatment with Ion Exchange Media, and On Site Regeneration, Distillation, and Plasma Destruction
- ER18-1482 Chemical Decomposition Combined with Physical Adsorption for the Treatment of Investigation-Derived Waste Containing PFASs
- ER18-1633 Lines of Evidence to Assess the Effectiveness of PFAS Remedial Technologies
- ER18-1306 Combined In Situ/Ex Situ Treatment Train for Remediation of PFAS-Impacted Groundwater
- ER18-1289 Treatment of Legacy and Emerging Fluoroalkyl Chemicals in Groundwater with Integrated Approaches: Rapid and Regenerable Adsorption and UV-Induced Defluorination
- ER18-1497 High-Performance Treatment of PFASs from Investigation-derived Waste: Integrating Advanced Oxidation-Reduction and Membrane Concentration
- ER-201729 Field Demonstration to Enhance PFAS Degradation and Mass Removal Using Thermally-Enhanced Persulfate Oxidation Followed by Pump-and-Treat

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 2012, 2018), including methods to quantify the environmental footprint (USEPA 2019). 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, 2012, 2013).

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 2011, 2011, 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 2012). Lastly, climate change vulnerability and adaptation measures of remedial technologies should also be considered to ensure resiliency in the implemented remedial action (USEPA 2013, 2014).

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 (2018).

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

Updated August 2021.

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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 have the opportunity to influence site characterization, remedy selection, and long-term site management. Because PFAS 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 challenging, because there are many misconceptions about PFAS. The lack of scientific knowledge about many of these PFAS further enhances the need to educate 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. Section 14 addresses tools for PFAS-specific risk communication challenges, and provides some examples of PFAS risk communication issues.

This section identifies the concerns of stakeholders who have been or may be affected by PFAS contamination. Because PFAS are emerging contaminants and have been detected in ecological receptors (animals and plants, see sections 5.5 and 5.6) and blood serum in many humans (Section 7.1), 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. **This section 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.**

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. Series-specific lists 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 which is published as a separate document.

The following concerns were identified during preparation of this document, with details of these concerns in the following sections.

• Lack of comprehensive regulatory standards or advisories for thousands of PFAS for the following (13.1.1): Drinking water (13.1.1.1) Environmental media other than drinking water (13.1.1.2) Human consumption of food (13.1.1.3) Ecological risk (13.1.1.4)	• PFAS in food packaging (13.1.12)
• Desire for one standard or screening level for PFAS (13.1.2)	• Potential PFAS contamination in recycling, compost, and fertilizer (13.1.13)
• Lack of Occupational standards (13.1.3)	• Lack of disclosure by product manufacturers (13.1.14)
• Lack of comprehensive monitoring information (13.1.4)	• Limited availability of information on the health effects of PFAS (13.1.15)
• Need to apply a precautionary approach in decision making (13.1.5)	• Responsibility for sampling and treatment on private property (13.1.16)
• Safety of short-chain substitutes (13.1.6)	• The potential for PFAS emissions from cleanup methods (13.1.17)
• Contamination from AFFF release sites (13.1.7) and unused AFFF disposal (13.1.8)	• Lack of scientific evidence that current PFAS treatment and disposal methods and remedies are fully protective of human and ecological health and prevent toxic emissions (13.1.18)
• Duty to warn AFFF responders (13.1.9)	• Stormwater and PFAS manufacturing discharges that may contain PFAS (13.1.19)
• Limitations in sampling and analysis methods (13.1.10)	• Psychological effects (13.1.20)
• Limited programs for health monitoring and blood testing (13.1.11)	• Economic consequences of local PFAS contamination (13.1.21)

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 Comprehensive Regulatory Standards or Advisories for Thousands of PFAS

This section discusses the lack of advisory standards or screening values for various environmental media and exposure pathways.

13.1.1.1 PFAS in Drinking Water

As of December 2021, USEPA has set health advisories for only two of the thousands of PFAS compounds: PFOA (perfluorooctanoic acid) and PFOS (perfluorooctane sulfonic acid). 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.

Several states have rules on these and other PFAS compounds, but the majority of PFAS compounds are not included in any of the states' regulations. Information about available current regulatory standards and guidance values for PFAS in drinking water are provided in Section 8, with a summary table linked on the PFAS fact sheet page.

Stakeholders are concerned because the health consequences of these other compounds remain uncertain. Firm conclusions relating individual PFAS compounds to specific health outcomes remain elusive (Guelfo et al. 2018). Information about health impacts for other PFAS is provided in Section 7.1.

13.1.1.2 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 evaluating environmental media (air, soil, and surface water and groundwater not used for drinking) and limited federal requirements that compel such monitoring at the time of publication. USEPA has developed interim recommendations for screening and remediation of groundwater for PFOS and PFOA at CERCLA and RCRA regulated sites (USEPA 2019). Section 8 includes information about regulations, guidance, and advisories for PFAS, including a summary table of available current regulatory standards and guidance values for PFAS in groundwater, drinking water, surface water, effluent (wastewater), and soil linked on the PFAS fact sheet page.

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. PFAS, such as PFOA and PFOS, have been detected in biosolids produced at wastewater treatment plants (WWTPs), and in soil, surface waters, and leachate from landfills. WWTP biosolids are commonly applied to land as a soil amendment. Stakeholders are concerned about uptake by crops such as corn, hay, and soybeans. Section 2 introduces PFAS sources at landfills and WWTPs, and Section 5.6 and Section 6.5.1 discuss plant uptake of PFAS.

There are few regulatory or guidance limits for PFAS in surface water that may affect fish and consumers of fish. In addition, PFAS in surface water also creates an exposure pathway that potentially affects ecological and human health. For more information on PFAS in surface water, see Section 16.

While recognizing that drinking water is the dominant exposure pathway, Vestergren and Cousins (2009) identified that PFAS impacts to other media need to be considered because "there is a clear need of investigations of how to remediate the hotspot areas with focus on the unsaturated zone," because "PFAS that are pooled in the unsaturated zone will continue to infiltrate and spread from contaminated areas as long as the source is not removed, or infiltration of precipitation is inhibited."

13.1.1.3 Human Consumption of Food

Many stakeholders want clear advisories or standards on PFAS in food due to the occurrence of PFAS in a variety of food. In Europe important sources of human exposure to PFOA and PFOS have been found to include the consumption of fish, meat, and eggs (EFSA 2018). The US Food and Drug Administration (FDA) has published information on their PFAS studies on their website (USFDA 2019). Few screening levels or advisories have been posted; for example, Maine has developed screening levels for fish for PFBS, PFOS, and PFOA, and for milk and beef for PFOS (ME DEP 2021). Further information about development of standards for food consumption is found in Section 8.2.2.11. PFAS are found in a variety of foods, including homegrown produce and wildlife. Some areas of concern regarding foods include the following:

- PFAS have been found in food purchased at stores. Some occurrence information for foods collected as part of the FDA's Total Diet Study is published in Genualdi et al. (2021).
- Some states have issued fish consumption advisories for specific 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." As a result, health risk assessments were undertaken and health advisories were issued (Environmental Protection Authority Victoria 2019), p.1).
- In Wisconsin, the Department of Natural Resources (DNR) recommended not consuming the liver of deer killed within a 5-mile radius of an industrial site where elevated levels of PFOS were found. "DNR And DHS Issue Do Not Eat Advisory for Deer Liver In Five-Mile Area Surrounding JCI/Tyco Site In Marinette", September 15,

2020, https://dnr.wisconsin.gov/newsroom/release/37921.

- Alaska Community Action on Toxics (ACAT) (Byrne 2009) reported that "A study (by Martin et al. 2004) 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 (Ostertag et al. 2009) 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." 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 (Byrne 2009).

13.1.1.4 Ecological *Risk*

There is wide stakeholder 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). Stakeholders are asking for expanded 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 (see Section 16.3).

13.1.2 Desire for One Standard or Screening Level for PFAS

Among stakeholders there is a difference of opinion regarding how standards for PFAS should be established. Many stakeholders believe that PFAS should be treated as a class of chemicals (Kwiatkowski et al. 2020), similar to how PCBs or dioxin are currently regulated. In 2021, Vermont concluded that further information is needed to evaluate the feasibility of regulating PFAS in drinking water as a class (VT ANR 2021.). Section 7.1 includes information about approaches for assessing toxicity of PFAS mixtures.

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 (see Section 7.1.5), many stakeholders support evaluating the mass of total PFAS as a preferred screening method, rather than limited compound-specific testing using target analyte lists (CSWAB 2018). However, it is noted that given the lack of a method to test for total PFAS (see Section 13.1.10), screening might need to be completed using a method such as the TOP assay, total organic fluorine, or non-target analysis as descried in Section 11. 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, other stakeholders and some interested parties do not support treating PFAS as a class of chemicals, because some PFAS, such as certain fluoropolymers, like PTFE, might need less toxicological information because they are unable to enter cells, they are not mobile in the environment, they do not bioaccumulate, and they are therefore not available to cause adverse health effects (Henry et al. 2018), although this issue needs further study (Lohmann et al. 2020). See also Section 2.2.2.1.

13.1.3 Lack of Occupational Standards

There are few standards or guidance values for occupational exposure for PFAS. NIOSH identified occupations that might have a higher potential exposure to PFAS, and identified occupational exposure studies and other research (NIOSH 2021). Stakeholders are concerned that paper mills and wastewater treatment plants where PFAS have been documented in indoor air, and manufacturers and industrial users of PFAS, do not have specific occupational standards for all of the PFAS that the workers might be exposed to during workplace activities.

13.1.4 Lack of Comprehensive Monitoring Information

Many stakeholders are concerned that most individuals and communities do not have any testing for PFAS. Moreover, there is no comprehensive federal requirement for PFAS testing of all drinking water systems and private wells. Based on publicly available data, there is an estimate that up to 80 million people in the United States might have drinking water with PFOA and/or PFOS concentrations greater than 1 nanogram per liter (Andrews and Naidenko 2020).

Limited testing has occurred in some public water systems, and USEPA's Unregulated Contaminant Monitoring Rule (UCMR) and other regulatory programs have provided more (see Section 8). Some significant points regarding the status of a comprehensive monitoring effort follows:

- As described in Section 8.2.2.4, the third round of USEPA's required monitoring program (UCMR3), which occurred between 2013 and 2015, sampled for only six of the thousands of PFAS. UCMR3 was limited to public water systems (PWS) serving more than 10,000 people and a limited number of smaller systems, but smaller PWSs and private wells were not included. More information about the UCMR3 data is included in Section 8.2.2.4. From this data set, it was estimated that approximately 6 million residents of the United States have drinking water that exceeds the health advisory for PFOA or PFOS, or both (APHA 2016).
- Sampling for UCMR4 (USEPA 2016), which occurred between 2018 and 2020, did not include any PFAS in its analyte list (USEPA 2020). Many stakeholders are concerned that an opportunity to better understand the magnitude of PFAS contamination on PWSs was not taken.
- Summarizing information about the Unregulated Contaminants Monitoring Rule (UCMR), Siros (2018) stated, "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 [UCMR]. Prior to this new law, only drinking water systems that served more than 10,000 people were required to monitor for unregulated contaminants. …Th[e] 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." UCMR5, scheduled for 2023–2025, is going to test for 29 PFAS chemicals (for which there is a validated USEPA testing method) in systems serving more than 3,300 people using lower detection limits than previous UCMRs (USEPA 2021).
- Some states (for example, New Hampshire and Vermont) have initiated testing of private wells in certain locations where there is a high potential for PFAS contamination, and require testing of public water systems subject to maximum contaminant level (MCL) regulations. The Washington State Department of Health 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).

13.1.5 Need to Apply a Precautionary Approach in Decision Making

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.

13.1.6 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 substitute them with shorter chain PFAS (see Section 2.4). Although some short-chain PFAS appear to be less bioaccumulative, the publicly available data are limited. Some short-chain PFAS can be persistent, 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." Precursor compounds for some short–chain PFAS are also of interest in future monitoring studies; for example, perfluoro-1-butane-sulfonamide (FBSA, a precursor to PFBS), has been documented with high detection frequency (32 out of 33 samples) in fish from North America (Chu et al. 2016; Ericson, Jogsten, and Yeung 2017). 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.

13.1.7 Contamination from 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 and in Section 3.

13.1.8 Contamination from Unused AFFF Disposal

Stakeholders are concerned that incineration of unused AFFF is not always specifically regulated with PFAS-specific emission conditions and limits, and that incineration may generate dangerous byproducts (see Section 3.10 on AFFF Disposal; USEPA 2020; Earthjustice 2020). The U.S. military indicated plans to collect and destroy unused firefighting foam that contains PFOS and PFOA (USDOD 2018). 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.” Stakeholders are concerned that there are no federally mandated protocols that require incineration to reach certain temperatures to specifically target PFAS. (See https://theintercept.com/2019/01/27/toxic-firefighting-foam-pfas-pfoa/)

The National PFAS Contamination Coalition (an assembly of stakeholder groups from across the U.S.) opposes incineration (and similar thermal treatment technologies) for disposal of PFAS-contaminated wastes and collected PFAS products because stakeholders are concerned that thermal treatment technologies may not be specifically permitted to treat PFAS, and that demonstration is needed that treatment will fully destroy PFAS, that is, reduce the molecules to carbon, fluoride salts, and/or other constituents (National PFAS Contamination Coalition Statement on Incineration of PFAS – National PFAS Contamination Coalition (pfasproject.net)). See Section 13.1.18 below.

The USEPA’s Interim Guidance on Destroying and Disposing of Certain PFAS and PFAS-Containing Materials That Are Not Consumer Products (USEPA 2020) indicates that thermal treatment (which includes incineration) is commercially available and potentially has the capability to destroy PFAS or manage the migration of PFAS in PFAS-containing materials, but that further research activities are needed. Some facilities in the United States have been permitted by state regulatory agencies for the thermal treatment of PFAS.

The Foam Exposure Committee (FEC), a subgroup of the Fire Department Safety Officers Association (FDSOA 2021), whose objective is to reduce firefighter/first responder exposures to PFAS in firefighting foams, reports that the absence of federal and state regulations addressing disposal provides more opportunities for fire departments to expose their firefighters and contaminate their own communities with AFFF products. Current regulatory programs that address use and disposal of AFFF are provided in Section 8.2.

13.1.9 Duty to Warn AFFF First Responders

Aside from standard workplace safety requirements regarding hazardous materials right-to-know, stakeholders are concerned that 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 the 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 the blood serum of 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; Jin et 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), 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, or other sources.
- IPEN (International Pollutants Elimination Network) released a report that presents information from recent studies that firefighters using AFFF have elevated blood levels of both PFHxS and PFOS; see also NIOSH (2021) for links to additional research. Earlier IPEN reports describe fluorine-free firefighting foam alternatives that can replace uses of toxic fluorinated firefighting foams (IPEN 2018, 2019). The FEC recommends replacing older stocks of AFFF with fluorine-free foam solutions (FDSA 2021).

13.1.10 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 fraction of these chemicals.

A related concern is that the specification for shorter chain AFFF published by the Department of Defense (USDOD 2018; 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 DOD has recently published a draft analytical method, DOD AFFF01, to quantify PFOA and PFOS with a limit of quantitation of less than 25 ppb (Willey 2021). The modern short-chain AFFF formulations are fluorotelomer-based, so PFOS (and other PFSAs) 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 and Section 3 include more information about AFFF specifications.

13.1.11 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 (see Section 7). Many communities where PFAS have 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. ATSDR established a multi-site study with seven partners across the country to better understand the connection between PFAS exposures and health effects (ATSDR 2020).

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. Only limited long-term programs have been established to monitor the health outcomes of exposed populations (for example, C8 Science Panel (C8 Science Panel 2020). If there is no assistance from the government, many community members cannot afford to have their blood tested.

13.1.12 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 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. For more information about FDA’s PFAS activities and food contact materials (FCM) PFAS phaseouts, please see Section 8.2.

Although there are no enforceable PFAS limits in food or water at the federal level as presented above in Section 13.1.1.3, some states and cities are moving forward with bans. Several states, including Washington, Minnesota, Maine, New York, and Vermont, have enacted laws to ban PFAS use in some food packaging. See Section 8.2 and the regulatory programs table (*coming soon*) for a summary of regulatory programs. Stakeholders are concerned because 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 PFAS are potentially transferred to certain food crops, and may leach to groundwater. If compost goes to a landfill, PFAS potentially ends up in the landfill's leachate.

13.1.13 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 is has PFAS contamination. Biosolids from wastewater treatment plants are used in some composts and fertilizers and PFAS sampling may not be part of the screening process for these products. However, this is changing; New Hampshire and Maine both require testing. Additionally, stakeholders are calling for more testing and regulation for land-applied or disposed paper mill waste due to potential PFAS impacts. Stakeholders are concerned that 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 that contain PFAS.

13.1.14 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 because some formulations are proprietary and may not be listed on a Safety Data Sheet. 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, because AFFF suppliers claim that formulations are proprietary.

13.1.15 Limited Availability on 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 2018 release of ATSDR's Draft Toxicological Profile for PFAS was reportedly delayed because of concerns about the public response. This example, if replicated, may lead to distrust and reduce the efficacy of risk communication. Additionally, collected health data may not be clearly and fully shared or explained to stakeholders.

13.1.16 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 USEPA limits, stakeholders maintain that 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.

13.1.17 Potential PFAS Emissions from Cleanup Methods

Stakeholders believe that treatment systems (from large public water treatment systems to small private point-of-use systems) should be monitored for effectiveness, as the type and frequency of monitoring may vary for all systems. There is also concern that disposal or regeneration of GAC canisters, resins, and byproducts will add contaminant loads of PFAS to the air, land, and water. Stakeholders are concerned that companies that thermally treat spent carbon filters that contain PFAS do not provide publicly accessible information that documents full destruction of all PFAS; some companies claim all PFAS are destroyed, yet the research appears to be focused on targeted PFAS (for example, PFOS and PFOA) destruction. More concerns about thermal treatment are discussed in Section 13.1.8, with further information provided in Section 12.4.

13.1.18 Lack of Scientific Evidence that Current PFAS Treatment and Disposal Methods and Remedies Are Fully Protective of Human and Ecological Health and Prevent Toxic Emissions

Historically, the three standard practices for PFAS waste management are landfilling, wastewater treatment, and incineration. Stakeholders' concerns with these disposal practices are highlighted in a study sponsored by the Environmental Working Group (EWG) (https://www.ewg.org/news-insights/news-release/study-disposal-pfas-waste-increases-contamination). One of the conclusions of that study is that all three methods have been found to not effectively contain or destroy PFAS. Tasha Stoiber, EWG senior scientist and primary author of the study, found that "The three common 'disposal' options for getting rid of PFAS do not eliminate these contaminants but rather end up just returning either the same chemicals or their byproducts back into the environment." Additionally, USEPA has confirmed that while "Thermal treatment technologies are common remediation approaches for contaminated media and waste, limited information exists on the efficacy, potential atmospheric emissions, operational conditions, costs, etc. for thermal treatment technologies specifically targeted for PFAS" (Mills et al. 2020).

Additionally, USEPA stated that "Research on thermal stability of PFAS compounds, the ability to fully capture and identify PFAS compounds and their thermal decomposition byproducts, and the efficacy of emission control technologies are areas of targeted research. These efforts, in cooperation with states and industries, [are] aimed at proper disposal of PFAS-laden wastes without media-to-media transfer or environmental release" (USEPA 2019). In USEPA's Interim Guidance (USEPA 2020), they identified areas for further study to assess the efficacy of destruction and disposal of PFAS-containing materials (that are not consumer products) to help protect public exposure to PFAS.

An example that demonstrates the stakeholders' concerns about adequate protection provided by disposal options is the Holston Army Ammunition Plant (Holston) in Tennessee. In a July 16, 2019, letter to USEPA Region 4 Administrator Mary Walker (https://cswab.org/wp-content/uploads/2019/07/Holston-Citizen-Petition-Region-4-PFAS-July-2019.pdf), several environmental groups stated that Holston will present a risk to human health and the environment by burning polymer-bonded explosives (PBXs) containing PFAS. The groups cited a recent decision by the neighboring State of Kentucky to prohibit the Blue Grass Army Depot from open-air burning or detonation (OB/OD) of "munitions wastes that are a potential source of Per- and polyfluoroalkyl substances (PFAS), including Teflon, Viton, and Viton-A. This includes both short and long chain PFAS." Both bases are located in USEPA Region 4. The groups stated: "Open air burning and detonation do not provide either sufficient or sustained temperatures times to achieve destruction. OB/OD activities at Holston are very likely resulting in the ongoing release and dispersion of PFAS to the environment, posing a potentially substantial health risk to workers and residents."

13.1.19 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 discharges remains unknown. Older and inactive facilities' discharge areas, many of which have not been sampled for PFAS, may also act as long-term sources of stormwater and/or groundwater contamination due to residual PFAS in soil at stormwater discharge areas.

13.1.20 Psychological Effects

It was reported at one USEPA community forum that children in some communities are scared to drink water. See the USEPA community meetings information provided on USEPA's website: https://www.epa.gov/pfas/pfas-community-engagement. This has occurred in communities where contaminated drinking water supplies have the effect of deterring children from drinking clean water. Additionally, blood level values have become an identity, and there are pictures of people holding up signs identifying their blood levels.

13.1.21 Economic Consequences of Local PFAS Contamination

Individuals have voiced concerns about significant economic consequences on property values and businesses. See the USEPA community meetings information provided on USEPA's website: https://www.epa.gov/pfas/pfas-community-engagement. In one case in Massachusetts, the Board of Health added PFAS to the list of substances homeowners with private wells in certain areas of town must test for before selling their homes (Town of Harvard, MA 2020). In New Jersey, PFOA, PFOS, and PFNA were added to a list of chemicals that private well owners must test for prior to selling their homes under the NJ Private Well Testing Act. This also applies to landlords who rent homes with private wells (see https://www.nj.gov/dep/rules/adoptions/adopt_20200601a.pdf). In another instance, because PFAS was detected in water used by dairy cattle, the farmer 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. Many tribes sustain themselves through hunting, fishing and gathering of foodstuffs. 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 available at the time of publication. 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 around PFAS. These websites have not been reviewed for accuracy or to determine if they are up to date.

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

PFASCentral.org

https://greensciencepolicy.org/highly-fluorinated-chemicals/

https://www.sixclasses.org/videos/highly-fluorinated-chemicals

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://theintercept.com/2019/09/19/epa-new-pfas-chemicals/

https://stories.usatodaynetwork.com/unwellwater/foam-1995/

https://www.ewg.org/pfaschemicals/what-are-forever-chemicals.html

https://pfas-exchange.org

https://silentspring.org/project/women-firefighters-biomonitoring-collaborative

https://www.epa.gov/pfas/basic-information-pfas

https://health.ri.gov/water/about/pfas/

https://www.fdsoa.org/resourcepage (click on resources)

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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 2015); 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 mangagement 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 2005, 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 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.
- Athough 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 priotities 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.

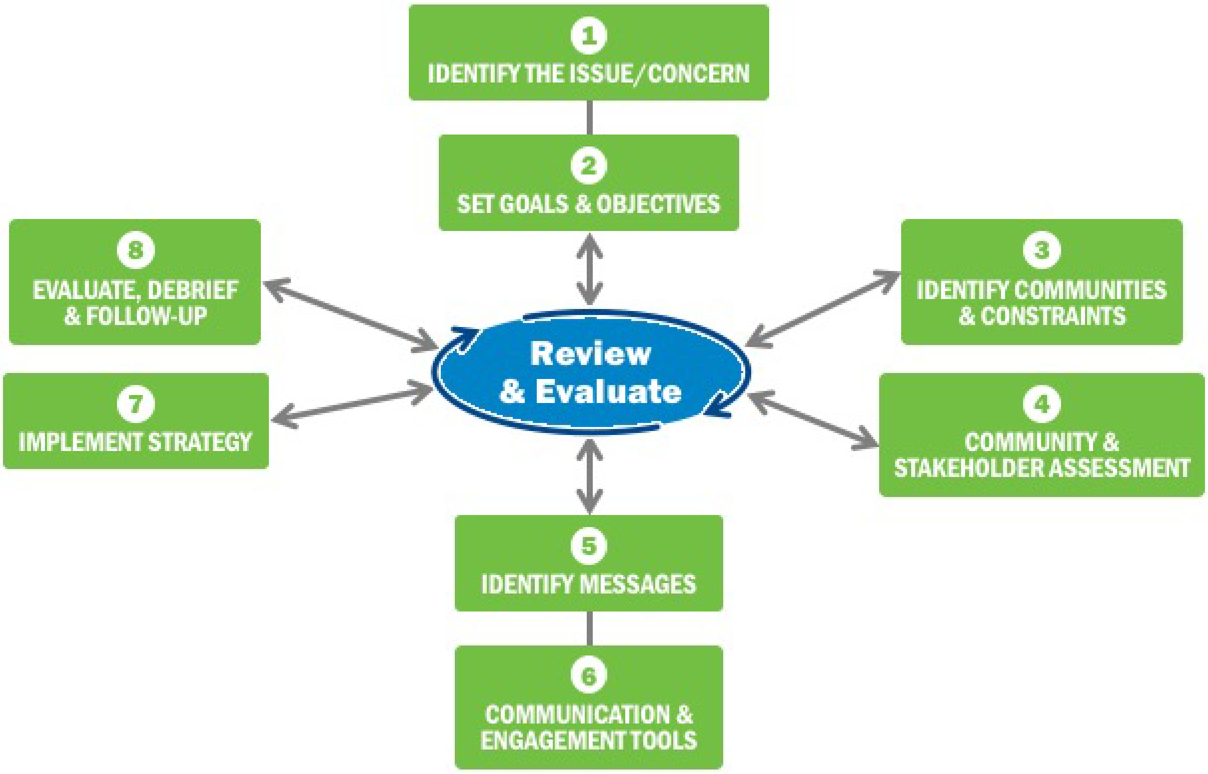

Figure 14-1. Communication plan process diagram.

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
- attainable: 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).

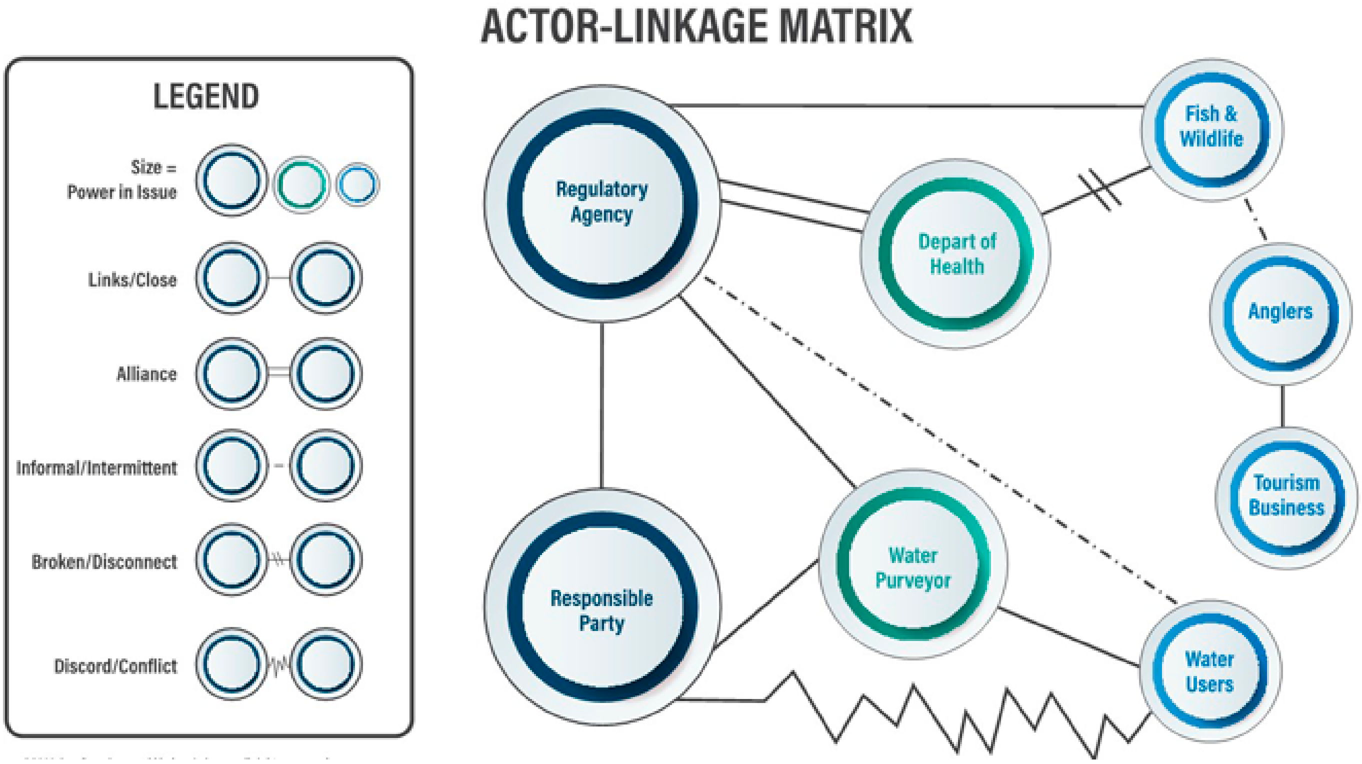

Figure 14-2. Example actor-linkage matrix.

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).

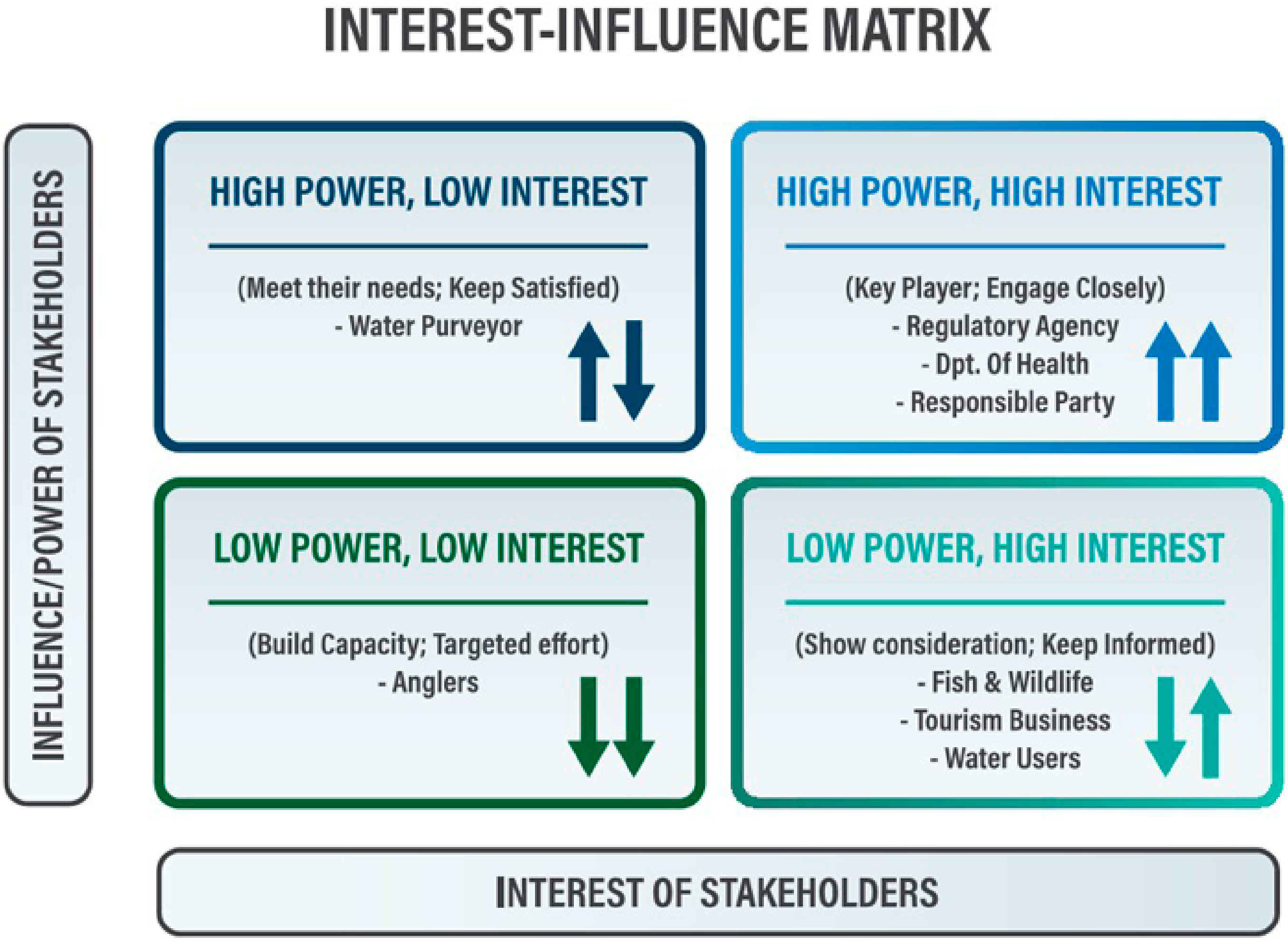

Figure 14-3. Example interest-influence matrix.

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.

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.	**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.	**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.
Keywords: Supporting Facts 1.3 PFAS are found throughout the environment, in people, and in animals and fish.	**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.	**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.

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 Petersburgh, 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, Petersburgh, 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; Petersburgh 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.

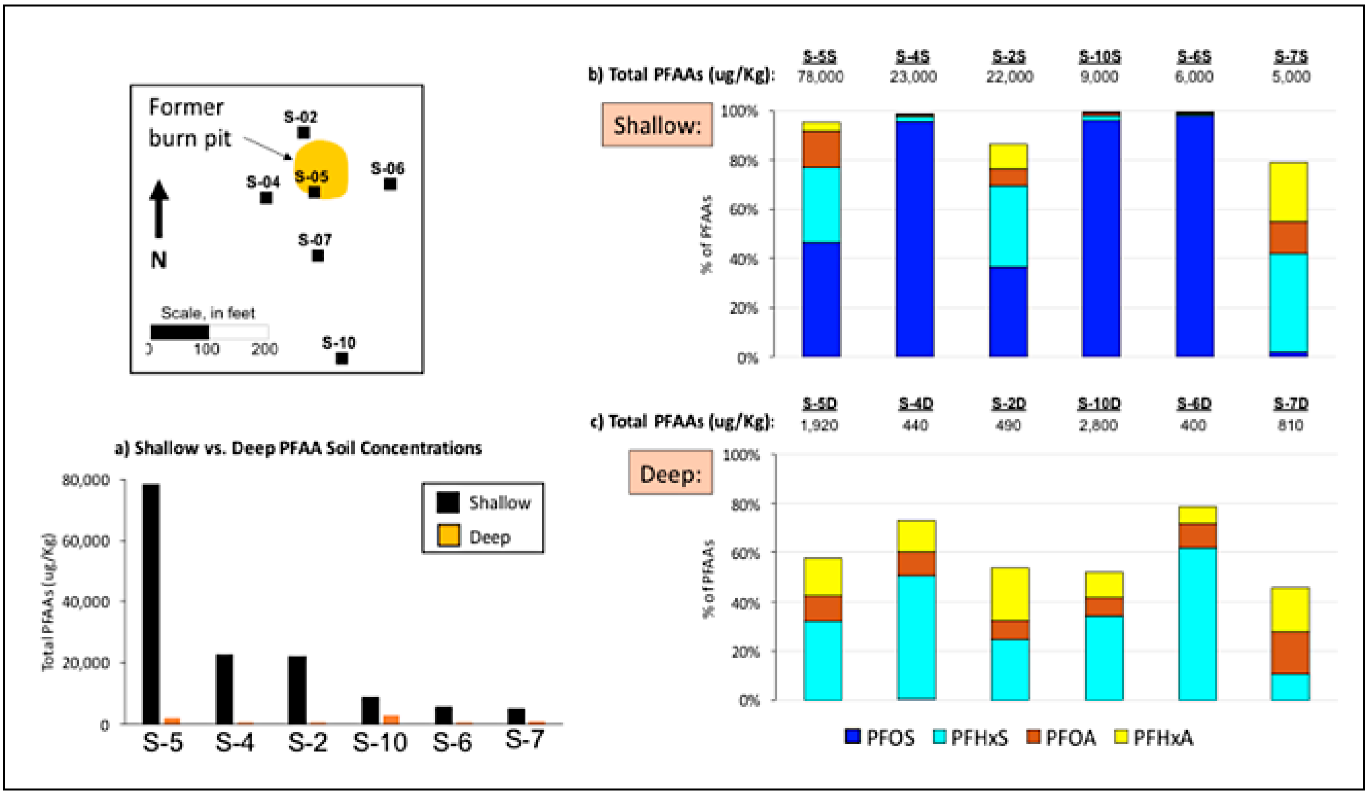


Figure 15-1. Comparison of shallow and deep soil samples at an AFFF release site.

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 PFSAs (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.

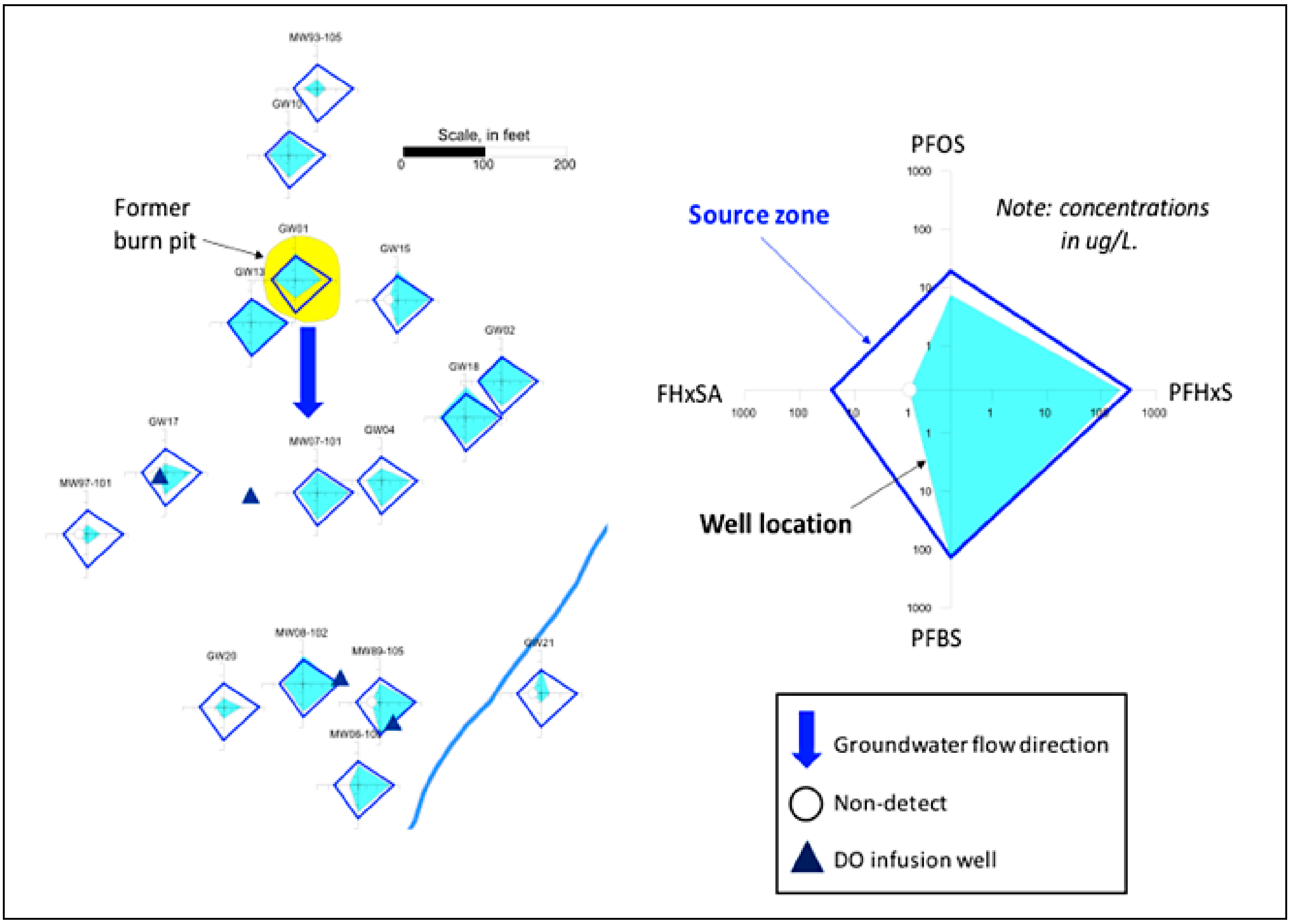


Figure 15-2. Radial diagrams illustrating PFSA trends at an AFFF release site.

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 then 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 PFSAs, 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.

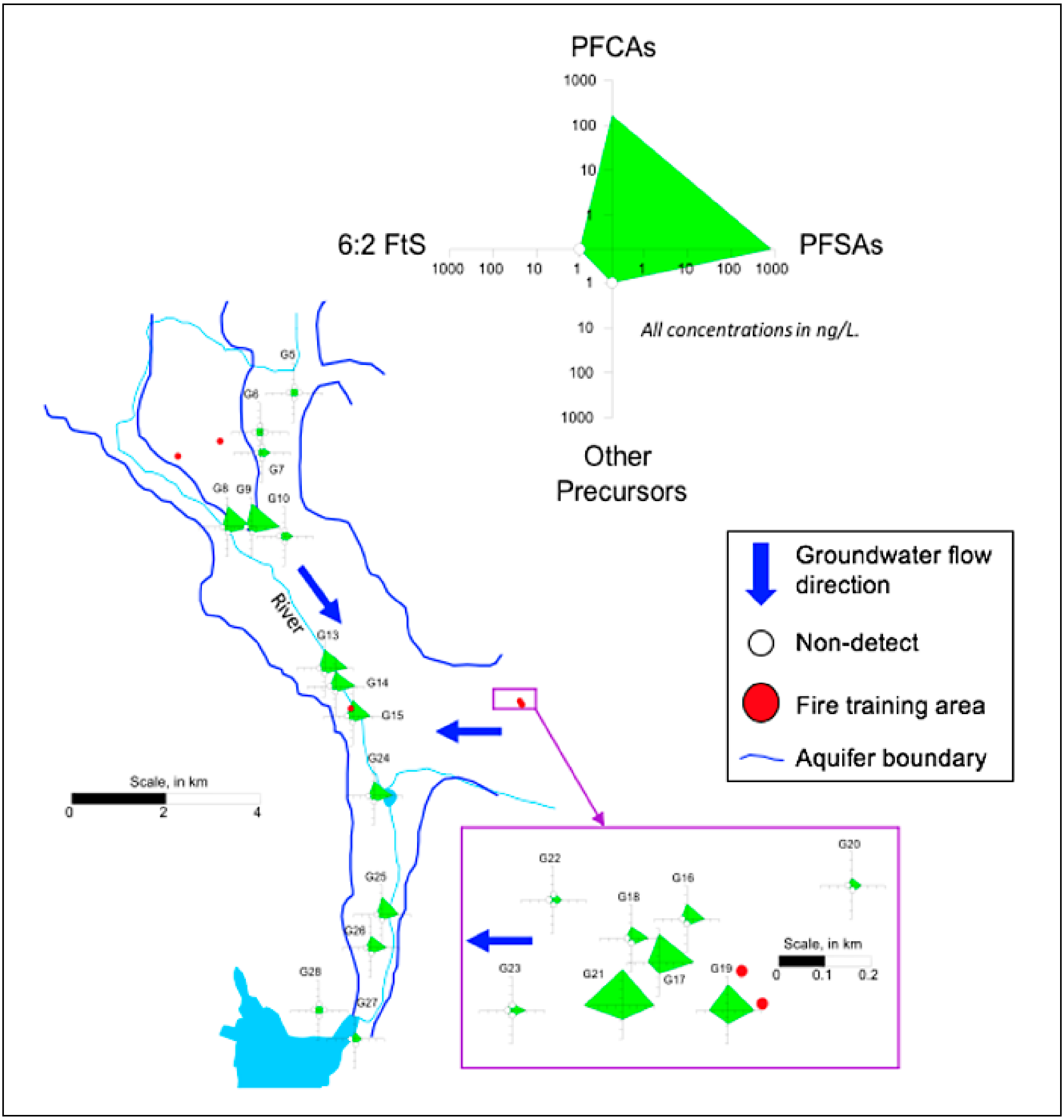


Figure 15-3. PFAS composition in groundwater.

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.
- PFSA 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, 1940–1960) 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 1980 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 ft^2 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.

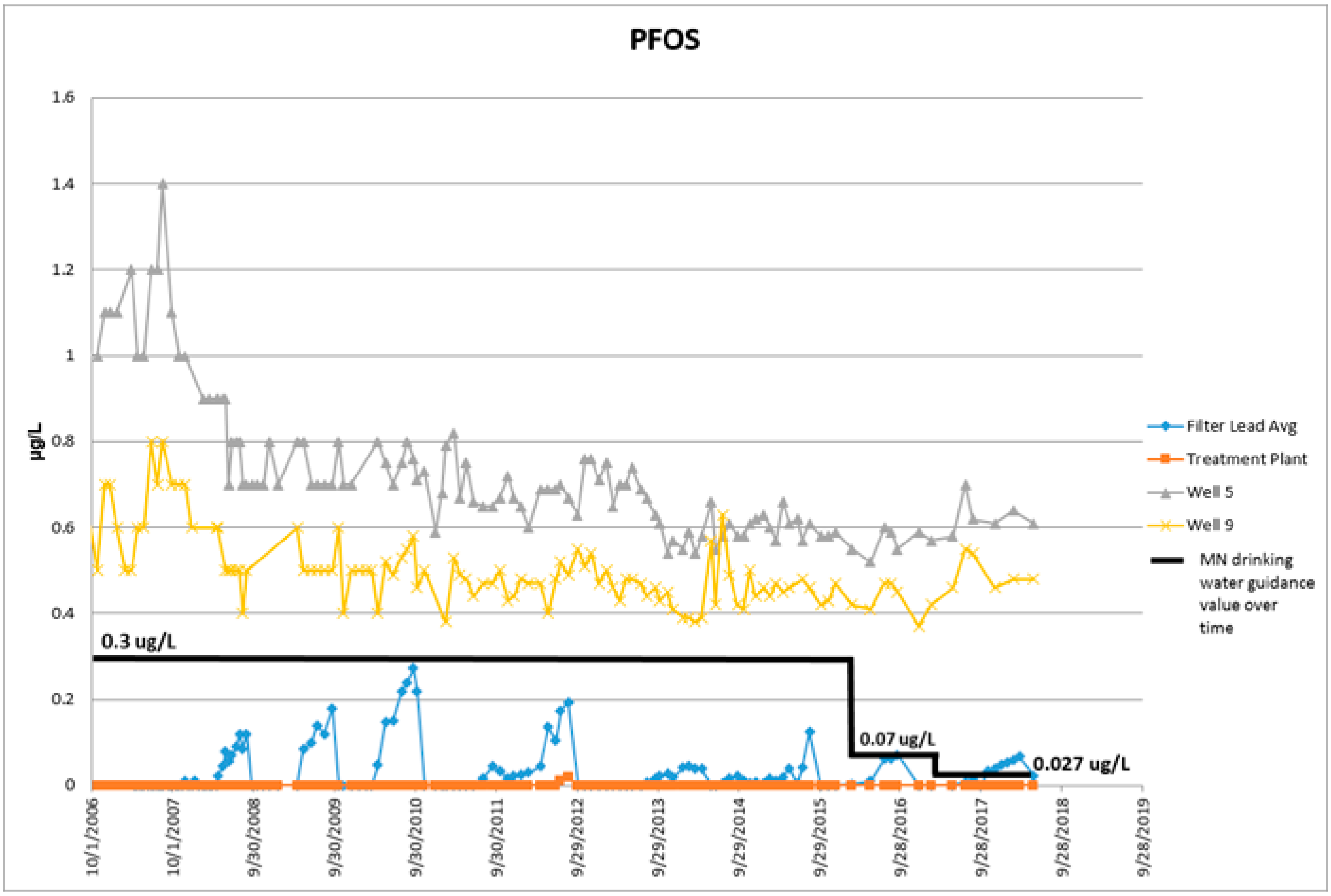


Figure 15-5. Influent and effluent concentrations for PFOS.

Source: Courtesy of the Minnesota Department of Health.

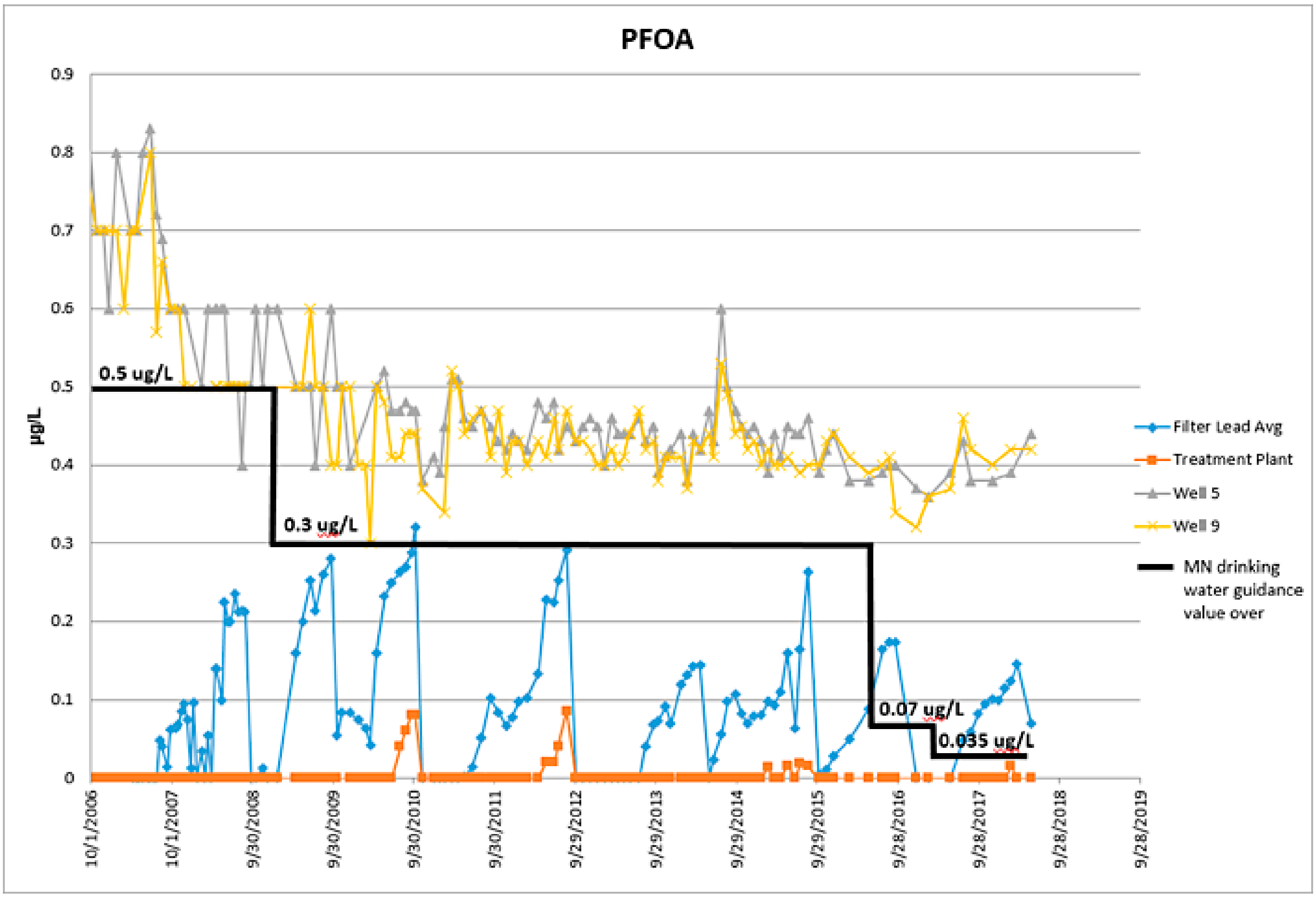


Figure 15-6. Influent and effluent concentrations for PFOA.

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/ft^2. 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/ft^2 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.

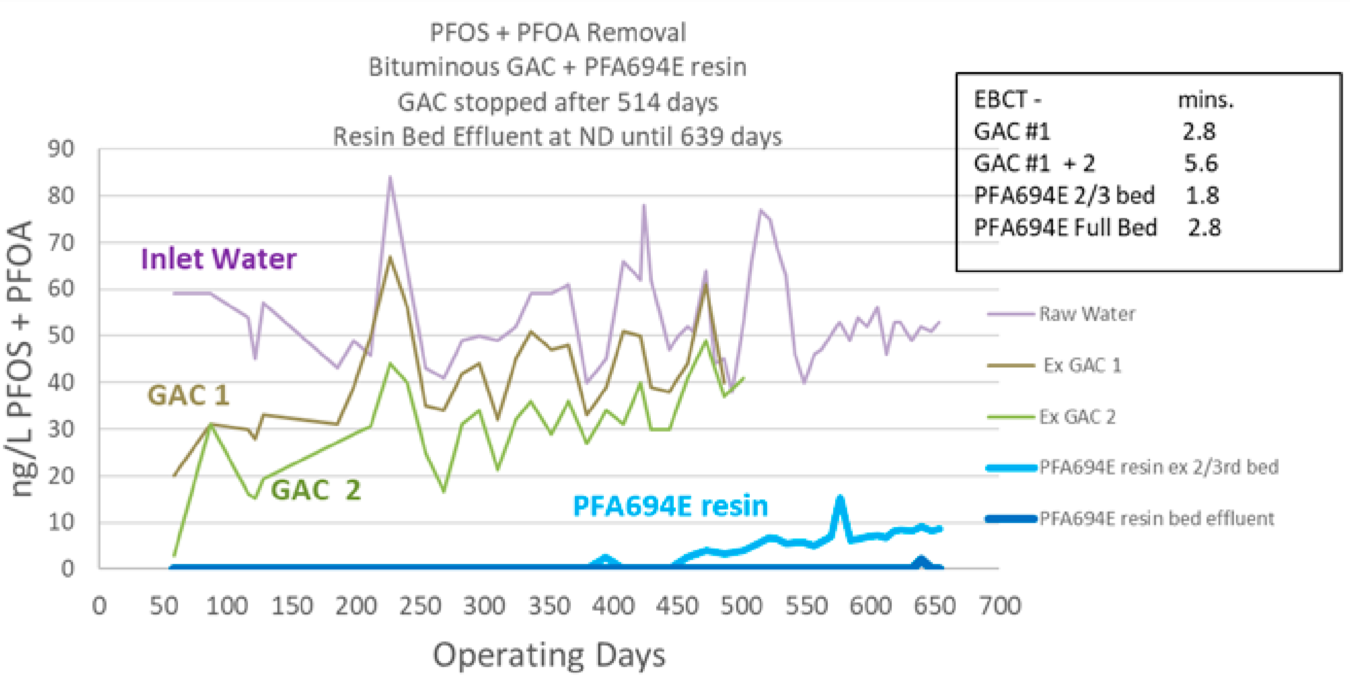


Figure 15-7. Combined PFOS/PFOA breakthrough.

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.

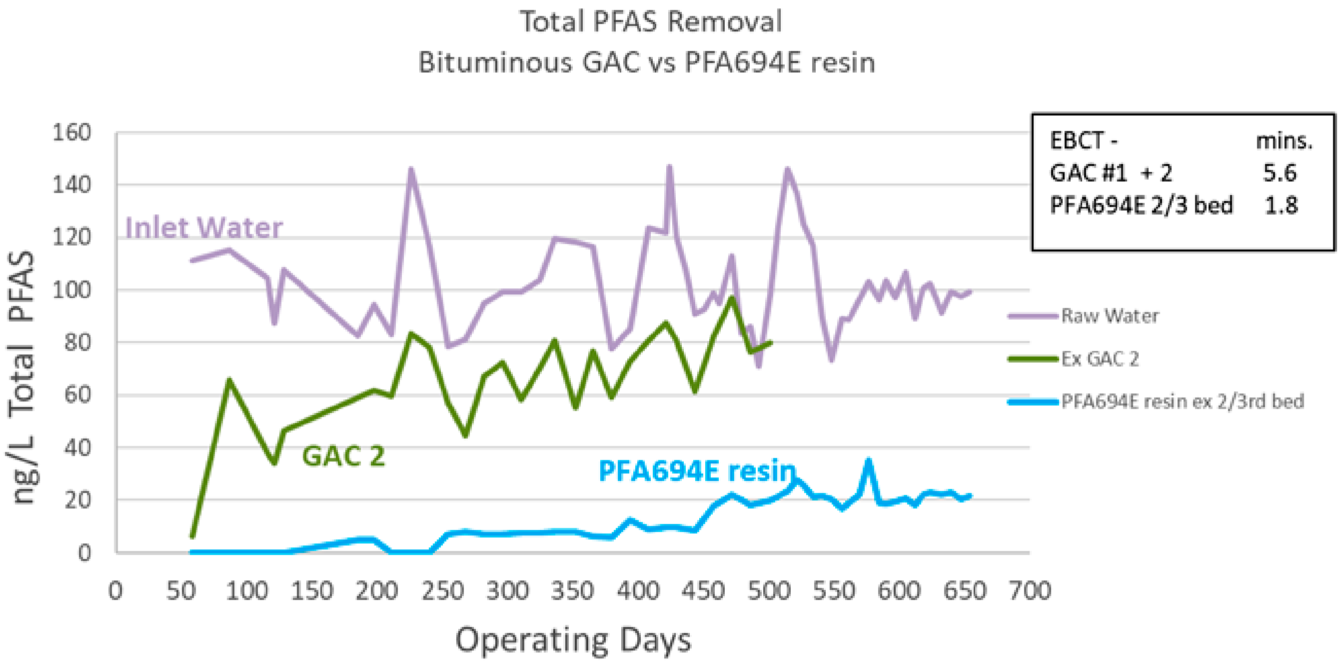


Figure 15-8. Combined breakthrough of total PFAS.

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 (µg/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.

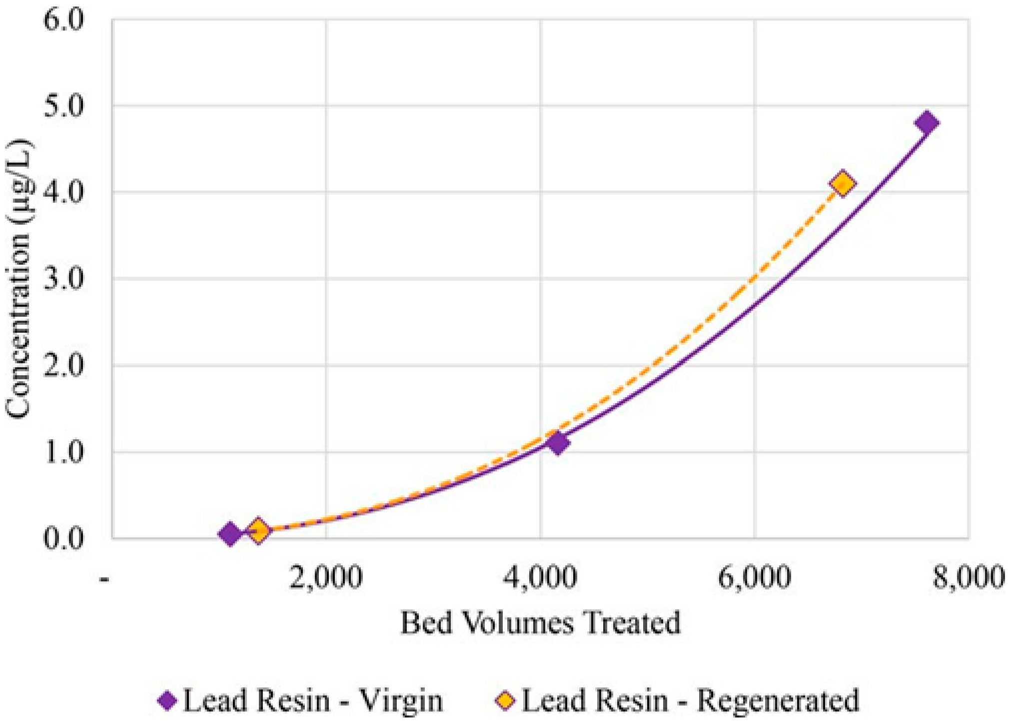


Figure 15-9. Postregeneration breakthrough curve (total PFAS).

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

		Influent Concentration Observed During Pilot Test (µg/L)		
Analyte	**Analyte Acronym**	**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
Perfluorononanoic 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 m^3/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.

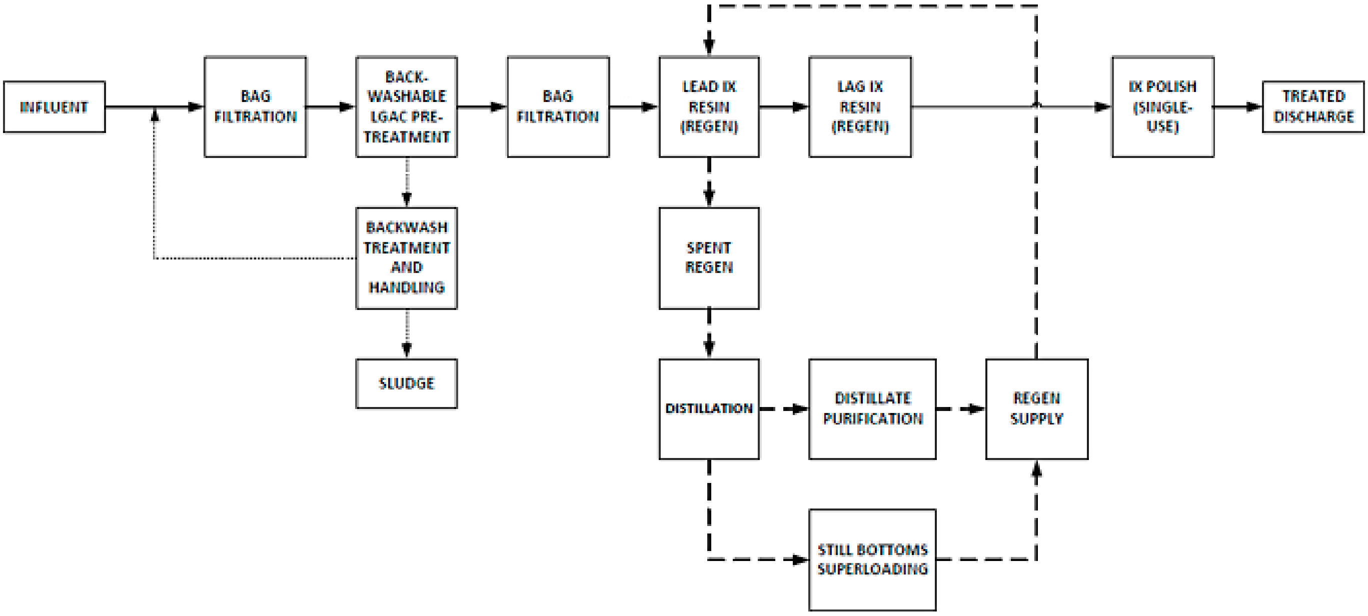


Figure 15-10. Block flow diagram of full-scale treatment system.

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.

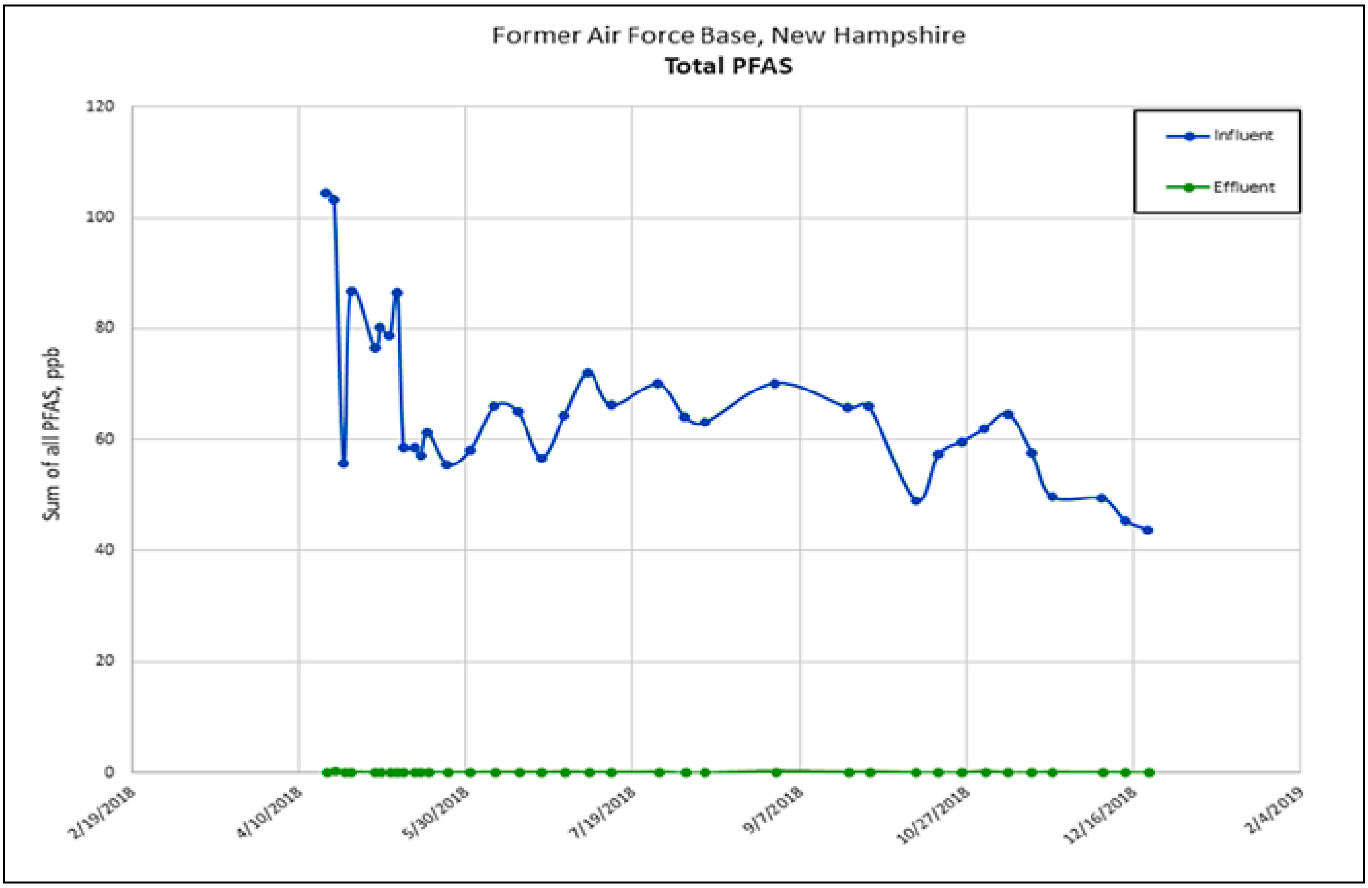


Figure 15-13. Influent and treated effluent total PFAS concentrations.

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.

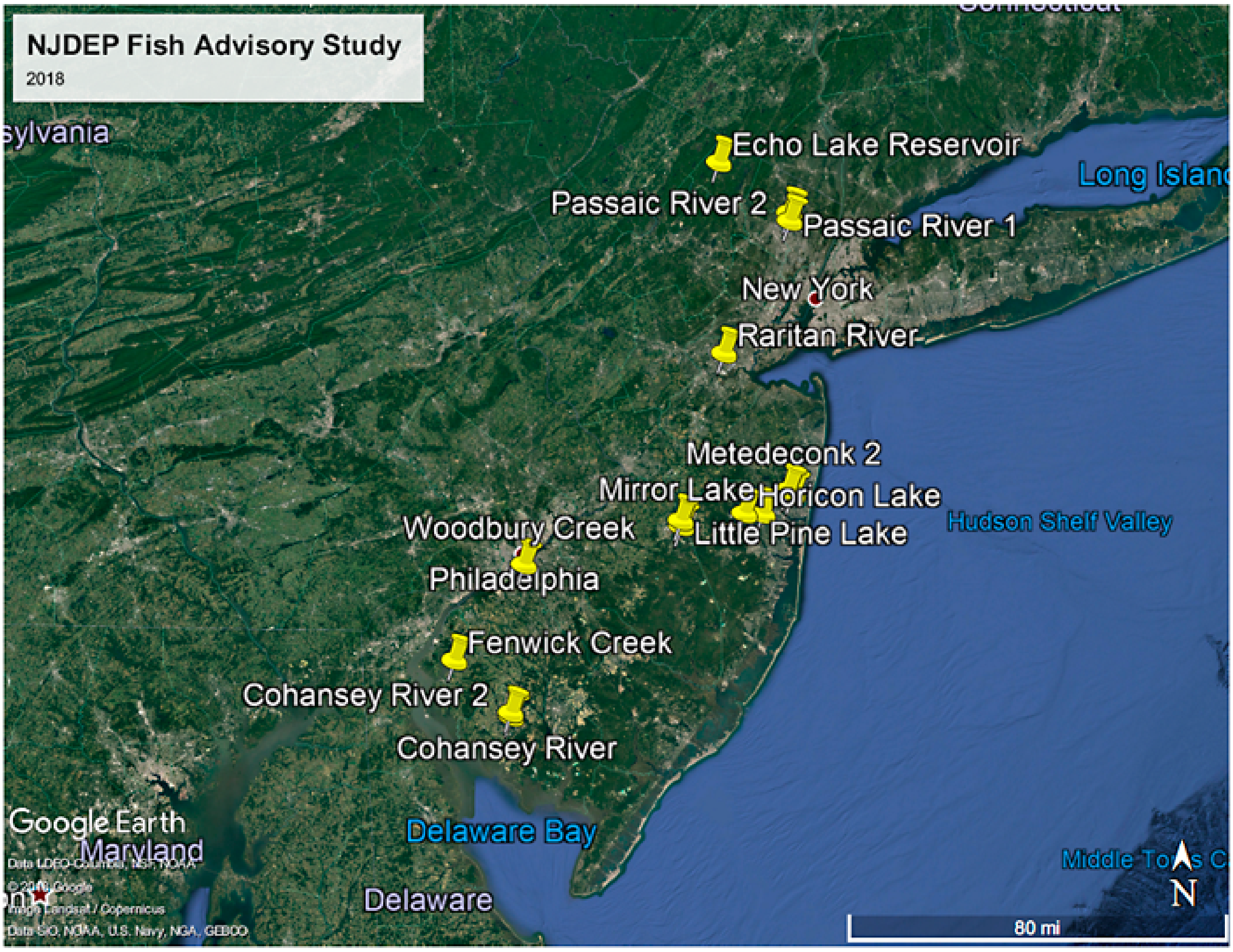
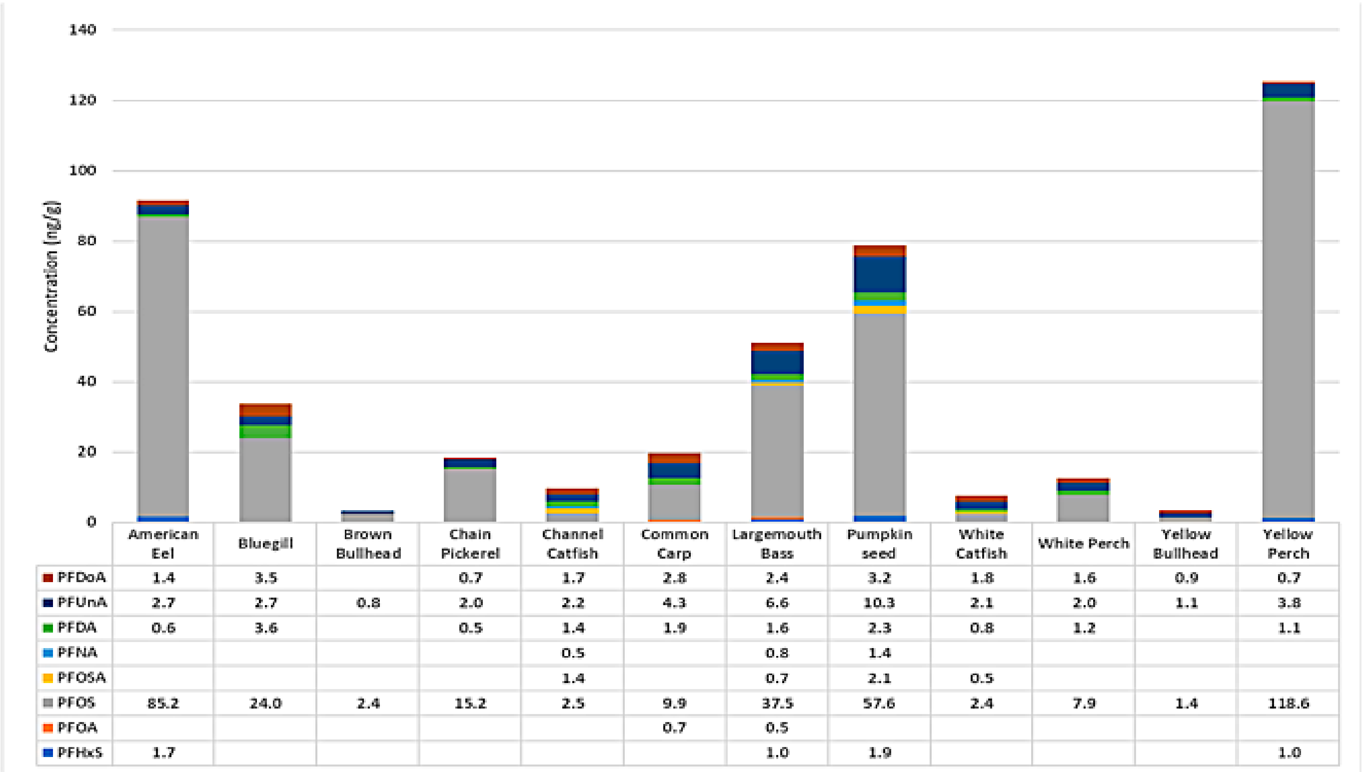


Figure 15-14. Map of water bodies included in NJDEP fish tissue study.

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.



	American Eel	Bluegill	Brown Bullhead	Chain Pickerel	Channel Catfish	Common Carp	Largemouth Bass	Pumpkin seed	White Catfish	White Perch	Yellow Bullhead	Yellow Perch
PFDoA	1.4	3.5		0.7	1.7	2.8	2.4	3.2	1.8	1.6	0.9	0.7
PFUnA	2.7	2.7	0.8	2.0	2.2	4.3	6.6	10.3	2.1	2.0	1.1	3.8
PFDA	0.6	3.6		0.5	1.4	1.9	1.6	2.3	0.8	1.2		1.1
PFNA					0.5		0.8	1.4				
PFOSA					1.4		0.7	2.1	0.5			
PFOS	85.2	24.0	2.4	15.2	2.5	9.9	37.5	57.6	2.4	7.9	1.4	118.6
PFOA						0.7	0.5					
PFHxS	1.7						1.0	1.9				1.0

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 2017)], PFOS [1.8 ng/kg-day; (NJDWQI, 2018)], 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):

$$C_{fish} = HQ \cdot RfD\left(\frac{BW \cdot AT_{nc}}{M \cdot CR}\right)$$

where

– C_{fish} is the risk-based fish concentration (ng/g)

– HQ is the target hazard quotient = 1 (unitless)

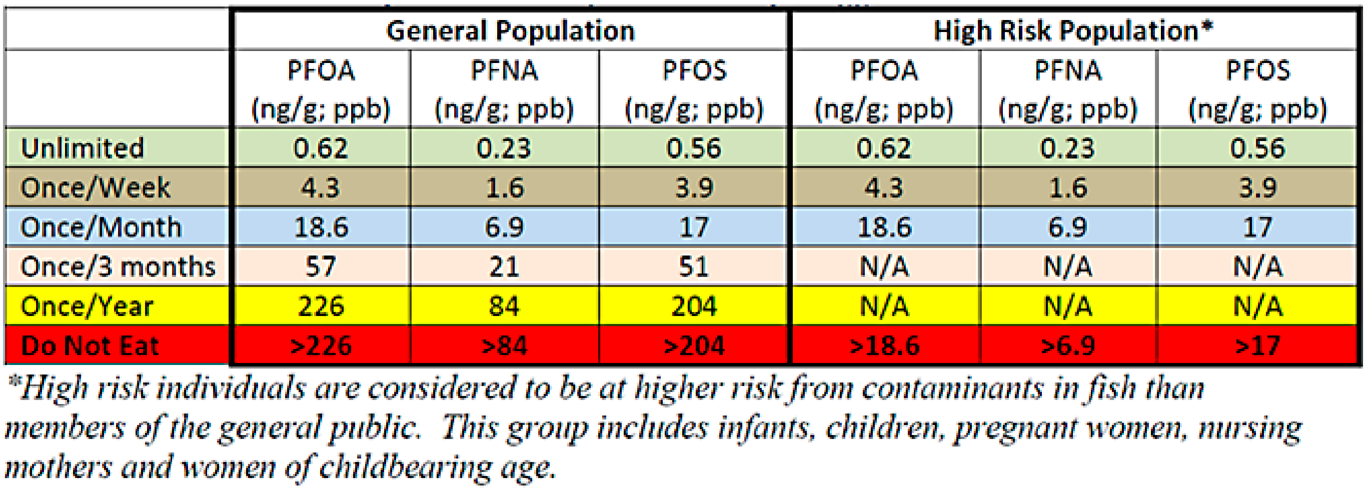
– M is the number of meals during the exposure period

– 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

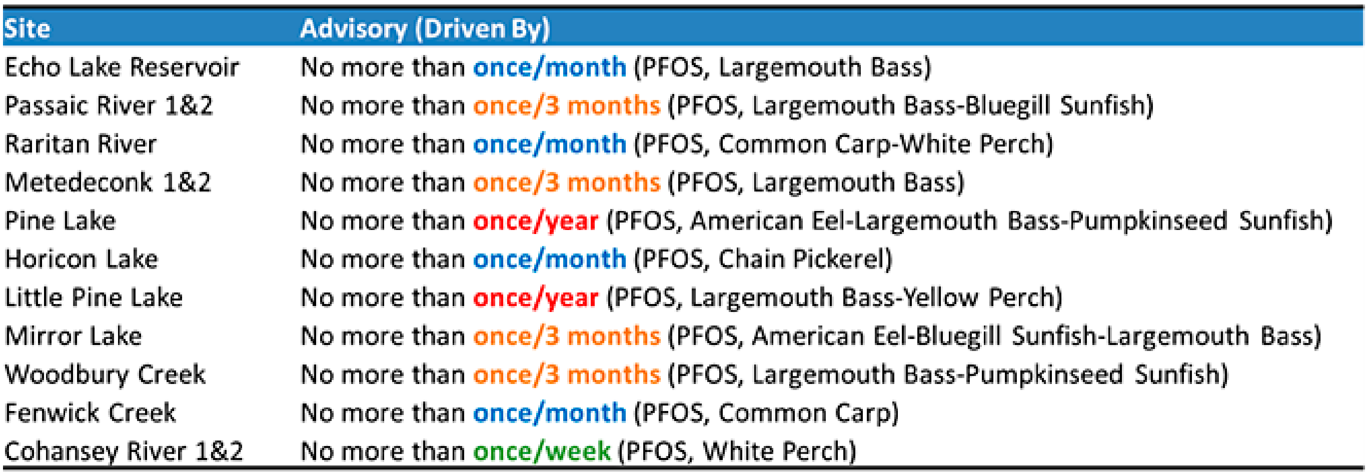
*High risk individuals are considered to be at higher risk from contaminants in fish than members of the general public. This group includes infants, children, pregnant women, nursing mothers and women of childbearing age.

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 risj 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 Dearry 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 1950, 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.

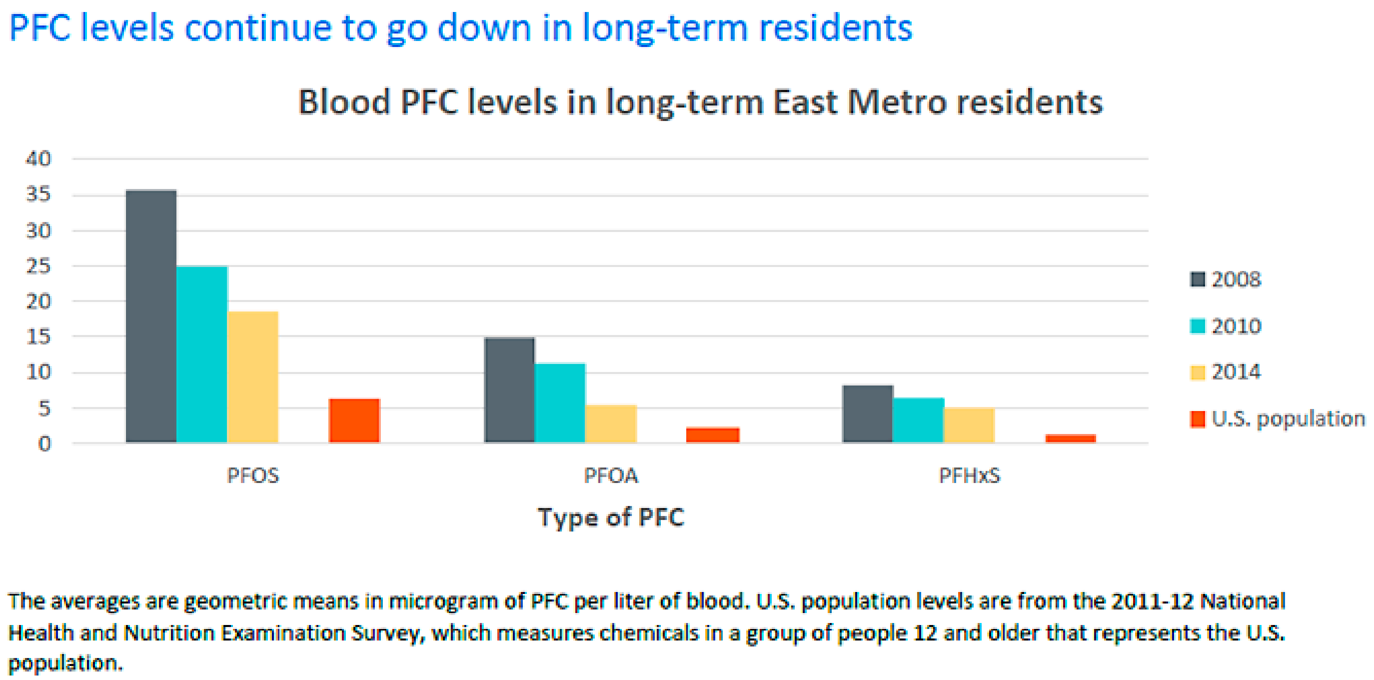
MDH notes the importance of discussing the scientific method with stakeholders to remain transparent about their course of action. They also share new knowledge as it becomes available and do not wait until they have a perfect message or until they know all of the facts to engage with the community. 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.

Updated September 2020.

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16 Surface Water Quality

The purpose of this section is to support the PFAS Technical and Regulatory Guidance Document (PFAS Guidance Document) users (state and federal environmental staff, stakeholders, project managers, and decision makers) to gain a working knowledge of the current state of PFAS science and practice for surface water quality. The section does not include calculated criteria, rather it provides available information and references that can then be used to support development or review of criteria or guidance values to protect surface water quality.

Section Number	Topic
16.1	Introduction
16.2	Protection of Human Health
16.3	Protection of Biota
16.4	Sampling and Analysis
16.5	Surface Water Foam

16.1 Introduction

This section provides information to help fill in the gaps related specifically to concerns with PFAS-impacted surface water and associated receptors. Several states have expressed a need for technical information to support the development of surface water quality criteria (WQC) or guidance values for uses other than drinking water, including but not limited to habitat for fish and other aquatic life. USEPA (2020) developed recommendations and provided derivation methods for surface water criteria “for determining when water has become unsafe for people and wildlife using the latest scientific knowledge.” States and tribal governments may, and sometimes do, develop their own numerical criteria. To protect human health, the states and tribal governments may also establish water body–specific fish consumption advisories for certain aquatic species. These advisories are recommendations and not enforceable. This section provides technical information regarding PFAS in surface water that individual states and tribal governments can consider individual states and tribal governments when developing criteria according to their own processes and policies. This information focuses on two main issues. First is the protection of human health from a variety of potential exposures to PFAS in surface water, such as drinking water, consumption of fish and other aquatic species, and from recreational activities. Second is the protection of biota, based on available ecotoxicity data, bioaccumulation and concentration factors, and aquatic-dependent wildlife considerations, among others.

As of the writing of this document, there are few formally established surface water criteria for any PFAS that are protective of uses of surface water other than as drinking water. Florida, Minnesota, and Michigan are examples of states that have aquatic life protection values (see the Water and Soil Values Tables that are posted on the fact sheets page).

In addition to the well-established issues associated with PFAS in surface water, such as use of the surface water as a source of drinking water and accumulation of PFAS in biota, this section also includes a discussion of a relatively new issue related to surface water: PFAS-containing foam. Investigations in at least three states—Minnesota, Michigan, and Wisconsin—have found that concentrations of PFAS in surface water, or discharging to surface water, at sufficient levels can generate foam on surface water. That foam acts to remove PFAS from the water column, but also acts as a secondary source of PFAS as the foam leaves the surface water and is deposited in other locations.

16.1.1 Beneficial Uses

One of the first steps in developing the criteria is to determine the beneficial uses that are to be protected for the water body of concern. These have usually been developed by the state organization responsible for water quality and/or water resources for the state. That regulatory agency assesses potential beneficial uses and assigns appropriate designated uses for a water body. As examples, in Massachusetts this task is the responsibility of the Massachusetts Department of Environmental Protection, while in California it is under the purview of the nine Regional Water Quality Control Boards that establish potential beneficial and designated uses for the water bodies for each region. The process for establishing these beneficial uses in most instances follows protocol developed by USEPA (2020).

With the potential adverse health effects associated with the ingestion of certain levels of various PFAS, negative impacts on beneficial uses of surface water may occur. Table 16.1 provides a fairly comprehensive list of potential beneficial uses for surface water. This table is a compendium taken from the *Water Quality Control Plan (Basin Plan) for the California Regional Water Quality Control Board, Central Valley Region, Fourth Edition, Sacramento and San Joaquin River Basins* (RWQCB-CVR 2016). Different jurisdictions use different lists of beneficial uses. The list in Table 16-1 is used for illustration. For an evaluation of PFAS, the list may be substantially reduced in order to focus on those that are appropriate, as the presence of PFAS may not have an impact on a particular use (for example, navigation). In the table the list has been reduced by separating the beneficial uses that may be impacted by PFAS (light blue) and those that are not likely to be (light green). The list can be further reduced by combining several of the uses that evaluate similar issues, such as aquatic toxicity. As an example, the beneficial uses listed as WARM, COLD, EST, WILD, BIOL, and RARE (see Table 16.1) are each designed to protect aquatic species that have a range of attributes. The beneficial use for shellfish could be added to that grouping by expanding the evaluation under it to include benthic organisms and sediment quality.

Table 16-1. Beneficial Uses

Source: Adapted from RWQCB-CVR (2016)

	Beneficial Use	**Description**	**Does PFAS Have Impact on Use? Covered in this Section**
1.	Municipal and Domestic Supply, Use as Drinking Water (MUN)	Uses of water for community, military, or individual water supply systems, including, but not limited to, drinking water supply.	Yes
2.	Agricultural Supply (AGR)	Uses of water for farming, horticulture, dairy operations, or ranching.	Yes
3.	Primary Water Contact Recreation (REC-1)	Uses of water for recreational activities involving body contact with water, where ingestion of water is reasonably possible.	Yes
4.	Groundwater Recharge (GWR)	Uses of water for natural or artificial recharge of groundwater.	Yes
5.	Commercial and Sport Fishing (COMM)	Uses of water for commercial or recreational collection of fish, shellfish, or other organisms.	Yes
6.	Aquaculture (AQUA)	Uses of water for aquaculture or mariculture operations.	Yes—not all components covered under other beneficial uses—harvesting of aquatic plants for human consumption
7.	Warm Freshwater Habitat (WARM)	Uses of water that support warm water ecosystems.	Yes—combine with COLD
8.	Cold Freshwater Habitat (COLD)	Uses of water that support cold water ecosystems.	Yes—combine with WARM
9.	Estuarine Habitat (EST)	Uses of water that support estuarine ecosystems.	Yes—combine with WARM and COLD for ecotoxicity for all of the aquatic species
10.	Wildlife Habitat (WILD)	Uses of water that support terrestrial or wetland ecosystems.	Yes—food chain issues, in addition to WARM, COLD, and EST
11.	Spawning, Reproduction, and/or Early Development (SPWN)	Uses of water that support high quality aquatic habitats suitable for reproduction and early development of fish.	Yes
12.	Shellfish Harvesting (SHELL)	Uses of water that support habitats suitable for the collection of filter-feeding shellfish.	Yes

	Beneficial Use	**Description**	**Does PFAS Have Impact on Use? Covered in this Section**
13.	Hydropower Generation (POW)	Uses of water for hydropower generation.	No—PFAS not expected to impact POW
14.	Industrial Process Supply (PRO)	Uses of water for industrial activities that depend primarily on water quality.	No—as below for IND
15.	Freshwater Replenishment (FRSH)	Uses of water for natural or artificial maintenance of surface water quantity or quality.	No—issues covered under other beneficial uses
16.	Non-contact Water/Secondary Contact Water Recreation (REC-2)	Uses of water for recreational activities involving proximity to water, but where there is generally no body contact with water, nor any likelihood of ingestion of water.	No
17.	Preservation of Biological Habitats of Special Significance (BIOL)	Uses of water that support designated areas or habitats, such as established refuges, parks, sanctuaries, ecological reserves, or Areas of Special Biological Significance, where the preservation or enhancement of natural resources requires special protection.	Not covered individually—covered under WARM, COLD, EST, and WILD
18.	Rare, Threatened, or Endangered Species (RARE)	Uses of water that support aquatic habitats necessary, at least in part, for the survival and successful maintenance of plant or animal species established under state or federal law as rare, threatened, or endangered.	Not covered individually—covered under WARM, COLD, EST, and WILD
19.	Migration of Aquatic Organisms (MIGR)	Uses of water that support habitats necessary for migration or other temporary activities by aquatic organisms, such as anadromous fish.	No—issues already covered under other beneficial uses
20.	Industrial Service Supply (IND)	Uses of water for industrial activities that do not depend primarily on water quality, such as mining and cooling water.	No—concern is the discharge of the water to another location
21.	Navigation (NAV)	Uses of water for shipping, travel, or other transportation by private, military, or commercial vessels.	No—PFAS not expected to impact navigation

Refining the list of beneficial uses reduces the number of evaluations to the following groupings:

1. Aquatic toxicity to both water column and benthic organisms. This beneficial use combines those listed as WARM, COLD, EST, WILD, BIOL, RARE, and SHELL in Table 16-1.
2. Protection of human health from ingestion of PFAS when surface water is used as drinking water. Listed as MUN in Table 16-1. The values for this are already covered in Section 8 and in updated tables (fact sheets page), and discussed further below.
3. Protection of human health from exposure to PFAS in the consumption of aquatic organisms, including benthic organisms. In Table 16-1 this encompasses the beneficial uses listed as COMM, AQUA, and SHELL.
4. Protection of human health from contact with and ingestion of PFAS in surface water during recreational activities such as swimming and fishing. This beneficial use is listed as REC-1 in Table 16-1.
5. Use of the surface water as an agricultural supply (AGR). Use of the surface water in this manner would allow for

the uptake of PFAS into plants used for human and animal consumption, stock watering of animals used for human consumption and animal consumption, as well as recharge of excess water to groundwater or other surface water bodies (return water).

6. Groundwater recharge is also included, but the issues are the same as those for MUN, AGR, and IND as listed in Table 16-1.

These beneficial use groupings were used to identify the topics to be included in the remainder of this section.

16.1.2 Existing Methods of Protecting Surface Water for Beneficial Uses

This section provides information about the existing methods that regulatory agencies or organizations with jurisdiction use for protecting surface water bodies from discharges of various pollutants. This information provides context for what may be implemented to address potential sources of PFAS in surface water.

After establishing the beneficial uses for a given body of water (lake, stream, creek, estuary, ocean) the regulatory agency or organization implements processes designed to protect those beneficial uses. Typically, this begins with establishing water quality protectiveness standards/criteria or guidance values to protect those specific beneficial uses. As an example, to protect aquatic species, values are established for protection of the health of the fish to allow them to continue to exist in the environment and breed without curtailment. If the fish species is fished for human consumption, then values are also established to allow for fishing to occur without unacceptable effects on those consuming the fish. As values are established for each of the beneficial uses assigned for the water body, the most stringent of the values can be used as the value that is protective of all the designated beneficial uses. In that instance, that value would be used for comparison to other beneficial use values instead of individual values for drinking water and fish protection. For PFAS those values are just beginning to be established.

Once the protective value for the water body has been established, regulatory mechanisms exist to protect the water body to maintain or reduce the concentrations to below the protective values. Discharges to surface water are regulated by state- or federally issued permits. Effluent limits are established in those permits for constituents that could pose a threat to water quality. Establishing appropriate chemical-specific effluent limits protects beneficial uses. The effluent limitations are set so that the concentrations in the surface water body stay below the protective values. In addition to chemical-specific effluent limitations, the permits typically establish acceptable toxicity limitations that must be met in the total effluent. Both effluent and toxicity limitations can take into account mixing with the surface water body within a permitted mixing zone (dilution).

If a water body already has concentrations that are greater than the protective value, then the regulatory agency can establish total maximum daily loads (TMDLs). The TMDLs identify maximum mass discharges for the chemicals that exceed protective values and are used to identify mass loading limits on discharges in the watershed for that water body. Additionally, TMDLs have a component for evaluation of nonpoint sources of discharge within the watershed that include the chemical of concern. If needed, regulations of these nonpoint discharges could be adopted to also limit those discharges. Often, best management practices are established as the control mechanism for nonpoint discharges. If nonpoint discharges are the primary contributor of the pollutant, alternate approaches, such as watershed restoration plans, may be established in lieu of TMDLs. These plans can include best management practices and pollutant minimization components.

During times when a protective value is exceeded and before corrective measures are taken to bring concentrations down below those values, temporary use restrictions can be issued to protect users of the water body. Examples of such restrictions include banning recreation or issuing fish advisories that recommend restricting consumption of various fish species. If the water is being used as a source of drinking water, additional water treatment could be required.

Effluent limitations, TMDLs, watershed restoration plans, and use restrictions have been effective in protecting beneficial uses and reducing risk to receptors for numerous chemicals. It is likely that these measures will also be useful in addressing PFAS.

16.1.3 Status of State and Federal Surface Water Protection Efforts Regarding PFAS

At the time of publication, there were no national surface water values for PFAS in the U.S., and only a handful of states have addressed PFAS in surface water; a more recently updated summary of values is available on the fact sheets page. Many of the challenges or obstacles to developing surface water criteria are the

Enforceable vs. Nonenforceable Federal and State Values

Standard – Promulgated values that are enforceable. Example: primary drinking water standard or maximum contaminant level

Criteria – Recommended nonenforceable values that can be used to establish a standard. Example: USEPA water quality criteria
Screening/Guidance Levels – Nonenforceable values that usually represent a de minimus risk and can be used to determine if further action may be necessary. Example: USEPA regional screening levels, action-levels.

same as for groundwater, including the large number of individual PFAS, many of which lack toxicity and published physical and chemical properties data. In addition, surface water is used in a greater number of ways than groundwater, representing potential direct exposure routes through dermal contact and water ingestion, and indirect exposure through consumption of fish and shellfish. On October 18, 2021, the USEPA announced its PFAS Strategic Roadmap (USEPA 2021). The Roadmap includes actions that are planned to be undertaken by USEPA. These planned actions include publishing final recommended ambient water quality criteria for aquatic life (expected Winter 2022) and human health (expected Fall 2024), and increasing the availability of data on PFAS in fish tissue (expected Summer 2022) that can be used to finalize the list of PFAS for establishing fish advisories (expected Spring 2023).

At the state level, surface water criteria development has taken a range of approaches. Alaska has adopted health advisory levels for surface water used as drinking water. These levels are used as action levels and are not enforceable under the Clean Water Act. Michigan, Minnesota, and Florida developed their own statewide criteria based on water and fish consumption using state-specific inputs and addressed PFOA and PFOS. Other states are in the process of collecting data or evaluating what approach to take to develop their own criteria in the absence of federal guidelines. Wisconsin is collecting surface water and fish tissue data to support calculation of surface water values. New Hampshire and Vermont have released detailed reports outlining potential strategies and associated costs and timing for developing state criteria. The plan from Vermont describes how its Agency of Natural Resources has developed a framework to establish water quality standards and how it may apply to developing such standards for protection of human health and aquatic life from PFAS. The report concludes that technical challenges and the constraints of deriving water quality criteria (WQC) for PFAS are “logistically difficult, would take a long time, and be very expensive.” It recommends developing fish consumption advisories, tracking USEPA development of aquatic biota criteria for PFAS, incorporating USEPA criteria when they are developed, and continued collaboration with New England states on developing plans for deriving water quality standards (Vermont DEQ 2020). The number of states that have established values for protection of aquatic life is small and includes Michigan and Florida. A table of state-established values can be found on the fact sheets page.

Surface water criteria are generally established by the states, either by adopting values recommended by USEPA per section 304(a) of the Clean Water Act, or by calculating state-specific criteria that must be approved by USEPA. States have specific responsibilities when setting surface water criteria and submitting that information to USEPA:

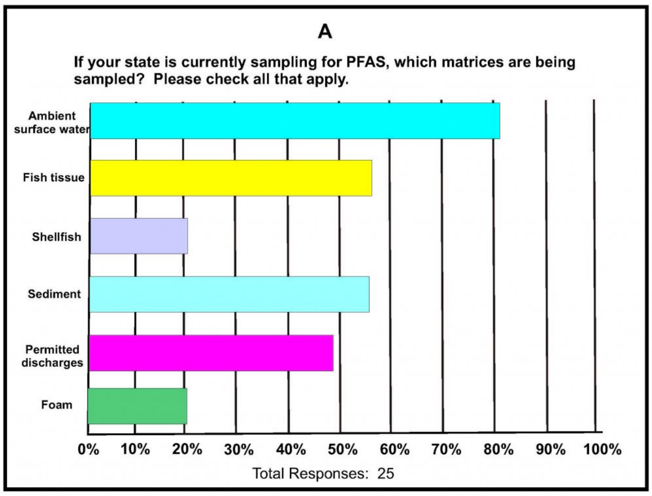
- Water bodies must have an appropriate designated use or uses.
- The WQC must support those uses.
- Antidegradation policies to protect high-value waters must be adopted.
- The status of waters must be monitored.
- The standards must be revisited on a regular basis and if a revision is required, the state must obtain USEPA approval.

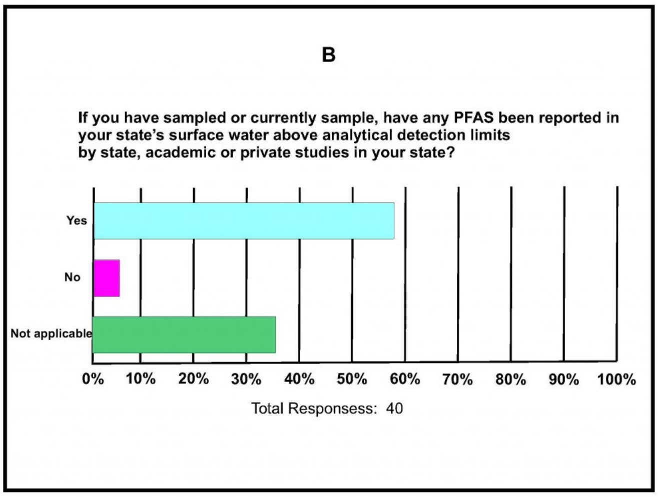
Most states are still in the process of assessing the extent of PFAS in their surface waters, some only at specific potential source areas.

16.1.4 Survey of States

In the spring of 2020, the ITRC PFAS team sent a survey to the states to gather information on their efforts to address PFAS in surface water. The survey included questions on what media states are monitoring for PFAS, whether PFAS have been detected in surface water, if the states have fish consumption advisories in place for any PFAS, and if the states are contemplating developing surface water quality criteria or guidelines. Other questions addressed the availability of data and information on sampling methods, PFAS-containing foam, and whether states have restrictions to minimize the discharge of PFAS to surface water.

A total of 42 states submitted responses. A summary of key responses is provided in Figures 16-1A-D. These show that of the different media being sampled, 80% of the states are sampling surface water (Figure 16-1A), and of those sampling for various PFAS in surface water, almost 60% detected one or more PFAS (Figure 16-1B). It was determined that 75% of states do not have any criteria, guidance, limits, or standards for PFAS in surface water (Figure 16-1C); however, it is noted that 16% do have some protective measure for surface water that is used as drinking water and 16% have guidance related to fish consumption advisories. Lastly, although 46% of the states were not considering development of criteria for PFAS in surface water, almost 40% felt they needed more information (Figure 16-1d); the remainder are currently developing criteria in response to proposed legislation, legislative mandates, or in response to department-level initiatives. For states that have developed surface water quality values, twice as many states reported using USEPA guidance for developing the values versus those using other procedures and methods.





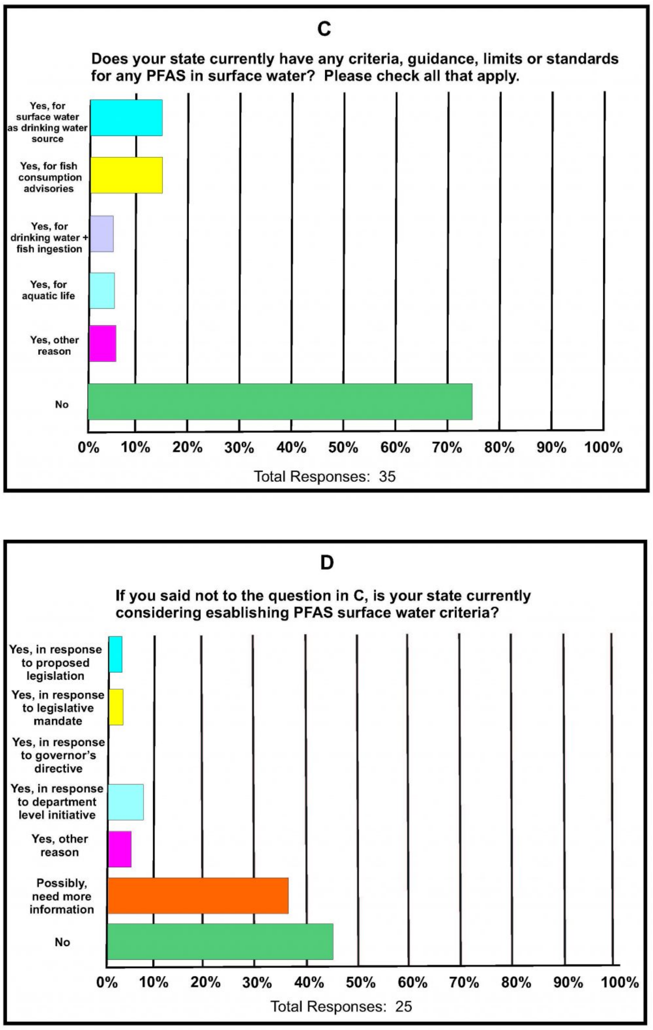


Figure 16-1A–D. Summary of Key Responses from the ITRC State Survey (2020)

Given the rapid pace in the state-of-the-science for PFAS and the desire for PFAS regulations in many states, it is likely there are updates since the time the survey was conducted. However, the PFAS team used the information from the survey to inform what areas to focus on in this surface water quality section and to document the fundamentals for states to consider when developing surface water quality protective values for PFAS. Where relevant, pertinent information from the survey is included in Sections 16.2–16.5.

For states that have developed standards/guidance/limits, these protective values can be found in tables produced by ITRC that are periodically updated on the fact sheets page.

16.2 Protection of Human Health

This section discusses the human health aspects of PFAS in surface water. There are other sections in this document that discuss general human health–related PFAS issues in detail that supplement the information in this section. Those sections are Section 7.1, Human Health Effects and Section 9.1, Site Risk Assessment, Human Health.

Under the federal Clean Water Act, states must adopt water quality standards that consist of both designated uses and numerical and/or narrative criteria to protect these uses. As described in Section 16.1, a designated use (also called a “beneficial use” or “designated beneficial use”) in some states is a use of surface waters that is considered desirable and should be protected. As noted in Table 16-1, surface waters have many different beneficial uses, some of which are relevant to human health and some that are not. Uses that are most relevant to human exposure and are considered for most chemicals include municipal and domestic supply (also referred to as drinking water use); agricultural supply (also commonly referred to as irrigation); primary contact recreation; secondary contact recreation/noncontact water recreation;

commercial, subsistence, and sport (recreational) fishing (referred to in some states as fish ingestion); and aquaculture (also focused on fish ingestion).

In relation to beneficial uses, the exposure pathways for contaminants in surface water that most warrant consideration of human health for PFAS are included in Table 16-2.

Table 16-2. Exposure Pathways in Relation to Beneficial Uses

Beneficial Use	Associated Human Exposure Pathway for PFAS
Municipal and domestic supply; use as drinking water	Drinking water ingestion and dermal contact during household use; secondary uses may include irrigation for home gardening and produce consumption
Commercial, subsistence, and sport (recreational) fishing	Consumption of aquatic organisms (fish and shellfish) that may bioaccumulate PFAS from surface water
Primary contact water recreation	Incidental ingestion and dermal contact with water and/or foam during immersion activities such as swimming, waterskiing
Non-contact/secondary contact water recreation	Dermal contact with water and/or foam during nonimmersion activities such as wading, boating, fishing; exposures considered to be insignificant for PFAS
Agricultural supply	Consumption of crops, dairy products, and meat that may bioaccumulate PFAS from irrigation water; some states may also consider direct contact with irrigation water
Aquaculture	Consumption of aquatic organisms (fish and shellfish) that may bioaccumulate PFAS from aquaculture water

Regulatory agencies use relevant and appropriate use-specific exposure factors combined with chemical-specific toxicity factors (reference doses; cancer slope factors) to develop ambient water quality criteria (AWQC) that are protective of human health for these uses and exposure pathways. The exposure pathways usually considered in development of AWQC are drinking water ingestion (for waters designated for drinking water use) and consumption of aquatic organisms.

At this time, exposure pathways involving ingestion are considered to be the most significant PFAS exposure sources. Recreational uses of surface waters for secondary contact activities, such as wading and boating, which do not involve immersion but may result in dermal contact with water, are considered to be insignificant sources of PFAS exposures. See Sections 17.2.2 and 17.2.3.

Human health criteria for contaminant concentrations in surface water that are protective of fish consumption are also relevant to PFAS exposures. Additionally, some states have developed fish consumption advisories that recommend the frequency of consumption for recreationally caught fish based on levels of contaminants, including PFAS, measured in fish tissue from certain geographic regions or in specific water bodies (Section 16.2.2.6).

The salinity of the surface water body influences the beneficial uses considered. Saline water criteria consider only the consumption of aquatic organisms (fish and shellfish), while freshwater criteria may consider exposure through consumption of aquatic organisms and/or drinking water. The designated uses for freshwater bodies may vary from state to state based on policy and/or actual uses as some water bodies may not support both potable use and aquatic biota consumption. Thus, criteria can be developed for the fish/shellfish consumption pathway alone or for the potable use and fish/shellfish consumption pathways combined. Surface water criteria are usually not developed for potable use alone and generally defer to guidelines such as maximum contaminant levels (MCLs) and maximum contaminant level goals (MCLGs) developed by USEPA and other agencies under drinking water programs. The combined use criterion will be more stringent than the criterion for consumption of organisms only for reasons detailed below.

16.2.1 Input Factors for Development of Surface Water Criteria and Fish Consumption Advisories

Section 16.2.2 includes information and an example equation used to develop human health criteria for relevant exposure pathways. Section 16.2.2.6 provides information and an example equation used to develop fish consumption advisory triggers.

16.2.1.1 Toxicity Values

The toxicity values used for both human health criteria and fish consumption advisories are reference doses (RfD, ng/kg/day or mg/kg/day) for noncarcinogenic effects and cancer slope factors (mg/kg/day) for carcinogenic effects. States may base their WQC and fish consumption advisories on toxicity values recommended by USEPA or toxicity values from sources other than USEPA, or develop their own toxicity values. The toxicity values used for PFAS vary among agencies based on different choices of critical toxicological effect, uncertainty factors, exposure assumptions, and other considerations.

Currently, the USEPA has not established surface water criteria for any PFAS, and toxicity values are available for only a limited number of PFAS. When information becomes available to develop surface water criteria for a PFAS, USEPA may follow a tiered process in selection of toxicity values, as it has done when developing criteria for other contaminants. When USEPA last updated its human health criteria (USEPA 2015), its primary source of updated toxicity values was the Integrated Risk Information System (IRIS), whose scientists are currently developing toxicity values for the following five PFAS: perfluorodecanoic acid (PFDA), perfluorononanoic acid (PFNA), perfluorohexanoic acid (PFHxA), perfluorohexane sulfonic acid (PFHxS), and perfluorobutanoic acid (PFBA) (USEPA 2020).

Other sources of toxicity values, for contaminants other than PFAS, reviewed by USEPA in its update of human health criteria include:

- USEPA Office of Pesticide Programs
- USEPA Office of Pollution Prevention and Toxics, USEPA Office of Water
- USEPA Office of Land and Emergency Management (for example, Provisional Peer Reviewed Toxicity Values (PPRTVs))
- S. Agency for Toxic Substances and Disease Registry (ATSDR)
- Health Canada
- California EPA’s Office of Environmental Health Hazard Assessment

The USEPA (2015) updates used a toxicity factor from one of the non-IRIS sources listed above if no IRIS toxicity factor was available, or if the toxicity factor from another source used a newer study or a more current risk assessment approach than IRIS.

For PFOS and PFOA, this document provides a table of toxicity factors (and their basis) currently used in water standards and guidance values developed by USEPA and individual states. This table is discussed and can be accessed from Section 8.3. In addition to the reference doses that it developed for its drinking water health advisories, the USEPA (2014) generated PPRTVs for PFBS, and more recently released draft toxicity assessments for PFBS and GenX for public comment (USEPA 2018). USEPA published the final PFBS toxicity assessment in 2021 (USEPA 2021). The USEPA’s PFAS Action Plan, which was first developed in 2019 and updated in 2020 (USEPA 2020), states that USEPA will evaluate additional PFAS for development of toxicity values, including the five PFAS being evaluated by IRIS that are mentioned above. Currently, USEPA IRIS has developed draft systematic review protocols for these five PFAS (USEPA 2019).

16.2.1.2 Protected Populations and Target Risk Levels

The protected populations that are considered in the development of surface water criteria for human health typically include adults. In some cases, other populations, such as lactating women, women of childbearing age, children, and infants, may also be explicitly considered separately, depending on the nature of the chemical and the exposure route. As discussed in Section 16.2, the human health criteria most relevant to PFAS consider ingestion of aquatic organisms (fish and shellfish) and/or drinking water. In general, exposure from ingestion of aquatic organisms will likely be greater than exposure from drinking water for PFAS such as PFOS that bioaccumulate in aquatic life.

In the development of human health WQC based on standard exposure assumptions, the relative doses from fish consumption and drinking water are dependent on the bioconcentration factor (BCF) or bioaccumulation factor (BAF). The assumed daily dose from fish consumption (22.5 g/day) is greater than the assumed daily dose from drinking water ingestion (2.4 L/day) for bioaccumulative PFAS such as PFOS (see Sections 16.2.1.3 and 16.2.1.4). However, exposures to bioaccumulative PFAS in drinking water are higher in infants, particularly in those that are breastfed, than in adults, and infants are considered to be a sensitive subpopulation for adverse effects of PFAS (Goeden, Greene, and Jacobus 2019). In contrast to human health criteria for surface water, drinking water guidelines for PFAS developed by USEPA (USEPA 2016, USEPA 2016) and some states are based on exposure assumptions or exposure modeling for sensitive life stages (for example, lactating women, infants (Post 2021)). Minnesota (MPCA 2020) has recently used modeling of early-life exposure in formula-fed and breastfed infants, as well as a higher fish consumption rate specific to women of childbearing age (MPCA 2020), to develop a human health surface water criterion for PFOS; they also developed a human health-based criterion for PFOS in fish tissue.

A target cancer risk level is used along with the cancer slope factor in calculation of criteria based on carcinogenic effects. The selection of the lifetime cancer risk level is a policy choice, not a scientific decision, and the target cancer risk level (for example, 1 in 100,000 or 10^{-5}; 1 in 1,000,000 or 10^{-6}) differs among states, which is one reason why criteria based on cancer risk can vary among different states.

When chemicals have the potential to exert both carcinogenic and noncarcinogenic effects (for example, PFOA), the final criterion may be based on the lower of the criteria based on cancer and noncancer effects. Criteria for noncarcinogenic effects are developed such that exposure to the contaminant will not exceed the RfD.

16.2.1.3 Exposure Factors

The exposure factors typically considered in development of criteria for ingestion of drinking water and/or aquatic organisms include assumed body weight, drinking water and/or aquatic organism (fish/shellfish) consumption rates, and relative source contribution (RSC). These exposure factors and their use in developing criteria are described below.

As previously stated, the default adult body weight is usually used when developing human health criteria. USEPA currently recommends a default adult body weight of 80 kg for development of human health criteria (USEPA 2015). However, some states' criteria are based on the older recommended value of 70 kg. Alternative body weight assumptions for specific ages, sexes, or other subgroups can be found in the USEPA Exposure Factors Handbook (USEPA 2011), and certain states may use these values.

States typically use default ingestion rates recommended by the USEPA for the specified environmental media, for example, drinking water or fish tissue; however, some states use state-specific values, especially for fish ingestion. The adult drinking water consumption rate is usually used for human health criteria. In 2015, USEPA updated its recommended default adult drinking water consumption rate for human health criteria from 2 L/day to 2.4 L/day (USEPA 2015). It is noted that the relevant body weight-normalized exposure parameter (L/kg/day) is 0.03 L/kg/day with the updated body weight and ingestion volume, which represents a very small change from 0.029 L/kg/day based on the older values. Similarly, USEPA also updated the default rate of 22 g/day for fish consumption from the previous value of 17.5 g/day (USEPA 2015). Some states consider state- or region-specific rates that have been developed based on consumption data from their region, including higher consumption rates by tribes and/or for subsistence fishing in some cases (USEPA 2014).

Under current (USEPA 2000) guidance, an RSC is used when a human health criterion is based on an RfD (noncancer effects), and USEPA used an RSC USEPA (2015) in its updates of noncarcinogenic criteria. The RSC is the percent of total exposure assumed to come from exposure arising from surface water (ingestion of water and aquatic organisms, or ingestion of organisms only) at the criterion concentration. It is intended to ensure that total exposure from all sources (surface water and non-surface water–related) does not exceed the RfD. USEPA guidance specifies an RSC of 20–80 percent, with a default of 20 percent (the most stringent possible value) when data to derive a chemical-specific value are not available (USEPA 2015). Some states and USEPA use the 20 percent default value in their PFAS drinking water guidelines, while other states (for example, MN, NH, NY) use higher RSC values based on estimates of non-drinking water exposures from human biomonitoring data or in consideration of certain life stages.

16.2.1.4 Bioaccumulation, Bioconcentration, and Biomagnification Factors

Three types of factors can be used by risk assessors to relate environmental concentrations of a chemical (for example, in water, sediment, soil, or prey) to concentrations within certain organisms. These factors include bioaccumulation factors (BAF), bioconcentration factors (BCFs), biomagnification factors (BMFs) and associated trophic magnification factors, each of which are defined in the text box below. These factors are frequently used for risk assessment of biota such as fish and shellfish consumption by human fish consumers, as well as wildlife. The USEPA has outlined methods for developing BAFs, which are recommended for risk assessment of most chemicals, whereas BCFs and BMFs typically provide useful information about the fate, transport, and ecological risks of chemicals (USEPA 2003).

Certain PFAS are highly bioaccumulative in aquatic organisms such as fish, and this is especially true for long-chain PFAS such as PFOS. For the risk assessment of bioaccumulative and bioconcentrating chemicals such as PFAS, BAFs or BCFs should represent the tissues that are consumed by humans (for example, fillets or muscle tissue) and should also represent the trophic level of the fish species of interest (for example, secondary consumer or top-level predatory fish). Both BAFs and BCFs are specific to the chemical and organism in which it is detected. For BCFs, BAFs, or BMFs, larger values indicate greater accumulation in organisms, which in turn result in lower surface water criteria. At this time BCFs, BAFs, and BMFs for PFAS are primarily based on measured data. Examples of these values for PFAS in aquatic organisms are available in Table 5-1 (as a separate Excel file) and discussed in Section 5.5.

Transfer Factors

Bioconcentration factors (BCF, L/kg) represent the direct uptake of PFAS by an organism from the water column (through the gills) and are measured as the ratio of the concentration in an organism to the concentration in water. Typically derived from laboratory studies.

Bioaccumulation factors (BAF, L/kg) represent the amount of PFAS taken up from bioconcentration plus the contribution of PFAS in the diet of that organism. Typically estimated from field studies.

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

Trophic magnification factors (TMF; typically unitless) express the change in contaminant level per trophic level, and therefore describe the biomagnification between different trophic levels of the food web.

When the standard USEPA equation shown in the text box in Section 16.2.2 is used with standard exposure assumptions (drinking water ingestion – 2.4 L/day; fish consumption – 22 g/day) to develop human health criteria, the assumed contribution to total exposure from fish consumption is greater than from drinking water when the BCF or BAF is >110. As the numerical value of the BCF or BAF increases, the proportion of assumed exposure from fish consumption continues to increase. Given the mathematical impact of BAFs, BCFs, and BMFs on resulting WQC, there are several considerations for data use and applicability. One example of these considerations is the applicability of values estimated from studies on nonnative species or from water bodies with different water chemistry from the sites intended for protection. The use of central tendency versus upper percentile values may result in less stringent criteria but may be less appropriate in cases where BAFs for a given compound vary by orders of magnitude. The USEPA encourages the use of site-specific modification to BAF, BCF, and BMF selection where such decisions are appropriate and scientifically defensible (USEPA 2000).

16.2.2 Human Health Criteria Development for Beneficial Uses of Surface Water

This section outlines issues that are relevant to development of surface water criteria for specific beneficial uses. These criteria are based on the protection of human health from exposure via intentional ingestion of contaminated media, including:

- drinking water use, 16.2.2.1
- subsistence, commercial, and sport fishing, 16.2.2.2
- drinking water combined with subsistence,

Standard USEPA Equation for Combined Drinking Water + Fish/Shellfish Consumption

$$SWC = \frac{RfD \times BW \times RSC}{DI + ((BCF \text{ or } BAF) \times FIR)}$$

SWC = surface water criterion (mg/L)

commercial, and sport fishing, 16.2.2.3
- contact recreation (incidental ingestion of and skin contact with surface water, sediment, and PFAS-containing foam), 16.2.2.4
- use for agriculture, 16.2.2.5
- fish consumption advisories, 16.2.2.6.

Using USEPA methodology, the surface water criteria described in Sections 16.2.2.1, 16.2.2.2, and 16.2.2.3 can be derived using a variant of the equation in the text box to the right. As described in Sections 16.2.2.1 and 16.2.2.2, terms accounting for exposure from drinking water or fish consumption can be removed as appropriate for the designated use of the water body.

RfD = reference dose (mg/kg/day)

BW = body weight (kg)

RSC = relative source contribution (unitless)

BCF = bioconcentration factor (L/kg)

BAF = bioaccumulation factor (L/kg)

FIR = fish ingestion rate (kg/day)

DI = drinking water ingestion rate (L/day)

USEPA (2000)

16.2.2.1 Waters Designated for Domestic/Municipal Supply (Drinking Water Use)

As noted earlier, surface waters that are designated only for drinking water use may use drinking water guidelines already developed by USEPA or state agencies as WQC. Current state and federal drinking water guidelines for PFAS are found in ITRC’s Tables of PFAS Water and Soil Values (https://pfas-1.itrcweb.org/fact-sheets/). Some states derive this type of surface water criterion using the equation above but omit the denominator terms for bioaccumulation/bioconcentration factors and fish ingestion rates. This equation determines a drinking water value based on human health risk assessment but does not include consideration of analytical or treatment removal factors. Additional discussion of drinking water guidelines may be found in Section 8.3.3.

Numerically, surface water quality criteria for the protection of drinking water may be the same as or differ from drinking water standards such as MCLs, which apply to public water systems, or ambient groundwater quality standards. Drinking water standards such as MCLs are often higher than the strictly health-based goals derived by the previously described equation due to analytical and treatment limitations, while surface water criteria do not consider these factors. However, almost all the current state and federal drinking water guidelines for PFAS are set at health-based goals because analytical and/or treatment removal considerations are not included as limiting factors in the development of the guidelines. Some states may have the authority to adopt existing drinking water values, such as MCLs, as surface water quality criteria for the protection of drinking water sources. This varies due to states’ regulatory authorities and definitions of surface waters considered acceptable for potable use. Alternatively, some states may derive criteria that differ from drinking water guidelines due to consideration of drinking water use combined with other designated uses such fish/shellfish consumption.

16.2.2.2 Waters Designated for Subsistence, Commercial, and Sport (Recreational) Fishing (Consumption of Aquatic Organisms [Fish and Shellfish] Only)

Surface water criteria for fish and shellfish consumption rely on assumptions about consumption rates as well as the relationship between chemical concentrations in water and the resulting tissue concentrations in consumed aquatic organisms.

Default fish consumption rates recommended by USEPA and choices made by states to reflect regional consumption patterns were discussed in Section 16.2.1.3. The quantifiable relationship between chemical concentrations in water and the concentrations in tissue is represented by transfer factors such as BCFs, BAFs, or BMFs, which are defined in Section 5.5 and included in the text box in Section 16.2.1.4.

The equation used to derive this type of criterion, using USEPA methods, would be the equation in the box above but omitting the drinking water ingestion rate. This equation relies on toxicity values (Section 16.2.1.1) and exposure factors (Section 16.2.1.3), as well as BAFs or BCFs for the specified chemical. More stringent toxicity values, higher exposure factors (for example, fish consumption rates), or larger BAFs or BCFs result in lower surface water criteria. For example, criteria based on the higher fish intake rates for subsistence fish consumers would be more stringent than criteria based on the average intake rates for U.S. consumers or sport fishers. Depending on state level or regional policies, such criteria may be developed separately for sport (recreational) and subsistence fishing practices. Aquaculture operations may be required to meet similar criteria for rearing, harvesting, or selling fish depending on the regulatory authority of certain states. This type of surface water criteria is typically developed in consideration of fish, especially predatory fish, as these are more commonly caught and consumed by the public than are shellfish. However, similar criteria can be developed for shellfish (for example, bivalves and crustaceans) using similar risk assessment methods.

16.2.2.3 Waters Designated for Combined Use as Drinking Water and for Subsistence, Commercial, and Sport (Recreational) Fishing

Freshwaters may support and/or be designated for both drinking water and fish consumption beneficial uses. This requires consideration of factors discussed in Sections 16.2.2.1 and 16.2.2.2. The full equation in the box above provides the USEPA method for deriving this type of criteria. Default input values would be similar to those listed for each use separately. Surface water criteria established for both drinking water and fish consumption will be more stringent than criteria for either use alone.

16.2.2.4 Waters Designated for Contact Recreation

WQC for recreational contact, such as swimming and wading, consider exposure primarily due to incidental ingestion and dermal contact with surface water, sediments, and potentially PFAS-containing foams. There is no standardized equation for development of criteria protective of exposure to recreational water, but certain equations in the USEPA’s Risk Assessment Guidance for Superfund (RAGS) provide a framework for developing screening levels for recreational contact (USEPA 2004). Specifically, equations for estimating chemical intake by incidental ingestion of water and dermal absorption from water during swimming or wading are available in Chapter 3 of the RAGS Part E, Supplemental Guidance for Dermal Risk Assessment (USEPA 2004). There are several gaps in the current literature that limit the application of these equations, including scant information on skin permeability of several PFAS and how distribution in the water column influences dermal contact. Currently available information on partitioning of PFAS to air and the air/water interface is reviewed in Sections 5.2.4 and 5.2.4.1.

Dissolved-Phase PFAS

At this time, primary or secondary contact recreation with surface water is not expected to be a significant pathway for human exposures to PFCAs and PFSAs (for example, PFOS) as compared to drinking water or to consumption of aquatic organisms. Current evidence suggests that PFAS are poorly absorbed through the skin (discussed in Section 17.3.1.2). Studies performed by some state agencies estimated the risks associated with observed PFAS concentrations in water via recreational exposures such as swimming, and concluded that the risks were low (MDHHS 2019, MDH 2019, Vermont DEQ 2020, MPCA 2020). Recreational screening levels are likely to be orders of magnitude higher than concentrations that are protective of consumption fish/shellfish, drinking water use, or some estimates of toxicity toward aquatic wildlife. However, there is uncertainty regarding dermal absorption capabilities (for example, skin permeability coefficients) of most PFAS, both short- and long-chain, that would have a significant impact on derived guidance values. One additional area of concern may come with inhalation in an environment where water-to-air transfer may occur from aerosol-borne PFAS in sea sprays or dam mist near known source areas (Johansson et al. 2019). Knowledge in these areas and knowledge regarding the volatilization and inhalation potential of PFAS is very preliminary, still evolving, and subject to change (see Section 5.3).

PFAS in Foams

In contrast to dissolved-phase PFAS, PFAS-containing foam may occur at and above the air-water interface on surface waters. Observations concerning PFAS-related foams present in surface waters have been reported in several states and present concerns for exposure from prolonged skin contact or incidental ingestion by small children. Unlike PFAS dissolved in water, foams may remain on the skin for a longer period, which may elicit public concerns. There are currently no WQC for the formation of foams, but some states may consider developing contact standards for exposure to foams. As noted above, a critical parameter in developing risk-based screening levels for recreational contact is the skin permeability coefficient, which is a measure of dermal absorption. There is currently high uncertainty and limited information available regarding skin permeability for PFAS (see Section 17.3.1.2), and this lack of data poses major challenges to risk assessment for human dermal contact with PFAS. It is anticipated that exposure to PFAS-containing foam on surface waters poses a significantly lower risk to human receptors than direct ingestion from food and water, but if combined with drinking water or occupational exposure, could pose an added toxicological burden.

Using a similar approach to that described above, along with USEPA guidance (USEPA 2000, 2011, 1989), some states may decide to develop surface water criteria for PFAS-related foams. However, these surface water criteria would likely be far higher than any criteria needed to protect surface water for other uses by humans and wildlife and would be applicable to a limited number of sites. Some states, such as Minnesota, have published qualitative guidelines (MPCA 2020). In the future, some states may develop human health-based criteria for PFAS-containing foams in surface waters that would be protective of recreational exposures such as swimming and wading. It is also challenging to sample foam in surface waters, as described in Section 16.5.

16.2.2.5 *Waters Designated for Agricultural Supply*

One of the beneficial uses of fresh water is agricultural supply, for irrigation of crops for direct human consumption and silage for dairy or beef livestock that may ultimately lead to indirect human consumption (milk or beef ingestion). Since PFAS are known to bioaccumulate and have been detected in edible crops, produce, dairy, and meats (Section 5.6) (ATSDR 2018; USFDA 2019), there are potential concerns regarding acceptable levels of PFAS in surface water that will be protective of human health if used for irrigation of crops and silage.

The rapidly expanding literature about PFAS uptake into crops is useful in identifying a few general trends and is discussed in depth in Sections 5.2.3 and 5.6. The potential for PFAS bioaccumulation in plants ranges from low (0.1) to approximately 10 times the soil concentration in many studies, although plants with high water content (for example, lettuce) could exhibit considerably higher bioaccumulation of certain PFAS (see Table 5-2, provided as a separate Excel file and discussed in Section 5.6.2). Chain length is a significant factor in availability for uptake into plants. While both longer chain and shorter chain PFCAs and PFSAs may be taken up by plant roots, there is generally greater translocation and distribution of shorter chain PFAS into the remainder of the plant, including the aboveground tissues (Section 5.6.2). In general, there is greater accumulation in vegetative tissues (for example, leaves and stems) than in storage tissues such as fruits and seeds (Section 5.6.2).

There is currently no USEPA guidance for development of surface water criteria for irrigation and livestock watering. However, approaches have been developed by some states, and other countries such as Canada (ECCC 2017), that consider human dermal and inhalation exposure to irrigation water and consumption of irrigated produce (for example, University of Florida (2018)). These references may be consulted for additional information on irrigation and livestock protection.

16.2.2.6 *Fish Consumption Advisories Based on Consumption Frequency*

Fish consumption advisories are health-protective recommendations developed by states for frequency of consumption of recreationally caught fish meals. These advisories may be applicable statewide, in certain regions of a state, or to specific water bodies or reaches/segments of water bodies. Fish consumption advisories are not surface water criteria and are not regulatory in nature. The advisories may be issued for the general public, and they may be more stringent for specific groups of people at higher risk, such as women of childbearing age, pregnant or nursing women, or children. At the time of publication of this document, several states (for example, AL, CT MI, MN, NJ, WI) have issued fish consumption advisories for PFAS, particularly PFOS.

Advisories are developed by comparing fish tissue concentrations in wet weight ("triggers") that do not result in unacceptable risks for consumption of meals at different frequencies (for example, unlimited [daily]; once per week, once per month, once per year) with concentrations of the contaminant measured in fish tissue. The advisories may be species- and water body–specific, based on data for PFAS tissue concentrations from the species in the water body, or they may apply regionally and/or to multiple species. Typically, limits are developed for muscle fillets of commonly caught and consumed fish, often accompanied by a recommendation to avoid consumption of skin, fat, and other nonmuscle parts of the fish. If there are populations whose consumption patterns exceed the assumptions of the advisory (for example, consumption of whole fish), there may be a potential for insufficient protection.

Assumptions and parameters used in the calculation of fish tissue trigger levels include:

1. the reference dose for each PFAS

Standard USEPA Derivation of Fish/Shellfish Tissue Trigger Concentrations Used in Development of Consumption Advisories

$$DTC = \frac{RfD \times BW}{MS}$$

Where:

DTC = trigger concentration for daily consumption (µg/g)

BW = assumed human body weight (kg)

RfD = chronic oral reference dose (µg/kg/day)

MS = meal size (g/day)

Trigger concentrations for less frequent meal consumption are calculated by multiplying trigger concentration for daily consumption by appropriate factor (for example, daily – 7; monthly – 30).

2. a consumer's body weight (BW)
3. the size of the fish meal

USEPA (2000)

The generalized equation for development of fish tissue trigger concentrations based on noncancer effects used for fish consumption advisories are shown in the text box; a different equation (not shown) would be used for advisories based on cancer risk.

16.3 Protection of Biota

16.3.1 Overview and Purpose

This section presents the technical methods and information needed to develop or review surface water criteria for PFAS that would be protective of aquatic life and their uses. There are other sections in this document where general ecological issues associated with PFAS are discussed in detail, and that information supplements the information contained in this section. That additional information can be found in Section 7.2, Ecological Toxicology, and Section 9.2, Ecological Risk Assessment.

The types of aquatic life to be protected are usually defined by the various beneficial uses related to surface water that are described in Section 16.1.1. USEPA guidance (USEPA 1985) for derivation of such criteria are primarily intended to protect all but the most sensitive aquatic organisms from exposure to chemicals in surface water or sediment porewater. Considerations also exist to derive criteria for protection of aquatic-dependent avian and mammalian wildlife via calculation of a "final residue value" that can factor into final selection of the chronic criterion (USEPA 1985), or a more explicit "wildlife criterion" using methods presented for the Great Lakes Initiative (GLI; (USEPA 1995)).

Aquatic life criteria share the levels of protection afforded by the Clean Water Act and USEPA guidelines (USEPA 1985) in that criteria are derived using toxicity tests with aquatic organisms in which survival, growth, and reproduction are measured. These data are compiled to derive criteria intended to protect against unacceptable adverse effects to most animal taxa in the aquatic community, which is most commonly calculated to represent protection of approximately the 95th percentile of tested aquatic genera. As a result, acute and chronic criteria concentrations are generally said to represent protection of all but 5% of the most sensitive aquatic species. Criteria can also be lowered to protect particularly important species such as recreationally or economically important species or listed threatened or endangered species.

The following sections summarize the general USEPA methods available for derivation of aquatic life criteria for PFAS, with a focus on how to select the most appropriate toxicity test endpoints related to USEPA guidance (USEPA 1985). Available ecotoxicity data are then summarized for all freshwater and marine aquatic species relevant for derivation of aquatic life criteria, including invertebrates, vertebrates, and algae/vascular plants. This section closes with a summary of information necessary to develop criteria to protect aquatic-dependent wildlife such as birds or mammals, including permissible tissue PFAS concentrations, bioaccumulation and bioconcentration factors, and other food chain effects.

16.3.1.1 Derivation of Aquatic Life Protection Criteria—Methods Summary

The general approach for derivation of aquatic life criteria, according to USEPA guidance (USEPA 1985), is briefly summarized below, along with the definition of key terms. The first step is to compile acute and chronic toxicity data that meet the USEPA (1985) guidelines for the relevance and reliability of each study. This evaluation for scientific relevance and reliability largely focuses on test duration, survival in the control treatment, and methods, with distinctions made between acute (short-term) or chronic (long-term) studies. For example, acute toxicity studies must have an exposure duration of 96 hours (although 48 hours is acceptable for more short-lived species, such as cladocerans and midges), organisms must not be fed during the study, and the endpoint must be mortality, immobilization, or a combination of the two. Chronic toxicity studies must be conducted using exposure durations that encompass the full life cycle or, for fish, early life stage and partial life cycle studies. The acceptable endpoints for chronic tests include survival, growth, and reproduction (see Section 16.3.1.4). The duration of chronic studies may be many days, weeks, or months.

To develop criteria that are protective of the diverse array of aquatic biota, an extensive database representing multiple test species, genera, and taxa is required. A minimum database of acceptable studies representing at least eight specific taxonomic families of aquatic organisms is also required. This is done to ensure that criteria are derived based on data that represent the widest possible range of likely sensitivities encountered in the environment. These minimum database requirements differ for freshwater versus saltwater species as presented in Table 16-3.

Table 16-3. Minimum database requirements for derivation of aquatic life criteria (USEPA 1985)

Freshwater	**Saltwater**
A bony fish in the family Salmonidae	Two families in the phylum Chordata
A second family of bony fish (preferably a commercially or recreationally important warm water fish)	A family in a phylum other than Arthropoda or Chordata
A third family in the phylum Chordata	Either the Mysidae or Penaeidae family
A planktonic crustacean	Three other families not in the phylum Chordata (may include Mysidae or Penaeidae, whichever was not used above)
A benthic crustacean	Any other family
An insect	
A family in a phylum other than Arthropoda or Chordata	
A family in any order of insect or any phylum not already represented	

For each species with acceptable acute toxicity data, the species mean acute value (SMAV) is calculated as the geometric mean of available 48- to 96-hr median lethal concentrations (LC50s) or median effect concentrations (EC50s) for each species. The genus mean acute value (GMAV) is then calculated as the geometric mean of available SMAVs for each genus. The lowest 5th percentile of the distribution of available GMAVs is identified as the final acute value (FAV), which is divided by two to determine the criterion maximum concentration, which is more commonly termed the “acute criterion.” The criterion continuous concentration, or “chronic criterion” can either be calculated using the same 5th percentile calculation as the FAV if all eight minimum database requirements are met, or if they are not met by dividing the FAV by the ratio of acute to chronic effects, termed the acute to chronic ratio (ACR). The ACR is determined from those species with both acute and chronic data available usually as a geometric mean of the available species ACRs. ACR values are one of the factors used to derive chronic surface water criteria for chemicals (USEPA 2008). They may also be used in the development of aquatic life screening values when acute toxicity data may be available but not enough chronic toxicity data are available for a chemical. Generally accepted ACR values have not yet been developed for PFAS and would need to take into account the diversity of chemical structures and behavior of PFAS. See the discussion in Section 16.3.2 regarding the availability of acute and chronic data for select PFAS.

16.3.1.2 Problem Formulation

Recently, USEPA has been developing ambient water quality criteria documents following an ecological risk assessment framework (USEPA 1992) to provide a logical approach to criteria derivation based on the chemical’s characteristics, fate and transport, and mode of toxic action. This information for PFAS is summarized below to assist with the development of a conceptual model and identification of endpoints needed for states to derive aquatic life criteria.

16.3.1.3 Conceptual Model

A conceptual model consists of a written and/or graphical representation of the linkages between the exposure characteristics of the chemical and the ecological endpoints of relevance to criteria derivation. PFAS will be transported to surface waters from direct soil runoff, groundwater discharge, atmospheric deposition, or point source discharges (see Figure 17-1). Once transported into surface waters, PFAS exposures to aquatic organisms will occur via two main pathways: direct from water (bioconcentration) and via the organism’s diet as well as water (bioaccumulation). These pathways are also described and quantified in Section 5.5.

Biomagnification is also an important factor for some PFAS (for example, those with carbon chain lengths of eight or more) (Section 5.5). Section 16.3.3 describes procedures to evaluate uptake of PFAS in aquatic-dependent wildlife.

This simple conceptual model suggests that aquatic life criteria for PFAS will need to consist of two different kinds of toxicological information:

- Toxicity data generated from water-only exposures
- Toxicity data with effects measured on the basis of receptor tissue concentration and diet, from which bioaccumulation and bioconcentration factors are estimated to back-calculate to a protective PFAS concentration in water (see Section 16.3.3.3).

Toxicity data measured on the basis of receptor tissue concentration can also be used to derive purely tissue-based aquatic life protection criteria for PFAS. Tissue-based aquatic life criteria would be subject to less uncertainty because the effects levels directly relate toxic dose and exposure pathways, and because BAFs or BCFs would not be needed to back-calculate to a water concentration. This approach has recently been used for methylmercury (USEPA 2010) and selenium (USEPA 2016) in fish in which tissue-based criteria concentrations take precedence over water column-based concentrations.

16.3.1.4 Assessment Endpoints

Assessment endpoints represent the expression of environmental values to be protected by the management framework (USEPA 1992). In the case of ambient water quality criteria, the values to be protected are aquatic life and their uses. As discussed in Section 16.3.1, the levels and types of protection are those afforded by the Clean Water Act and USEPA guidelines (USEPA 1985). These guidelines specify protection of all but 5% of the most sensitive aquatic organisms with respect to survival, growth, and reproduction.

16.3.1.5 Measurement Endpoints

Measurement endpoints represent the direct empirical measurements of chemical exposure and biological effects that are used to ultimately represent the assessment endpoint (USEPA 1992). For PFAS, the relevant measurement endpoints are as follows:

- Measures of exposure: Given the conceptual model noted above, PFAS measurements would need to include both direct aqueous concentrations and aqueous concentrations estimated using appropriate bioaccumulation or bioconcentration factors (see Section 16.3.3 and Section 9.2.2). Sufficient single chemical toxicity data for aquatic life criteria mainly exist for only PFOA and PFOS, although Tier II methods have been used by Giesy et al. (2010) for PFBS and by Divine et al. (2020) for acute and chronic values for 21 PFAS. Mixture studies for commonly detected PFAS are limited with no consensus on additivity, synergism, or antagonism. Thus, it is difficult to determine at this time whether measures of exposure could be considered additive for either PFOA + PFOS, or even for other PFAS.
- Measures of effect: According to USEPA guidance (USEPA 1985), measures of effect (either acute or chronic) are limited to those representing survival, growth, and reproduction. Therefore, only PFAS toxicity endpoints that either directly measure, or can directly represent, these endpoints should be used for derivation of aquatic life criteria. According to toxicity data summarized in Section 16.3.2 below (and in Section 7.2), available PFAS toxicity endpoints include several sublethal endpoints that could potentially be used to represent growth or reproduction. These include endpoints such as development, percent emergence, time to metamorphosis, and development of malformations. Therefore, states will need to determine whether or not these sublethal effects can be considered reliable quantitative measures of chronic effects of relevance to development of criteria. USEPA developed some logical considerations for this determination relative to endocrine-disrupting chemicals. These considerations may be applicable to PFAS (USEPA 2008).

16.3.2 Availability of Ecotoxicological Data

Toxicity data for establishing surface water quality criteria are available in peer-reviewed sources, mainly the primary literature. As noted in Section 7.2, most aquatic toxicity data are for PFOS, PFOA, and several other PFAS, including PFNA, PFBA, and PFBS. It is worth noting that USEPA has curated peer-reviewed sources of ecotoxicity data for PFAS into the USEPA ECOTOXicology Knowledgebase. As of August 2020, USEPA reported they had conducted a comprehensive literature search and systematic review for >300 PFAS and added ecological toxicity data to ECOTOX from 692 references. These efforts are continuing (USEPA 2019).

This section provides a high-level overview of the available ecotoxicity data retrieved at the time and does not represent an exhaustive literature review for the classes of organisms specifically required for developing aquatic life surface water quality criteria. As noted in Section 7.2, the ecological toxicology of PFAS is an active area of research and users are encouraged to query the literature for updated values. Furthermore, states that undertake criteria development should thoroughly review the studies discussed here and others that are subsequently published to determine if they meet regulatory requirements prior to using them for WQC development.

When developing surface water quality criteria protective of aquatic receptors, several criteria should be met when selecting appropriate studies, such as inclusion and adequate control animal responses and availability of details on experimental design. Test animals should be native and have reproducing wild populations. Also, note that many published endpoints are based on nominal rather than measured PFAS exposures; where measured concentrations are used, they can range from very low to very high percentages of the nominal values (<10–240%). Thus, it is recommended to use measured concentrations for establishing criteria.

The following sections highlight available data, or lack thereof, for the various taxonomic families required for WQC development (refer to Table 16-3 and Section 16.3.1.1).

16.3.2.1 Bony Fish

Aquatic criteria development requires toxicity data for a salmonid species and one other species of bony fish. Fish toxicity studies are mainly focused on PFOS, for which data for multiple bony fish species (for example, rainbow trout (*Oncorhynchus mykiss*), sheepshead minnow (*Cyprinodon variegatus*), fathead minnow (*Pimephales promelas*), and zebrafish (*Danio rerio*) are available. As discussed in Section 5.5, PFOS preferentially accumulates in fish tissue relative to other PFAS. Overall, the data for other PFAS are generally limited to a single species or are lacking entirely (see Table 7-1, link in Section 7.2).

16.3.2.2 Salmonids

Acute salmonid studies on the rainbow trout (*O. mykiss*) have been conducted under both fresh- and saltwater conditions for PFOS. EC50 range from 17 mg/L to 22 mg/L (Robertson 1986; Palmer, Van Hoven, and Krueger 2002); a no observed effect concentration (NOEC) was reported at 6 mg/L (Palmer, Van Hoven, and Krueger 2002). No chronic studies were identified for this or other salmonid species.

16.3.2.3 Other Fish Species

Several acute and chronic studies are available for non-salmonid species (see Table 7-1, link in Section 7.2) and for PFAS other than PFOS. Data from these studies indicate acute toxicity of PFOS on the same order of magnitude as that observed for the rainbow trout, with some species perhaps even more sensitive; LC50s for zebrafish (*D. rerio*; a freshwater native to Asia*)* and fathead minnow (*P. promelas*, a freshwater native to North America*)* were approximately 10 mg/L, with EC50 and NOECs ranging between 1.5 and 3 mg/L (Drottar and Krueger 2000; Ulhaq et al. 2013). Data from an acute test on the North American saltwater species sheepshead minnow (*C. variegatus*) for PFOS suggest this species is less sensitive than its freshwater counterparts, with EC50 greater than 15 mg/L (Palmer, Van Hoven, and Krueger 2002).

Chronic studies of PFOS toxicity are more limited; only two studies of *P. promelas* were identified and indicated a NOEC of approximately 0.3 mg/L and EC50 of 7 mg/L (Drottar and Krueger 2000; Oakes et al. 2005) for early life stage development.

Acute and/or chronic zebrafish toxicity studies are also available for PFOA, PFBS, PFNA, PFBA, and PFDA. Acute toxicity is highly variable, but in general, these compounds appear to be less toxic than PFOS, with LC/EC50 reported up to 3,000 mg/L; the exception to this generality is PFDA, where an EC50 of 5 mg/L was reported (Ulhaq et al. 2013). Chronic toxicity data in this species for these compounds are more limited, but the few available studies suggest chronic toxicity may occur at substantially lower concentrations; for example, Zhang et al. (2012) reported a LOEC of 0.01 mg/L for growth/weight was for PFNA.

16.3.2.4 Other Aquatic Chordates—Amphibians

Amphibians represent an alternative class of aquatic/semi-aquatic chordates for which PFAS toxicity studies have been conducted. There are currently limited PFAS toxicity data available for amphibians, but this class of organisms is becoming more widely studied. Nearly all the available amphibian studies entail acute studies in aquatic life stages (with mortality as the endpoint) on PFOS exposures to several species, including *Xenopus laevis (African clawed frog)*, *Rana pipiens (northern leopard frog)*, *Rana nigromaculata (black-spotted frog)*, *Pseudocris crucifer (spring peeper)*, and *Bufo gargarizans (Asiatic toad)*. Of these, *R. pipiens* and *P. crucifer* are native to North America. Amphibian data are discussed in Section 7.2 and summarized in Table 7-9 for PFOS and PFOA. These studies indicate mortality is observed in amphibians at water concentrations over 10 mg/L, with chronic toxicity occurring at lower levels (although within the range of acute toxicities), and that PFOA is less toxic than PFOS.

16.3.2.5 Crustaceans

Freshwater

Acute

Acute toxicity data for freshwater crustaceans are focused on various daphnids (see Table 7-1, link in Section 7.2), with some data on freshwater shrimps such as the cherry shrimp (*Neocaridina denticulate*) (Li 2009). The largest number of publications are on the water flea, *Daphnia magna*, where 24–48-hour survival data are available for PFBA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, and PFOS. For most other freshwater species, acute toxicity data are limited to PFOA and PFOS.

Chronic

A smaller number of specific PFAS have been assessed for chronic toxicity in freshwater crustaceans. This includes PFOA, PFBS, PFOS, and GenX salt (ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)-propanoate) (Drottar and Krueger 2001). The 21-day survival and reproduction assay with daphnids is reported for both PFOS and PFOA (see Table 7-1, link in Section 7.2). A series of studies evaluated bioavailability of certain PFAS with respect to exposure cofactors such as dissolved proteins, organic carbon composition, and other solutes (Xia, Dai, et al. 2015; Xia, Rabearisoa, et al. 2015; Xia et al. 2013). Although these studies do not estimate ECs or LCs for specified PFAS, they demonstrate that abiotic factors require consideration for exposure assessment and comparison across aquatic toxicity studies.

Saltwater

Acute

Two short-term studies (96 hours) provide some data on the acute toxicity of PFOS in marine crustaceans. The two tested species, both mysid shrimp, are *Siriella armata* and *Mysidopsis bahia,* for which NOECs of 0.550—1.25 mg/L (Drottar and Krueger 2000; Mhadhbi et al. 2012) were derived; however, the values for *S. armata* were based on nominal concentrations (Mhadhbi et al. 2012). Additional studies are needed to evaluate other PFAS, as well as to discern differences in acute toxicity among benthic, epibenthic, and pelagic crustacean species.

Chronic

There are very few laboratory-based chronic toxicity studies available for marine crustaceans. One study was a 35-day growth, reproduction, and survival assay for PFOS using mysid shrimps (*Mysidopsis bahia*) (Drottar and Krueger 2000); values summarized in Table 7-1, link in Section 7.2). Simpson et al. (2021) more recently conducted a comprehensive study of PFOS sediment, overlying water, and/or porewater exposure to various benthic marine/estuarine species, reporting chronic effects data for an amphipod (*Melita plumulosa*), a copepod (*Nitocra spinipes*), and a crab (*Macrophthalamus* sp.).

While there are multiple studies regarding the occurrence of PFAS in wild-caught crustaceans, there is little information on biological effects. There is one recent report on wild-caught eastern school prawn (*Metapenaeus macleayi*) that found associations between metabolomic profiles and certain PFAS, but the exposure history for the animals was unknown (Taylor et al. 2019).

16.3.2.6 Mollusks

Freshwater

Acute

For freshwater mollusks, toxicity studies of PFOA and PFOS are limited to five species: bladder snail (*Physa acuta*), fatmucket clams (*Lampsilis siliquoidea*), black sandshell mussels (*Ligumia recta*), *Unio ravoisieri,* and zebra mussels (*Dreissena polymorpha*) (Li 2009; Hazelton et al. 2012; Fernández-Sanjuan et al. 2013; Amraoui, Khalloufi, and Touaylia 2018). The fatmucket and black sandshells are native to North America, whereas the remaining three are nonnative to the U.S. or are invasive species, as in the case of zebra mussels. Following 24- to 96-hour exposures, Hazelton et al. (2012) estimated lower EC50s for PFOS than for PFOA in both fatmucket clams and black sandshell mussels, where larvae were more sensitive than juveniles toward PFOS.

Chronic

Assessments of chronic effects in freshwater mollusks are limited to a single study with water concentrations that were much higher than those detected at most remediation sites. Following a 28-day exposure to PFOS, Hazelton et al. (2012) observed impaired growth effects in larval and juvenile fatmucket clams as determined by reductions in larval viability (LOEC of 0.0045 mg/L) and impaired metamorphosis (LOEC of 0.0695 mg/L), respectively. Fernández-Sanjuan et al. (2013) evaluated the physiological responses of nonnative and invasive zebra mussels toward a mixture of PFOA and PFOS (0.001—1 mg/L, 10 days), but did not report any mortality.

Saltwater

Acute

Acute toxicity studies for marine mollusks are currently limited to PFOA, PFNA, PFOS, and PFDA. A larger body of literature exists on occurrence and tissue concentrations in mussels and oysters, but almost none of these assessed whole or suborganism level effects. Two 96-hour acute toxicity tests reported NOECs for mortality in *Unio complamatus* (20 mg/L) and eastern oyster (*Crassostrea virginica*) (18 mg/L) (Drottar and Krueger 2000).

Chronic

Chronic studies for sublethal effects of PFAS on bivalve mollusks are limited to a few marine species, including green mussels (*Perna viridis*), Mediterranean mussels (*Mytilus galloprovincialis*) and California mussels (*Mytilus californianus*). In vitro and in vivo studies of California and Mediterranean mussels offer some information relative to effects on xenobiotic transport proteins and enzymatic activities, respectively (Stevenson et al. 2006; Balbi et al. 2017; Gülsever and Parlak 2018), but do not quantify ECs, NOECs, or LOECs for whole-organism exposures. A series of studies using green mussels reported on multiple endpoints following 7-day exposures to PFOS, PFOA, PFNA, and PFDA. These studies evaluated biochemical markers of altered xenobiotic metabolism (Liu, Gin, and Chang 2014), genotoxicity (Liu et al. 2014), oxidative stress (Liu, Chang, and Gin 2014), and immunotoxicity (Liu and Gin 2018) and reported NOECs ranging from 0.010-0.100 mg/L (PFOA and PFNA) down to 0.001-0.01 mg/L (PFOS and PFDA). Simpson et al. (2021) reported chronic no-effects levels for two species of bivalve mollusks (*Tellina deltoidalis* and *Soletellina alba*) of 0.22 mg/L and ≥ 0.85 mg/L, respectively.

16.3.2.7 Aquatic Insects

Freshwater

Toxicity data for aquatic insects (for example, midges, mayflies, dragonflies) are available in the literature, although they mainly stem from acute studies of PFOS, PFOA, and PFNA in the freshwater midge species *Chironomous riparius* and *C. tentans* (see Section 7.2.2.1). Of the aquatic invertebrate species, the chironomids are currently reported as having the highest sensitivity to PFOS (MacDonald et al. 2004). Acute effects are observed to generally occur at water concentrations of approximately 60 mg/L or greater, with chronic effects induced at concentrations less than 0.002 mg/L (see Section 7.2.2.1).

Toxicity data for other orders of aquatic insects are very limited, although some studies indicate that the odonates may also be highly sensitive to PFAS exposures. Van Gossum et al. (2009) found behavior changes following long-term (4-month) exposure of PFOS to damselflies (*Enallagma cyathigerum*) with NOECs reported from 0.010 mg/L to 0.100 mg/L. Bots et al. (2010) conducted a lifetime exposure study of PFOS on *E. cyathigerum*, finding adverse effects on egg development, larval hatching, development and survival, metamorphosis, and body mass, with NOECs ranging from less than 0.010 mg/L (for metamorphosis) to over 10 mg/L (for egg hatching success).

Saltwater

No toxicity information was found on marine insects.

16.3.2.8 Algae/Vascular Plant Data

Section 7.2.4.1 provides a summary of aquatic plant toxicity data. Data on the toxic effects of PFAS on aquatic plants are limited to studies that evaluated PFOS exposures on several algal/microalgal species, on duckweed (*Lemna gibba*), and on watermilfoil (*Myriophyllum spicatum)*. Acute toxicity of PFOS in freshwater aquatic plants has been found to range from approximately 30–100 mg/L, with chronic values generally about tenfold lower.

In a chronic study on a saltwater species of diatom (*Skeletonema costatum*) Desjardins et al. (2001) reported observed effects at approximately 3 mg/L. Simpson et al. (2021) reported a chronic NOEC of > 4.2 mg/L for growth rate as an endpoint.

16.3.3 Aquatic-Dependent Wildlife

This section considers aquatic-dependent wildlife (primarily birds and mammals) in developing surface water criteria for PFAS. It is important to note that the development of such criteria is still in its infancy because (i) there are few laboratory or field studies with data on the toxicity of PFAS to wildlife, (ii) data of sufficient/appropriate quality on the concentration of PFAS in the diet of aquatic-dependent wildlife are limited, and (iii) the unique properties of PFAS make the modeling of food chain uptake complicated. The following sections briefly discuss why aquatic-dependent wildlife should be considered and present methods that can be used to derive surface water quality criteria for their protection.

16.3.3.1 Why Consider Aquatic-Dependent Wildlife?

As described in Section 16.3.1, the focus for deriving surface water quality criteria is primarily on protecting aquatic life (for example, plankton, benthic invertebrates, fish, shellfish). However, it has long been recognized that wildlife species may be more sensitive than aquatic species toward certain contaminants as a result of dietary exposure, particularly if the contaminant is bioaccumulative (USEPA 1985, 1989, 2005).

Because some PFAS are known to be bioaccumulative (see Section 5.5), it cannot be assumed that surface water quality criteria derived for the protection of aquatic life will also be protective of aquatic-dependent wildlife. Protection of aquatic-dependent wildlife is of importance at contaminated sites, particularly for wildlife with smaller home ranges that coincide with the extent of PFAS impacts (Conder et al. 2020; Divine et al. 2020). In developing risk-based screening levels (RBSLs) for different classes of receptors, Divine and coworkers found that for some PFAS, RBSLs for aquatic-dependent wildlife are lower than RBSLs for aquatic life. Lastly, due to the long-range transport for some PFAS (see Section 5.3), there could be a need for surface water quality criteria protective of aquatic-dependent wildlife in remote areas where management actions to address human exposure may not address ecological exposures.

16.3.3.2 Surface Water Quality for the Protection of Wildlife

The principal approach to developing protective surface water quality for wildlife is to use standard desktop wildlife exposure models to solve for a media concentration that results in exposure being equal to a selected toxicity threshold. In modeling exposure, such an approach either uses measured contaminant concentrations in the tissue of the prey/forage or relies on BAFs (to estimate prey/forage tissue concentrations). The same toxicity threshold can be used in either case. Another approach is to determine a critical concentration in the tissue of a prey item that is protective of the wildlife receptor. The advantage of this “body burden” approach is that it avoids the uncertainties associated with relying on BAFs; however, it entails the collection of site-specific tissue data for implementation.

These two approaches are discussed in the following sections.

16.3.3.3 Calculation of a Protective Surface Water Quality Value for Aquatic-Dependent Wildlife

In 1995, USEPA published the Great Lakes Water Quality Initiative (GLI) Technical Support Document for Wildlife Criteria (USEPA 1995). The GLI Technical Support Document provided technical information on the derivation of surface water quality criteria to protect birds and mammalian wildlife. The method is similar to that used to derive noncancer human health criteria and relies on the use of BAFs in a food chain model to back-calculate a surface water value (USEPA 2017). USEPA has used this method for chemicals such as DDT, PCBs, 2,3,7,8-TCDD, and mercury, for which aquatic life-based criteria were modified to become more stringent in order to incorporate adverse effects to wildlife (USEPA 1995). States and tribes bordering the Great Lakes, as well as other states, such as California, have since adopted this approach to derive aquatic-dependent wildlife surface water quality criteria.

The GLI Technical Support Document (USEPA 1995), Section III, provides the equations needed to calculate a protective surface water quality value for birds and mammals from exposure via food and water ingestion (see text box).

By extension, this method can be used in the development of surface water values for PFAS. The GLI approach uses five representative species (bald eagle, herring gull, belted kingfisher, mink, and river otter), because these species are likely to be subjected to the highest exposure from bioaccumulative contaminants through the aquatic food web. However, depending on the conceptual model under evaluation, it might be more appropriate to select different representative

Standard Equation for Derivation of a Protective Surface Water Quality Value for Aquatic-Dependent Wildlife

$$\text{WV (mg/L)} = \frac{\text{TD (mg/kg bw/d)} * (1/(\text{UF}_A * \text{UF}_S * \text{UF}_L)) * \text{BW (kg)}}{\text{W (L/d)} + \text{sum}\,[\text{FC}_i\ \text{(kg food/d)} * \text{BAF}_i\ \text{(L/kg)}]}$$

Where:

species (for example, sandpiper species given their relatively high incidental ingestion of sediment). Giesy et al. (2010) provided good examples of using the GLI approach to calculate surface water criteria for trophic level IV predatory birds for two compounds, PFOS and PFBS.

The GLI Technical Support Document includes tables with values for the exposure parameters (body weight, water and food ingestion rates, as well as prey/forage trophic level). Other sources of receptor-specific exposure parameters can be found in USEPA's Wildlife Exposures Factor Handbook USEPA (1993), Conder et al. (2020), and Divine et al. (2020). However, it is a best practice to select exposure parameters that are most representative of the populations living within the area to which the criteria will be applied. Climate, temperature, habitat, and many other factors specific to the region underlying the studies that are the basis of the exposure factors can vary significantly.

Key PFAS-specific components to this approach are the selection of, and sources for, BAFs to estimate prey or forage tissue concentrations, and the wildlife toxicity data for PFAS (no observed adverse effect levels [NOAELs] and lowest observed adverse effect levels [LOAELs]).

As noted in Section 16.2.1.4, given the influence of BAFs on calculation of a water quality value, their use and applicability need to be carefully considered. Information on a literature review and selection of BAFs is provided in Section 5, with a compilation of BAFs and their sources presented in Table 5-1 (see link in Section 5.5).

WV = wildlife value in milligrams of substance per liter (mg/L)

The bird WV is the geometric mean of the WVs calculated for the three birds and the mammalian WV is the geometric mean of the WVs calculated for the two mammalian wildlife species.

TD = test dose in milligrams of substance per kilogram per day (mg/kg-d) for the test species. This shall be either a NOAEL or a LOAEL (expressed either on a wet weight or dry weight basis for consistency with FC).

UF_A = uncertainty factor (UF) for extrapolating toxicity data across species (unitless). A species-specific UF shall be selected and applied to each representative species, consistent with the equation.

UF_S = UF for extrapolating from subchronic to chronic exposures (unitless)

UF_L = UF for LOAEL to NOAEL extrapolations (unitless)

BW = body weight in kilograms (kg) for the representative species

W = daily volume of water consumed in liters per day (L/d) by the representative species

FC_i = daily amount of food consumed from the i^{th} trophic level in kilograms per day (kg/d) by the representative species (expressed either on a wet weight or dry weight basis for consistency with TD)

BAF_i = bioaccumulation factor for the i^{th} trophic level in liters per kilogram (L/kg)

As noted, there are currently few PFAS toxicity data for wildlife in the scientific literature or standard toxicity databases. Furthermore, given the minimum toxicity database requirements for developing Tier I criteria (see USEPA (1995)), it is unlikely these requirements will be met for individual PFAS at the current time. Note that the GLI technical support document does provide guidance on developing Tier II wildlife values for contaminants with limited toxicity data (USEPA 1995). Conder et al. (2020) and Divine et al. (2020) are good sources of PFAS toxicity reference values (TRVs) for avian and mammalian wildlife that not only include tables of recommended values, but also provide guidance on reviewing toxicity studies reported in the literature and selecting the values. Additionally, Table 7-3 presents TRVs derived for mammalian wildlife.

16.3.3.4 Calculation of a Protective Prey/Forage Tissue-Based Value

USEPA published a science advisory board consultation document on tissue-based criteria for "bioaccumulative" chemicals as proposed revisions to aquatic life guidelines (USEPA 2005). The approach is based on the recognition that for bioaccumulative chemicals, there is a need to develop criteria that account for multiple routes of exposure such as the diet, sediment, and water.

The approach is similar to that for developing a water-based value in that it is based on a daily dietary dose of a chemical that is protective of most sensitive species and integrates it with exposure potential to estimate a chemical concentration in the dietary tissue of representative species, also referred to as a wildlife value (WV). The advantage of this approach over the water-based approach is that it eliminates the uncertainty associated with using BAFs but requires the sampling of appropriate prey biota for implementation.

The equation in the text box below used to develop a tissue-based WV is based on the GLI model for aquatic-dependent birds and mammals but expressed as the chemical concentration in the diet rather than in water (see USEPA (2005), Section 4.4). As discussed above, sources of exposure information can be found in USEPA (1993, 1995), Conder et al. (2020), and Divine et al. (2020).

Note that if the target aquatic-dependent wildlife is exposed via several trophic levels, a WV will need to be calculated for each trophic level using BAFs, or if available, applicable BMFs for the targeted aquatic-dependent wildlife receptor (see Table 5-2, Section 5.5). This will then guide which species of prey/forage to target when monitoring for compliance.

Because this approach was developed to address the bioaccumulation of lipophilic chemicals, it assumes the chemical contribution from water is negligible, which, as discussed in Section 5.5.2, may not be the case for some PFAS. Furthermore, it does not consider dietary intake via the incidental ingestion of sediment, which as noted above, can be included depending on the species of wildlife being evaluated. As indicated by Larson, Conder, and Arblaster (2018), incidental sediment ingestion could be a significant contributor to exposure to aquatic-dependent wildlife.

Standard Equation for Derivation of a Protective Prey Tissue Value for Aquatic-Dependent Wildlife

$$\text{WVww (mg/kg food)} = \frac{\text{TD (mg/kg bw/d)} * (1/(\text{UF}_A * \text{UF}_S * \text{UF}_L))* \text{BW (kg)}}{\text{sum [FC}_i \text{ (kg food/d]}}$$

Where:

WVww = wildlife value expressed as the chemical concentration in the diet of each representative species measured as wet weight

TD = test dose expressed as daily dietary dose (wet weight) from selected study, either a NOAEL or a LOAEL

UF = uncertainty factors for interspecies variation (UF_A), subchronic to chronic (UF_S), and LOAEL to NOAEL (UF_L)

BW = body weight of a representative species

FC_i = amount of daily food consumed for each species from the i^{th} trophic level

16.4 Sampling and Analysis

This section reviews the collection and analysis of surface water, biota, and surface sediment from aquatic systems. In most instances, the precautions taken to minimize biasing the concentrations of PFAS in the samples from sampling equipment and/or sampler protective clothing, among others, are the same as those described in Section 11.1 when sampling groundwater, surface soils, or fish. There are some unique aspects about where to collect a surface water sample that are discussed in this section. For analysis, the methods used for PFAS in drinking water, soil samples, plant material, and groundwater described in Section 11.2 are also used for surface water, biota, and surface sediment. Issues and recommendations unique to sampling PFAS-containing foam are covered in Section 16.5.

16.4.1 Surface Water Sampling

Surface water bodies include, but are not limited to, oceans, bays, estuaries, lakes, streams, ponds, creeks, springs, wetlands, reservoirs, and artificial impoundments. The sample collection for PFAS from a surface water body is essentially the same as for other chemicals or pollutants. Standard operating procedures for sampling equipment have the same limitations, such as PFAS-free samplers, that are used for collection of samples from potable water systems or groundwater monitoring wells. See Section 11.1 for general sampling techniques and equipment requirements for PFAS sampling, including examples of PFAS-specific sampling protocols, and Section 11.2 for analytical methods and techniques.

In addition to USEPA's Compendium of Superfund Field Operations Methods (USEPA 1987) for general guidance on sampling surface water, Michigan (MI EGLE 2021; MI DEQ 2018) and New York (NY DEC 2021) have recently developed guidance specifically for PFAS. Some examples of sampling consideration in a moving water body such as a creek include:

- sampling far enough downstream from the suspected source to allow for adequate mixing
- collecting samples from the upstream side of the sampler to minimize compromising the sample
- collecting the sample from mid-depth in the thalweg (that is, along the natural direction of water flow, below the air/surface water interface but above the surface water/surface sediment interface)

- depending on your sampling objectives, collecting samples from multiple depths to provide the necessary information. This is due to the potential for stratification of PFAS concentrations through the water column and the location of the receptors of concern (i.e., benthic organisms or fish).

Due to chemical properties of PFAS, concentrations in the surface water near the discharge location may be higher at or near the surface. Collecting samples only from the surface may inform you of the worst-case scenario but may not provide information on locations away from the discharge point, such as at a water intake for domestic and industrial use. The same concern applies to PFAS-containing foam. Including this foam in the sample will bias the PFAS concentration high due to the elevated concentrations in the foam (see Section 16.5.5).

Additional considerations for surface water sampling during site characterization are noted below in Section 16.4.5.

16.4.2 Biota Sampling

Because some PFAS are known to accumulate in aquatic biota and in some instances may drive the development of surface water quality criteria (see Sections 16.2.2.2 and 16.3.3), sampling for biota may be an important component of a monitoring program or health assessment. The species of biota to collect and the tissue types to sample will depend on the study objectives. For example, a human health–based study should focus on collecting species within a size range targeted by recreational anglers or crabbers (NJDEP 2018), while an ecological-based study should focus on species representing different trophic levels, as well as benthic and pelagic habitats, and be of a size range targeted by piscivorous birds and mammals. In addition, because it has been shown that some PFAS bioaccumulate to a higher degree in the blood and liver compared to the flesh (see Section 11.1.7.8), collecting and analyzing different tissue types might be an important consideration in a study design.

General guidance on the use of different sampling techniques for fish and shellfish such as gill nets, seines, trawls, and electrofishing, can be found in USEPA (2000), and many states have their own guidance, which should be considered. When sampling biota for PFAS analysis, the additional precautions described in Section 11.1 should also be followed, and some states, such as Michigan, have developed their own PFAS-specific guidance (MI DEQ 2019). For example, collected biota should be wrapped in HDPE or polypropylene bags and/or aluminum foil, and stainless-steel tables, knives, and weighing scale hooks should be used for sample processing (in the field or in the lab), as well as untreated wooden cutting boards. Given that PFAS are widely present in the environment and human-made materials, it will be important to collect equipment blanks during sample collection and processing. Close coordination with the analytical laboratories will be needed to ensure similar PFAS-specific precautions are followed at all times (see Section 11.2).

Additional considerations include sampling surface water and surface sediment within the same area from which the biota are collected. While it is recognized that many aquatic biota are migratory or exhibit extended home ranges, this information will help support identification of PFAS sources as well as potentially the development of site-specific BCFs, BAFs, and biota-sediment concentration factors (BSAFs). BSAFs represent the amount of PFAS taken up by an organism from the sediment and are measured as the ratio of the concentration in an organism to the concentration in sediment. BSAFs are typically developed for those organisms in close contact with surface sediment, such as benthic and epibenthic invertebrates, as well as benthic fish (Figure 17-1).

16.4.3 Sediment Sampling

Because sediment can be a contaminant sink, a transport mechanism, and a source of contaminants to a surface water body and to benthic organisms, it may be necessary to sample sediment for PFAS to support an understanding of its contribution to the surface water quality and/or biota tissue concentrations. Conventional sediment sampling and coring techniques and protocols can generally be used to obtain samples for analysis of PFAS. Section 11.1 describes sampling protocols for all types of samples, with additional detail for porewater in Section 11.1.7.4 and sediment samples in Section 11.1.7.5

Examples of seven different sampling protocols typically used are detailed below:

- Where the sediment is accessible and can hold its form without collapsing, a corer or “Dormer Piston” sediment sampler could be used.
- When collecting samples from shore or wading, the sample should be collected from the upstream side of the sampler to minimize potentially compromising the sample from stirred-up sediment or from a waterproof coating on waders.
- Sediment core samples are collected directly from single-use liners and are not reused.
- There can be sites where the sediment is accessible but either the sediment is sloppy and would not hold its

form, or there is a high density of tree roots or boulders and a corer or piston sampler would not be feasible. In these situations, a stainless-steel trowel could be used to collect surface sediment samples.

- For subtidal sediments, the depth below the sediment surface from which the sample is required determines what equipment is needed. For surface sediment samples, devices such as a modified van Veen grab, Ekman grab, or Ponar grab sampler can be used, while for deeper subsurface samples, devices such as a vibracorer should be used. This nondedicated equipment (equipment used for more than one water body or location) should be verified as PFAS free, and the sampling program should include collection of equipment blanks.
- For sampling subtidal sediments, the depth from which the sample is required dictates what specialized sampling equipment is needed.
- Samples should be collected in HDPE wide-mouth bottles provided by the laboratory, and fitted with an unlined (no Teflon) polypropylene screw cap. A minimum of 50 g of sample is needed. Field observations, including sediment type, texture, and color, should be recorded.

16.4.4 Analytical Methods

Analytical methods for the analysis of PFAS in a surface water share many of the same components as those used for PFAS in other non-drinking water media. A discussion of these analytical methods is found in Section 11.2. Most surface water samples for PFAS are analyzed by Modified EPA 537.1 and use the DOD’s Quality Systems Manual (QSM) for Environmental Laboratories, Version 5.3, Appendix B, table B-15 (USDOD 2019), providing the most current and comprehensive set of quality standards for PFAS analysis. In June 2019, USEPA validated EPA SW-846 Method 8327 for the analysis of PFAS in surface water, groundwater, and wastewater (USEPA 2021). Method 8327 is available for use but has not yet been fully incorporated into SW-846. Method 8327 has not been widely used because it creates laboratory cleanup and accuracy issues and is not accepted by DOD.

16.4.5 Site Characterization

Conducting site characterization of PFAS at a site with a surface water body should begin with determining the beneficial uses as described in Section 16.1.1. Those beneficial uses should be used to select the types of samples to be collected. For example, if evaluating PFAS-containing foam, sample collection will be required near the surface; if evaluating potential impacts to benthic organisms, samples closer to the sediment/water interface should be collected, and if evaluating pelagic fish, it may be necessary to collect a surface water sample integrated throughout the water column. Point sources such as stormwater discharge pipes or a publicly owned treatment works (POTW)discharge should be located and potentially targeted for sampling to evaluate sources of PFAS to the water body. Establishing the locations of natural and human-made water inflow and outflow points to the water body will also help guide sample points and potential exposure sites. Groundwater/surface water interaction may also play a role in establishing the conceptual site model and locating places to sample. Section 10 contains more specifics regarding site characterization and development of a conceptual site model.

16.5 Surface Water Foam

PFAS-containing foam (discussed in this section) is differentiated from AFFF (discussed in Section 3) in that it is the result of dissolved-phase PFAS in surface waters that have been agitated by wind or wave action and aggregated into a mass at or above the surface of the water, irrespective of the PFAS source type.

16.5.1 Foam Above Water Interface

PFAS-containing foam may occur at and above the air-water interface on surface waters. In this context, surface water is subdivided and defined below. This subdivision describes vertically downward the air-water interface, surface micro layer (SML), neuston, and underlying water column. See Figure 16-2.

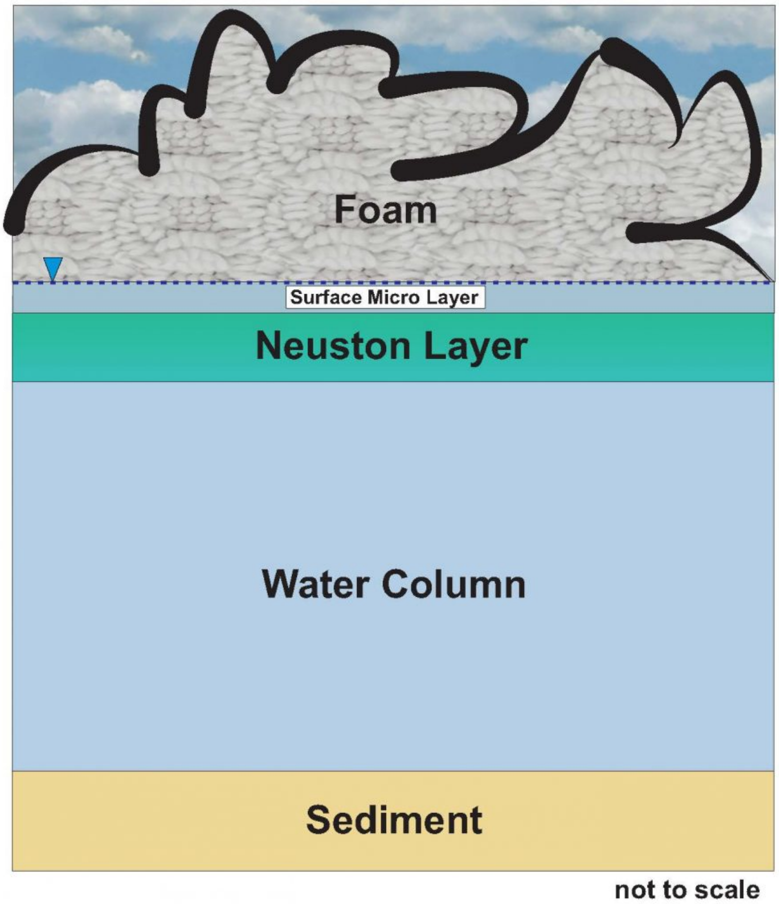


Figure 16-2. PFAS foam on surface water

Although it is typical to find PFAS-containing foam near release source areas, it may also occur some distance away when surface water bodies are interconnected. Source proximity may impact the concentration of PFAS analytes in the foam column itself. However, concentrated PFAS-containing foam may occur on surface water bodies containing low to nondetect PFAS concentrations immediately below the foam itself some distance from the source areas (MPCA 2020; Schwichtenberg et al. 2020). Underlying partitioning considerations are discussed in Section 5.2.2, Considerations for PFAS Partitioning.

Variable surface water depth, flow conditions, and co-contaminant mixtures may affect the presence, aggregation, and physical movement of PFAS-containing foam in the SML and above the air-water interface. These factors may be considered when evaluating fate and transport of PFAS-containing foam, as it may partition back into solution in the water column as it moves with the flowing water. A foam column at and above the surface may be affected by physical forces, including precipitation, wind, and wave action, causing it to separate and travel as smaller foam source material “islands” or collapse and dissolve back into the water column as it travels with the wind and waves.

16.5.2 Foam Characteristics

PFAS-containing foam has wide-ranging visual and textural appearances. These characteristics range from deflated, dry, or aged in appearance, as small aggregations of bubbles accumulating into larger islands of billowed piles, frozen in standard bubble foam appearance or frozen in thin sheetlike membrane appearance, frozen on top of snow and ice, dark coloration due to detritus or organic content, and bright white, with an aerated shaving cream or whipped cream texture.

“High turbulence generated foam tends to be fluffy, actively regenerates, and does not appear to contain high levels of organic material; while older, deflated foam does not actively regenerate and appears to be rich in organic or non-organic particulates. Foam observed along creeks and streams tend to vary in appearance and can occur with any combination of the above-listed characteristics. Wind-generated foam has only been observed on lakes, has generally been white and fluffy, and has actively accumulated along a downwind shoreline. Both organic-rich foam and unfrozen foam with a wrinkled appearance have been observed to accumulate along ice dams or ice shelves” (MPCA 2020).

16.5.3 Stratification Within Foam

Surface water foam is known to be laden with bacteria, detritus, and other naturally occurring material. However, stratification of concentrations of PFAS within the foam column or pile may be due to a number of physical and chemical conditions. For example, co-contaminants may impact the degree of stratification in the surface water column and the foam itself. Additionally, the foam may be aged and in a dry condition toward the top of the foam column/pile, creating a concentration gradient toward the base of the column/pile.

Sampling should be conducted so as to maximize consistency and reproducibility during PFAS surface water sampling to understand PFAS stratification in the surface water column and the foam. The Michigan Department of Environment, Great Lakes, and Energy (EGLE) has published a surface water foam sampling guidance, a surface water foam study report, and has published other PFAS sampling guidance (MI EGLE 2019, MI EGLE 2021, MI EGLE 2021).

As of the date of this publication, the state of Minnesota is working with technical support from the USEPA Office of Research and Development to evaluate foam sampling techniques aimed at understanding the concentration variability within the foam, at the surface micro layer, and the underlying near-surface water column.

16.5.4 Frozen Foam

PFAS-containing foam has been confirmed in frozen form on surface water in Minnesota, Michigan, and Wisconsin (MPCA 2019). Appearance of the foam is difficult to distinguish from snow and ice along stream or lake embankments. PFAS-containing ice has been confirmed in Michigan and can visually take the form of thin film-type islands or within massive ice (MPCA 2020). The ice appears to stratify vertically in concentration where located in massive ice. Confirmation of the degree of stratification in massive ice is an on-going study at this time. Early results from Michigan indicate it appears to increase in concentration with elevation in the ice cores, indicating the ice/air interface may be where the highest concentrations exist, similar to the propensity for PFAS to travel at the air/water interface.

16.5.5 Surface Micro Layer

As previously discussed, PFAS in solution tends to accumulate at the air/water interface, also known as the surface water micro layer or SML. The SML in this context, is generally understood to mean the layer in contact with ambient air and is approximately 50µm thick (MPCA 2020). Variability in sample collection techniques and the extent to which this interface is included or omitted in the collection of a bulk water sample may result in biased analytical results. This can further lead to incorrect conclusions about PFAS concentrations in surface waters at source areas and in the downgradient direction. Where the SML is not characterized and only the deeper water column is sampled, PFAS concentrations may be biased low . The SML may be the location of the highest PFAS concentration in the water column. Omitting collection of the SML could potentially lead to an inaccurate assessment of the risk to human and ecological receptors. Therefore, when preparing a sampling plan, it is important to consider the depth of the water column that is most relevant to the human and ecological receptors that may be exposed to PFAS; different receptors may require unique sampling strategies. At this time, methods to characterize PFAS concentrations and the nature of exposed biota in the SML are still under study (https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Risk-Assessment/ER19-1205).

Due to the physical and chemical properties of PFAAs, including their hydrophilic heads and hydrophobic tails, a given molecule may preferentially exist within the SML. Section 4 includes information about PFAS physical and chemical properties. Sampling the SML in relative isolation from the neuston layer below it or the foam column above it may become an important factor in accurate representation of the concentrations emanating from the SML into foam above when physical agitation occurs. The Michigan EGLE guidance for sampling PFAS-containing foam provides a starting point to understanding the considerations of this sampling protocol in varied circumstances (MI EGLE 2019). Michigan EGLE has also published other PFAS sampling guidance that may be relevant for a project (MI EGLE 2021).

16.5.6 Neuston Layer

The neuston layer may be defined, for the purposes of studying PFAS-containing foam, as the zone directly underlying the SML that is typically enriched with biological life and aligns with the larger definition by Wurl et al. (2017), which was related to strata thicknesses. Wurl et al. (2017) indicated

> “The sea surface microlayer is the boundary interface between the atmosphere and ocean, covering about 70% of the Earth’s surface. The SML has physicochemical and biological properties that are measurably distinct from underlying waters. Because of its unique position at the air-sea interface, the SML is central to a range of global biogeochemical

> and climate-related processes. Historically, the SML has been summarized as being a microhabitat comprised of several layers distinguished by their ecological, chemical and physical properties with an operational total thickness of between 1 and 1000 µm."

While this 1,000 µm SML definition is large enough to encompass the neuston, the refined definition of 50 µm thick SML provided above is considered the state-of-the practice for the purposes of understanding and evaluating PFAS-containing foam and layers of significance immediately underlying it. Liss and Duce (1997) clarify the neuston below the 50 µm SML as two distinct biological layers, "[The] neuston can be divided into epineuston and hyponeuston. The epineuston includes more than 40 species of water striders, *Halobates*, inhabiting the open ocean and coastal areas. The hyponeuston are organisms in the surface centilayer including hydrozoa, mollusks, copepods, isopods, decapod crustaceans, fishes, and the seaweed *Sargassum*."

Section 11.1.7.3 includes generalized surface water sampling guidance references. For PFAS-containing foam on surface water, it appears that the neuston layer is of particular importance in understanding dissolved-phase PFAS within the water column that may be available to the SML for aggregation and concentration into foam at the air-water interface. The neuston may also provide insight into the stratification of PFAS in the water column below the interface.

16.5.7 Analytical Methods

Analytical methods for the analysis of PFAS-containing foam are essentially the same as those used for PFAS in other non-drinking water media. A discussion of these analytical methods is found in Section 11.2. As with all non-drinking water samples, there is no USEPA-certified method for the analysis of PFAS at the time of this publication. Efforts are being undertaken to develop the various analytical methods for the various non-drinking water media. Since there may be very high levels of PFAS in PFAS-containing foam, the laboratory should be warned of this potential so that it can take the necessary precautions during analysis. In the Minnesota case study (MPCA 2020), a commercial laboratory analyzed PFAS-containing foams using their proprietary method of LC/MS/MS. These foam samples were collected following the Michigan foam sampling guidance noted above, with caution taken to prevent dilution of the sample by minimizing contact with the water during foam sample collection.

16.5.8 Enrichment Factors

Enrichment factors are defined for the context of this document as "the calculated fold increase (or decrease) of PFAS concentrations in foam compared to the co-located surface water sample. These values are unitless and are determined by dividing the foam concentration of a specific PFAS compound by the concentration of the same compound detected in the surface water sample. The foam enrichment factor for a given PFAS compound indicates whether that compound is preferentially concentrating into the foam from the bulk water column" (MPCA 2020).

As reported by McMurdo et al. (2008), "Kaiser et al. (2006) observed that surface foam created by bubbling air through an aqueous solution was enriched in perfluorooctanoate PFO by up to 3.2 times." However, simple enrichment factors have been documented in PFAS analytical samples from sites in Minnesota with factors ranging up to >32,000 times (MPCA 2020).

Currently, the extent to which the presence of foam may deplete PFAS concentrations in surface water is unclear. Enrichment factors of short-chain versus long-chain PFAS differed in one Minnesota case study (MPCA 2020) where 33 PFAS analytes were provided. With few exceptions, "short chain PFAS did not tend to enrich into the foam. Often the four, five, and six-carbon length chains were not detected in the foam samples. If they were detected, their concentrations were lower compared to concentrations measured in the surface water sample. Long-chain PFAS were found to have relatively higher foam-to-water enrichment factors than short chain PFAS. In a majority of the samples, 2-(N-ethyl-perfluorooctane sulfonamide) acetic acid (ETFOSAA) and perfluorooctanesulfonamide (PFOSA) had the largest foam enrichment" (MPCA 2020).

The ability of surfactants to concentrate in surface water foam is well known, but may be particularly of interest near source areas due to the ability of PFOA to partition into air circumstantially. Both terminal PFOA and PFOS may become entrained in these foams at high concentration, posing particular risk to ecological receptors in the neuston, SML, and those species reliant on the biological life above and below these zones. In support of this notion, Battelle (2018) indicated, "Foams in the natural environment are metastable and generally dissipate within seconds to days. Compositionally, foams are very similar to the SML, they are formed from the air entrapment on SML and they destabilize back to form SML. Compared to bulk water, foams are significantly enriched in many dissolved and particulate components, including particulate and organic matter, clay minerals, lipids, hydrocarbons, proteins, bacteria, hydrophobic contaminants, and heavy metals. As such, foams can provide a mechanism for fast transport of the contaminants through aquatic systems and a potential exposure pathway for aquatic animals and humans.”

Updated October 2021.

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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 PFSAs 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 ∑PFAS = 21.5, in Okinawa ∑PFAS = 7, in Kanazawa ∑PFAS = 13. In Hong Kong, the concentration varied from ∑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)]: • 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 ΣPFAS 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)]: • 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 ± standard deviation (SD) (range): • PFHxS: 0.31 ± 0.39 (ND–1.2) • PFOS: 3.1 ± 1.2 (ND–4.3) • PFBA: 1.9 ± 1.8 (ND–5.0) • PFPeA: 1.9 ± 1.4 (ND–4.0) • PFHxA: 1.5 ± 1.5 (ND–3.6) • PFHpA: 0.042 ± 0.10 (ND–0.30) • PFOA: 5.4 ± 3.8 (1.5–15) • PFNA: 0.49 ± 0.33 (ND–1.0) • PFDA: 0.48 ± 0.38 (ND–1.2) • PFUDA: 0.018 ± 0.064 (ND–0.22) • PFDoA: 0.20 ± 0.19 (ND–0.54) • Overall ΣPFAS: 15 ± 8.8 (3.4–34) 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 ΣPFAS 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 ΣPFAS.
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: • 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)]: • 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)]: • 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)]: • 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): • ΣFTOHs: 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: • ΣFTOHs: 47 • ΣFTCAs: 3.6 • ΣFASAs: 7.6 • ΣFASEs: 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: • ΣFTOHs: 0.8–27 • ΣFOSAs: 3.7–19 • ΣFOSEs: <25–88 The concentrations of FTOHs and FOSEs were found to increase with altitude.
Parkersburg, West Virginia. USA (Barton, Kaiser and Russell 2007)	Concurrent rain and air samples collected at nine locations at a manufacturing facility during a single precipitation event and analyzed for PFOA.	PFOA predominantly associated with particulates and detected as high as 1,100.
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: • 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: • 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): • ΣFTOHs: <0.4–32 • MeFOSE: <1–25 (g)/<1–21 (p) • EtFOSE: <1–8.7 (g)/<1–6.9 (p) • N-EtFOSA: <0.4–12 (g)/<0.4–12 (p)
Parkersburg, West Virginia USA (Barton et al. 2006)	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): • 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 (NEtFOSA, NEtFOSE, and NMeFOSE).	Reported PFAS concentration range: • ΣFTOHs: 11–165 • Σ(N-EtFOSA, N-EtFOSE, and N-MeFOSE): 22–403
ND = Nondetect		

Table 17-1B. Observed PFAS concentrations in indoor air

Location	Information	Concentrations (pg/m^3)
Northern Germany (Fromme et al. 2015)	Measured volatile PFAS in residences and schools in Northern Germany in 2014.	In schools, reported concentrations of PFAS [mean (range)]: • 6:2 FTOH: 7,853 (1,428–46,867) • 8:2 FTOH: 5,717 (2,480–13,888) • 10:2 FTOH: 2,066 (1,166–4,774) • 8:2 FTCA: 4,554 (128–47,739) • 10:2 FTCA: 1,800 (47–17,360) • N-EtFOSA: 274 (62–692). In residences, reported concentrations of PFAS [mean (range)]: • 6:2 FTOH: 2,058 (289–5,424) • 8:2 FTOH: 9,007 (4,702–21,698) • 10:2 FTOH: 3,296 (759–10,306) • 8:2 FTCA: 422 (58–1,040) • 10:2 FTCA: 205 (27–560) • N-EtFOSE: 69 (27–155) • N-MeFOSE: 552 (27–3,796)
Boston, USA (Fraser et al. 2012)	Indoor office air was sampled in the winter of 2009 in 31 offices in Boston, MA.	Reported mean concentrations of select PFAS: • 8:2 FTOH: 9,920 • N-MeFOSE: 289

Location	Information	Concentrations (pg/m^3)
Birmingham and Harwell, United Kingdom (Goosey and Harrad 2012)	This study reports atmospheric concentrations of a range of PFAS in homes, offices, and outdoor locations in Birmingham and Harwell, UK, during 2008 and 2009. (PFAS reported as MeFOSA, EtFOSA, MeFOSE and EtFOSE).	In homes, reported concentrations of PFAS [mean (range)]: • PFOS: 38 (<1–400) • PFOA: 52 (<1.9–440) • PFHxS: 36 (<1.1–220) • MeFOSA: <2.5 (<2.5–19) • EtFOSA: 120 (14–350) • MeFOSE: 950 (77–3,100) • EtFOSE: 600 (80–1,900). In offices, reported concentration of PFAS [mean (range)]: • PFOS: 56 (12–89) • PFOA: 58 (<1.9–200) • PFHxS: 94 (<1.1–330) • MeFOSA: 6 (<2.5–50) • EtFOSA: 59 (12–150) • MeFOSE: 480 (39–1,200) • EtFOSE: 490 (180–950)
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.	Reported concentration range for ΣFTOHs in homes was 890–47,000. The geometric mean concentrations for other PFAS: • MeFOSE: 380 • EtFOSE: 60 • MeFOSA: 30 • EtFOSA: 20 • PFOA: 28 • PFHxA: 9.7 • PFHpA: 5.1
Hamburg, Germany (Langer, Dreyer, and Ebinghaus 2010)	Air samples were collected in 16 residential and commercial buildings in Hamburg, Germany, in 2009–2010 and analyzed for a range of neutral PFAS.	Reported concentrations of PFAS ranged from: • ΣFTOHs: 3,300–307,000 • ΣFTCAs: 200–15,2000 • Σ(FASAs + FASEs): 4,400–148,000

Location	Information	Concentrations (pg/m^3)
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.	Reported total air concentrations (gas phase + particle phase) [mean (range)]: • MeFOSE: 2590 (11.1–8,315) • EtFOSE: 770 (4.75–1,917)
ND = Nondetect		

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; PFOS and PFOA the most frequently detected.	• ΣPFCAs: 0.029–14.3 • ΣPFSAs: ND–3.27 (only one sample was ND) Remote area (Lake Bonney, Antarctica): • PFOA = 0.048 • PFOS = 0.007
Global, locations not associated with known PFAS sources (Strynar et al. 2012)	Evaluated 60 soil samples from six countries and reported global median concentrations. PFOS detected in 48% and PFOA detected in 28% of the samples. Note that concentrations < LOQ (~0.5 µg/kg) were assigned a value of LOQ/√2 for the median calculations.	Global median concentrations: • PFOA: 0.124 • PFOS: 0.472
Point Sources		

Location	Information	Concentrations (µg/kg)
Location near industrial PFAS source (Davis et al. 2007)	Concentrations of ammonium perflurooctanoate (APFO) in two soil borings located within an impacted well field; concentrations decreased rapidly with depth.	APFO: 110–170
Fire Training/Fire Response (Houtz et al. 2013)	PFOS and PFOA in soils at an unlined fire training area.	Median concentrations: • PFOS: 2,400 • PFOA: 21
Fire Training/Fire Response (Anderson et al. 2016)	In a survey of 40 sites impacted by PFAS, the most frequently detected compounds were PFOS (99% of surface samples), PFHxS (77%), and PFOA (79%). PFOS was detected at the highest concentrations.	PFOS: • Median: 53 • Max: 9,700
Industrial Areas (Zareitalabad, Siemens, Hamer, et al. 2013)	PFOA and PFOS concentrations in soil were compiled.	Max: • 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: • 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		

Location	Information	Concentrations (µg/kg)
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 (∑PFAS)
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 (∑PFAS)
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 ∑PFAS 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): • 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: • PFOA: 6,570,000 • PFOS: 2,300,000
Landfill Impacts		

Location	Information	Concentrations (ng/L)
Firefighting Foam Sites		
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 %): • 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 %): • PFOA: 30–206,000 (36.8) • PFBS: 20–55,300 (40.8)
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.	Water maximum: • PFHxS: 281 • PFOS: 2,920 • PFHxA: 757 • PFHpA: 277 • PFOA: 767 • PFNA: 539 Particle maximum: • PFHxS: 0.15 • PFOS: 339 • PFOA: 4.05 • PFOSA: 0.44
Landfill Leachate and Groundwater (NY DEC 2017)	PFOA was detected in public and private drinking water in Petersburgh, NY. In the site investigation groundwater and leachate from the Petersburgh/Berlin landfill was tested.	PFOA groundwater range: • 1.4–1,600 PFOA leachate: • 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.	Range: • 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 2018)	Analysis of groundwater monitoring wells around landfills in Bennington, VT, for PFOS and PFOA. Nine locations were tested in 2016.	Median (maximum): • PFOA: 18 (900) • PFOS: 4.98 (140)
MSW Landfill Leachate		

Location	Information	Concentrations (ng/L)
Firefighting Foam Sites		
Raw and Treated Landfill Leachates (Busch et al. 2010)	22 landfill sites in Germany were included in a study of 43 PFAS in treated and untreated landfill leachate	**Raw leachate** Mean contribution (%): • PFBA: 27% • PFBS: 24% • PFHxA 15% • PFOA 12% • PFPeA 6.0% • PFHpA 4.0% • 6:2 FTS 3.7% • PFOS 2.7% • PFHxS 2.3% **Treated leachate** Range: • PFBA: ND-2,968 • PFBS: ND-1,356 • PFHxA ND-2,509 • PFOA: ND-926 • PFPeA: ND-829 • PFHpA: ND-280 • 6:2 FTS: ND-82 • PFOS: 0.01-235 • PFHxS: ND-178
Raw Landfill Leachates (Huset et al. 2011)	Concentrations of 24 PFAS were measured in six leachate samples collected from four US MSW landfills prior to leachate treatment	**Raw leachate** Range: • PFBA: 170-1,700 • PFPA: 120-1,500 • PFHxA: 270-790 • PFHpA: 100-340 • PFOA: 380-1,000 • PFBS: 280-890 • PFHxS: 160-700 • PFOS: 56-160 • 6:2 FtS: 29-370 • 8:2 FtS: 11-120 • Me-FBSAA: 58-440 • Me-FOSAA: 16-290 • Et-FOSAA: 21-480

Location	Information	Concentrations (ng/L)
Firefighting Foam Sites		
Raw MSW Landfill Leachate and a Evaporation Pond (Allred et al. 2014)	Concentrations of 70 PFASs were measured in seven landfill leachate samples from six landfills	**Raw leachate** Range: • PFBA: 69-3,700 • PFPeA: 54-3,200 • PFHxA: 190-8,900 • PFHpA: 62-3,100 • PFOA: 150-5,000 • 6:2 FTCA: 230-2,000 • 5:3 FTCA: 320-18,000 • 7:3 FTCA: 22-1,700 • PFBS: 38-3,200 • PFHxS: 45-1,100 • PFOS: 25-590 • MeFBSAA: 41-2,900 • MeFHxSAA: 16-1,900 **Evaporation Pond** Concentration: • PFBA: 24,000 • PFPeA: 39,000 • PFHxA: 50,000 • PFHpA: 14,000 • PFOA: 9,200 • 6:2 FTCA: 300 • 5:3 FTCA: 3,200 • 7:3 FTCA: 60 • PFBS: 830 • PFHxS: 3900 • PFOS: 14 • MeFBSAA: 8,000 • MeFHxSAA: 44
Raw and Treated Landfill Leachates (Yan et al. 2015)	Five municipal landfill sites in China were included in a study of 14 PFAAs concentrations in raw and treated leachate.	**Raw leachate** Range (mean contribution %): • PFOA: 281–217,000 (28.8) • PFBS: 1,600–41,600 (26.1) • PFPeA: 640–10,000 (15.9) • PFOS: 1,200–6,000 **Treated leachate** Range (mean contribution %): • PFOA: 30–206,000 (36.8) • PFBS: 20–55,300 (40.8)

Location	Information	Concentrations (ng/L)
Firefighting Foam Sites		
Raw MSW Landfill Leachate (Lang et al. 2017)	70 PFASs were included in a study of 95 leachate samples from U.S. landfills	**Raw leachate** Range: • PFBA: 30-4,791 • PFPeA: 23-3,194 • PFHxA: 41-8,858 • PFHpA: 32-3,133 • PFOA: 30-4,989 • FHEA: 30-6,547 • FOEA: <LOQ-1,150 • FPePA: <LOQ-41,309 • FHpPA: <LOQ-5,331 • PFBS: <LOQ-3,410 • PFHxS: <LOQ-1,328 • 6:2 FtS: <LOQ-2,248 • MeFBSAA: <LOQ-2,932 1. MeFHxSAA: <LOQ-1,898
Non-MSW Landfill Leachate		
Industrial Impacted Raw Landfill Leachate (Oliaei, Kessler, and Kriens 2006)	14 PFAAs were measured in leachate and gas condensate sampled from 3M–impacted landfills, Minnesota, USA	**Raw Leachate** Range: • PFBA: 1,400-2,200 • PFPeA: 2,700-9,200 • PFHxA: 13,100-28,900 • PFHpA: 4,000-14,700 • PFOA: 14,200-81,800 • PFBS: 1,800-4,800 • PFHxS: 2,200-7,400 • PFOS: 3,100-31,400 **Gas Condensate** Concentration: • PFBA: 4,570 • PFPeA: 5,480 • PFHxA: 37,900 • PFHpA: 15,100 • PFOA: 83,800 • PFBS: 6,300 • PFHxS: 9,480 • PFOS: 29,900

Location	**Information**	**Concentrations (ng/L)**
Firefighting Foam Sites		
Raw and Treated MSW/C&D/Ash Landfill Leachate (Solo-Gabriele et al. 2020)	12 samples were collected at five different landfill facilities within Florida, USA, and analyzed for concentrations of 11 PFAS species (7 carboxylic acids, 3 sulfonic acids, and 5:3 fluorotelomer carboxylic acid)	**C&D leachate** Range: • PFOS: 874-1,000 • PFOA: 1,680-1,720 • 5:3 FTCA: 1,650-1,930 **C&D MSW (25:75) leachate** Range: • PFOS: 557-770 • PFOA: 2,200-2,860 • 5:3 FTCA: 2,540-3,050 **MSW Ash Monofill (930-980C) leachate** Range: • PFOS: 120-166 • PFOA: 259-387 • 5:3 FTCA: ND
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.	PFOA: 1.5–3 PFOS: nondetect–0.8 PFNA: nondetect–1.1 PFHpA: nondetect–6
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.	Range: • 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		
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: • 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: • PFOA: 78,000

Location	**Information**	**Concentrations (ng/L)**
Firefighting Foam Sites		
Teflon Fabric Coating Facility (VT DEC 2018)	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: • 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: • 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 (Schaider, 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: • 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. %]: • 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 2017)	Results from finished groundwater testing by the EPA under UCMR3.	Range (freq. %): • 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 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

Location	Information	Concentrations (ng/L)
Fire Training/Fire Response (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 2017)	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: ∑PFAA 0.077–0.98 ∑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: ∑PFAA <0.21 to 5.8 ∑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
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: • 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: • 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: • 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: • 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 et al. 2010)	PFOS concentrations have been detected in fish collected near the outfall of wastewater treatment plants.	PFOS: 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 per- or polyfluorinated 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 PFECAs 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). PFSAs with more than eight fluorinated carbons (that is, PFOS and longer chain for PFSAs; PFNA and longer chain for PFCAs) are substantially more bioaccumulative than shorter chain PFAAs, with PFSAs 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 (2011) 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 2016), and in other nations, including Germany (Hölzer et al. 2008) and Sweden (Li et al. 2018) (Table 17-6). ATSDR (2019) 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 (≥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 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 = µg/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	—	—	—
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

Location	Study Population	Attributed Source	Year	PFOA			PFOS			PFHxS		
				Mean	***Median***	***Max.***	***Mean***	***Median***	***Max.***	***Mean***	***Median***	***Max.***
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 2016)	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 (95th)	5.5 (AM)	—	15.2 (95th)	1.3 (AM)	—	3.2 (95th)
	Private wells N=219			4.4 (AM)	—	26.6 (95th)	5.4 (AM)	—	16.4 (95th)	1.3 (AM)	—	3.4 (95th)

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 (2016). 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**
PFCAs								
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)	

	Mouse		**Rat**		**Nonhuman primate**		**Human**	
	Male	**Female**	**Male**	**Female**	**Male**	**Female**	**Male**	**Female**
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-4.3 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-12 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)	
PFSAs								
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)
Perfluoroether (Replacement for PFOA in fluoropolymer manufacturing processes)								
GenX	21 h[w]	18 h[w]	3 h[x]	<3 h[x]	~2 h[y]	~2 h[y]	—-	—-

	Mouse		Rat		Nonhuman primate		Human	
	Male	**Female**	**Male**	**Female**	**Male**	**Female**	**Male**	**Female**
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 et al. (2013) [h] Johnson and Ober (1979) Kemper and Jepson (2003) [i] Lau et al. (2006) [j] Butenhoff 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 (2011) [x] DuPont (2011) [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 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 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 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 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. 2016, 2016; MDH 2018, 2019; reviewed in NJDWQI 2015, 2017, 2018). 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 2011). 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 2016) and PFOS (USEPA 2016):

$$\text{Dose [ng/kg/day]} \times \text{CL [L/kg/day]} = \text{serum concentration [ng/L]}.$$

These clearance factors, which indicate bioaccumulative potential, are based on average values for human PFAS half-lives and volumes of distribution (Vd);

$$\text{CL [L/kg/day]} = \text{Vd [L/kg Body Wt]} \times \text{[Ln2/half-life in days]}.$$

Where Ln2 is the natural log of 2.

When combined with mean daily U.S. water ingestion rates (USEPA 2011), 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 2017; Post, Gleason, and Cooper 2017). For PFOA, this average serum:drinking water ratio is greater than 100:1 (NJDWQI 2017); 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 2018; 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 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.

Researchers who participated in the C8 Science Panel recently evaluated current epidemiologic evidence for PFOA and the diseases for which the C8 Science Panel had concluded in 2011–12 that there was a “probable link” with PFOA exposure (kidney and testicular cancer, high cholesterol, thyroid disease, pregnancy-induced hypertension, ulcerative colitis; C8 Science Panel Probable Link reports (C8 Science Panel 2017). They also reviewed evidence for associations of PFOA and additional health effects (Steenland et al. 2020).

Exposure assessment in most but not all of the epidemiology studies of PFAS 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 ovxtz 2012; Winquist and Steenland 2014, 2014; Dhingra et al. 2016; Dhingra et al. 2016; 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 2016, 2016; NJDWQI 2017, 2018; ATSDR 2021), PFNA (NJDWQI 2015; ATSDR 2021), and PFDeA (ATSDR 2021), 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 2012). 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 (2017) 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.

Steenland et al. (2020) noted continued consistent findings of an association between PFOA and high cholesterol. However, although high cholesterol is a risk factor for cardiovascular disease, the C8 Science Panel did not find a “probable link” for PFOA and heart disease, and subsequent studies have also not found an association. Relevant to this issue, Steenland et al. (2020) stated that this apparent inconsistency might be explained by associations of PFOA not only with increased cholesterol, but with increased high density lipoprotein (HDL) and decreased C-reactive protein, both of which decrease heart disease risk

Most reviews have concluded that PFOA (Gleason et al. 2015; Khalil 2015; USEPA 2016; NJDWQI; ATSDR 2021) and PFNA (NJDWQI 2015) are generally associated with increases in certain liver enzymes, particularly alanine aminotransferase (ALT). NJDWQI (2017) 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 2018, 2018; USEPA 2016). However, ATSDR (2021), p. 26, concluded that “increases in serum enzymes and decreases in serum bilirubin, observed in studies of PFOA, PFOS, and PFHxS, are suggestive of liver alterations.” 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. Steenland et al. (2020) also concluded that the limited currently available data do not support an association of PFOA and liver disease. However, Steenland et al. (2020) noted that the lack of human studies with sufficient power to detect this effect, well established liver toxicity of PFOA in experimental animals, bioaccumulation of PFOA in human liver, and extensive evidence for associations with markers of liver damage indicate the need for additional research, particularly in regard to potential associations with nonalcoholic fatty liver disease.

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 et al. 2015; Khalil 2015; NJDWQI 2015, 2017, 2018; 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, [glossary_exclude]head [/glossary_exclude]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 (2016, 2016) concluded that PFOA and PFOS are associated with decreased fetal growth, and ATSDR (2021) p.27, concluded that “evidence is suggestive of an association 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. Steenland et al. (2020) reviewed the factors considered in evaluation of epidemiologic studies of PFAS and birthweight that are discussed above and concluded that collectively, the studies of PFOA and birthweight that are currently available provide inconsistent results.

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 (2021), p. 27, concluded that “evidence is suggestive of an association between serum PFOA, PFOS, PFHxS, and PFDeA (meaning PFDA) levels and decreased antibody responses to vaccines.” USEPA (2016, 2016) 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 (2017) (2018) 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) , p 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.” Khalil (2015) stated that PFAS exposure has been associated with immunotoxicity, including decreased vaccine response, but that the data are inconsistent.

The C8 Science Panel concluded in 2012 that there was not a probable link between PFOA and common infections. Steenland et al. (2020) noted that there was insufficient evidence to infer such a probable link at that time, and that subsequent human and animal studies have evaluated the potential for PFOA to cause immunosuppression (for example, decreased vaccine response, increased infection) and hypersensitivity (for example, asthma, allergy). They reviewed the conclusions of several agencies (NTP 2016; ATSDR 2018 draft; EFSA 2018) and other recent reviews regarding the evidence for immune system effects of PFOA, as well as recent studies that are relevant to this topic. The overall conclusion made by Steenland et al. (2020) was that "a relatively large number of studies consistently report that PFOA impairs immune function," but that "evidence that PFOA increases the risk of infectious disease or asthma is 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 2012). USEPA (2016) 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 (2016) 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 2017, 2018) 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. Steenland et al. (2020) concluded that there is less evidence for an association of PFOA and thyroid disease than when the "probable link" conclusion for this effect was made, and that studies of PFOA and thyroid hormone levels report inconsistent results. Similarly, ATSDR (2021), p. 264, concluded that associations between PFOA, PFOS, PFHxS, PFNA, PFDA, and PFUnA and thyroid-related hormones and thyroid disease are inconsistent across studies, with the majority of studies not finding associations, and that most of the small number of studies of PFDoDA and thyroid hormones did not find "consistent associations."

Other Effects

The C8 Science Panel also found probable links for PFOA with ulcerative colitis (C8 Science Panel 2012) and pregnancy-induced hypertension [PIH] (C8 Science Panel 2012); 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 (2021), p. 26, concluded that "there is suggestive epidemiological evidence for an association between serum PFOA and PFOS and [PIH] and/or pre-eclampsia." In the opinion of Steenland et al. (2020), current evidence continues to support a link of PFOA and ulcerative colitis, although more research is needed for a definitive conclusion. For pregnancy-induced hypertension, Steenland et al. (2020) reported mixed results; one recent study found an association with preeclampsia, a related effect, while another did not.

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 (2012) 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.

A recent study by the National Cancer Institute (Shearer et al. 2021) evaluated associations of serum concentrations of PFOA and other PFAS with renal cell cancer in a subset of participants in a much larger ongoing cancer screening trial. The analysis included 324 subjects diagnosed with renal cell cancer and 324 individually matched controls. PFAS were measured in blood samples taken prior to cancer diagnosis, and serum PFOA concentrations were within the range that was prevalent in the general population at the time of sample collection (1993–2001). Increased serum PFOA was associated with increased risk of renal cell cancer. This association remained even when subjects with decreased kidney function were excluded, and when only subjects with serum PFAS levels measured ≥ 8 years before cancer diagnosis were included. Associations of serum PFOS and PFHxS with increased renal cell cancer risk were not statistically significant after adjustment for the other PFAS, while the association of increased risk with PFOA remained after this adjustment. The authors concluded that these results “add substantially to the weight of evidence that PFOA is a renal carcinogen and may have important public health implications.”

Steenland et al. (2020) concluded that the evidence for an association of PFOA and kidney and testicular cancer remains “supportive but not definitive.” They stated that although the results of three newer studies (published since the C8 Panel’s reports) are not consistent, the evidence for an association of PFOA with kidney cancer is strengthened by positive findings in the recent large case-control study in the general population (Shearer et al 2021).

As discussed in Section 9.1.3.2, PFOA, PFOS, and GenX chemicals were described as having suggestive evidence for human carcinogenicity by USEPA (2016, 2016, 2018) and NJDWQI (2017) – PFOA, NJDWQI (2018) – 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.

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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). As reviewed by Post, Gleason, and Cooper (2017), most PFAAs that have been evaluated for this effect can activate PPAR-α to some extent. Specific toxic effects of some PFAAs in rodent models occur wholly or partially via PPAR-α, while other effects are independent of PPAR-α. One important example is hepatic toxicity of PFAAs. For PFOS, hepatic effects are clearly primarily PPAR-α independent, while hepatic effects of PFOA and PFNA involve substantial contributions from both PPAR-α dependent and independent processes.

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 2017) and PFOS (Butenhoff et al. 2012; NJDWQI 2018), 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 PFECAs 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 2019; ATSDR 2021; NJDWQI 2018; 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 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 2018).

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 (2005) Guidelines for Carcinogen Risk Assessment, USEPA (2016, 2016, 2018) and NJDWQI (2017) – PFOA, (2018)–PFOS described PFOA, PFOS, and GenX as having suggestive evidence for human carcinogenicity. For PFOA, USEPA (2016) and ATSDR (2018), draft 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 (2016)and NJDWQI (2018) not discount human relevance of the hepatic tumors. USEPA (2005) and NJDWQI (2017) developed cancer slope (potency) factors for PFOA based on the incidence of testicular Leydig cell tumors in rats. USEPA (2016) 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 Health Effects Information for Some Additional PFAS of Current Interest

17.2.6.1 Information Relevant to Human Health Effects of Ether and Polyether PFAS

There is increasing awareness and interest in potential human exposure to PFAS other than PFAAs. These include ether and polyether PFAS and dicarboxylic acid polyether PFAS used as replacements for long-chain PFAAs. Additionally, ether and polyether PFAS and PFAS with other structures can be formed as unintentional byproducts of industrial processes. Health effects information for hexafluoropropylene oxide dimer acid (HFPO-DA, GenX), a 6-carbon perfluoroether, and ADONA, a 7-carbon polyfluoropolyether, which are both used as replacements for PFOA, is discussed in Sections 7.1.4 and 17.2.5. Information on the environmental occurrence, ecological effects, toxicology and toxicokinetics in laboratory animals, and bioaccumulation and potential health effects in humans is currently becoming available for additional non-PFAA PFAS at a rapid pace, particularly for additional ether and polyether PFAS (Wang et al. 2019). Collectively, this information indicates that the toxicological and bioaccumulative properties of some of these ether and polyether PFAS, particularly those with longer total chain lengths (carbons plus ether oxygens in the chain), are similar to those of the phased out long-chain PFAAs (for example, PFOA, PFOS, PFNA) (see Figure 2-4).

This section summarizes the currently available laboratory animal and human studies that are relevant to human health effects of some additional ether and polyether PFAS. This material expands the discussion of these groups of compounds beyond HFPO-DA (GenX) and ADONA that were discussed in Section 17.2.5. These additional ether and polyether PFAS include:

- per- and polyfluoroether carboxylates (PFECAs)
- per- and polyfluoropolyether carboxylates (PFPECAs)
- per- and polyfluoroether sulfonates (PFESAs)
- per- and polyfluoropolyether sulfonates (PFPESAs)

As discussed below, some of the most thoroughly studied PFESAs and PFPECAs have chlorine atoms on the terminal carbon (ClPFESAs and ClPFPECAs, respectively). Toxicity data for dicarboxylic acid PFPECAs are also discussed. Specifically, longer chain PFPECA analogues of GenX (HFPO-DA), including hexafluoropropylene oxide-trimer acid (HFPO-TA) and hexafluoropropylene oxide-tetramer acid (HFPO-TeA), and numerous other PFPECAs of various structures and chain lengths are of interest because they are used as replacements for phased-out long-chain PFAAs and/or formed as industrial byproducts. Many of these PFPECAs have been detected in the environment, including in drinking water in some cases (Pan et al. 2019; Munoz et al. 2019; Wang et al. 2019; Kotlarz et al. 2020). Industrial mixtures of ClPFPECAs of various chain lengths, as well as dicarboxylic acid polyether PFPECAs, are also of interest because they are used as alternatives for phased-out long-chain PFCAs, including PFNA (Solvay 2020; Wang et al. 2013), and ClPFPECAs have been detected in environmental media near industrial sources (McCord et al. 2020; Washington et al. 2020; Mazzoni et al. 2015).

F53B is a PFOS alternative that consists primarily of 6:2 chlorinated polyfluoroether sulfonate (6:2 ClPFESA), with smaller proportions of 8:2- and longer chain ClPFESAs (Munoz et al. 2019; see also Section 2.6.1.3). These ClPFESAs are used primarily in China, and are of interest because they have been found in multiple environmental media and, as discussed below, in human biomonitoring studies. Nafion byproducts are PFPESAs formed as industrial byproducts in the production of Nafion, a sulfonated tetrafluoroethylene-based fluoropolymer-copolymer, and are of interest because they have been found in drinking water impacted by industrial discharges (Hopkins et al. 2018). With some exceptions, the toxicity and bioaccumulative potential of PFAAs with similar structures (for example, PFCAs, PFSAs) generally increase with increasing carbon chain length (see Section 7.1.4). Similarly, currently available information on the ether and polyether PFAS with analogous structures (for example, HFPO-DA, -TA, -TeA; 6:2 and 8:2 ClPFESA) discussed in this section suggests that their toxicity and bioaccumulation also generally increase with increasing chain length (including both carbons and ether oxygens).

Human Biomonitoring and Health Effects Studies

PFECAs and PFPECAs

As discussed below, recent biomonitoring studies show that, as is the case for long-chain PFAAs, many ether and polyether PFAS are bioaccumulative in humans, although this may not be the case for some shorter chain members of this group such as GenX (HFPO-DA). Associations with changes in health-related endpoints (for example, clinical chemistry parameters) were also reported in some studies.

A biomonitoring study of Wilmington, NC, residents evaluated blood serum PFAS levels 5 months after cessation of exposure to drinking water from the Cape Fear River that was contaminated by multiple PFAS. Nafion byproduct 2 and two longer chain PFPECAs were detected in the blood serum of >85% of subjects; two other fluoroethers were less frequently detected. The shorter chain PFECA, GenX (HFPO-DA), which was also present in drinking water, and several other PFAS that were detected in the Cape Fear River, were not found in human serum (Kotlarz et al. 2020). This study did not evaluate potential associations of health effects and exposure to fluoroethers. Yao et al. (2020), whose study population lived near a fluorochemical plant in China, also detected multiple PFECAs and PFPECAs, as well as sulfonate ether PFAS (discussed below), in blood serum. They reported associations between PFO5DoA, a long-chain PFPECA that has 7 carbons and 5 ether oxygens, and increased serum lipids, liver enzymes, and uric acid. Two other PFECAs (HFPO-TA, 9 carbons and 2 ether oxygens; PFO4DA, 6 carbons and 4 ether oxygens) were associated with increases in one or more serum lipid parameters, and PFO4DA was also associated with increased uric acid.

A summary of an unpublished biomonitoring study of workers with occupational exposure to industrial mixtures of ClPFPECA congeners of various chain lengths reported an estimated human half-life of 2.5–3 years. Associations with increased serum lipids, liver enzymes, triglycerides, albumin, albumin/globulin ratio, thyroid stimulating hormone (TSH), free thyroxine, and prostate-specific antigen (PSA), and decreases in estradiol and indicators of immune system function (alpha-2-globulins and immunoglobulins) were reported (Solvay 2019). It was noted that the changes in serum lipids and liver enzymes may have been confounded by exposure to PFOA, and that associations with increased TSH and PSA were less reliable because they were based on fewer data points (Solvay 2019).

PFESAs and PFPECAs

6:2 ClPFESA was consistently detected in human blood serum in several recent biomonitoring studies in China (Jin et al. 2020; Liu et al. 2020; Pan et al. 2017; Yao et al. 2020). The median and mean human half-life of 6:2 ClPFESA were estimated as 15.3 and 18.5 years, respectively, as compared to an estimated median and mean of 6.7 and 7.7 years, respectively, for PFOS in the same study (Shi et al. 2016). 6:2 ClPFPESA was included in the suite of PFAS measured in blood serum of U.S residents in NHANES for the first time in 2017–18 (CDC 2021). It was found at the detection limit (0.100 ng/ml) in the 95th percentile of the total population, and at the same or similar levels in most racial/ethnic groups (Mexican Americans – not detected at 90th percentile, 0.100 at 95th percentile; non-Hispanic blacks – 0.100 ng/ml at 90th and 95th percentiles; non-Hispanic whites – not detected at 95th percentile; all Hispanics – not detected at 90th percentile, 0.100 at 95th percentile [values are geometric means]). The maximum level detected in any of these subgroups was 0.200 ng/ml. However, it was detected more frequently and at higher levels in Asians (0.200 ng/ml at 75th percentile; 1.00 ng/ml at 90th percentile; 2.30 ng/ml at 95th percentile; maximum – 10.9 ng/ml). It is not known whether the more frequent detections and higher serum levels in Asians results from their exposure while in Asia or from other sources such as consumption of foods contaminated with 6:2 ClPFESA that are imported from Asia.

As is the case for long-chain PFAAs, biomonitoring data demonstrate exposure to ClPFESAs in utero and through breast milk. Both 6:2 and 8:2 ClPFESA were found in matched maternal:umbilical cord blood samples, indicating fetal exposure, with 8:2 ClPFESA having a higher rate of transfer to cord blood (Cai et al. 2020; Chen et al. 2017; Pan et al. 2017; Xu et al. 2019). The only study that evaluated potential health outcomes associated with fetal exposure found no evidence of an association between ClPFPESAs exposure and birth outcomes (Xu et al. 2019). 6:2 and 8:2 PFESA were also found in human breast milk from several locations in China, but not from Sweden (Awad et al. 2020; Jin et al. 2020). Breast milk levels of these PFESAs were associated with decreased infant growth in one of these studies (Jin et al. 2020).

Rodent Toxicology Studies

PFECAs and PFPECAs

As discussed above, hepatotoxicity is an effect common to many PFAS. In mouse studies, HFPO-TeA, with 12 carbons, was more hepatotoxic than its shorter chain analogue HFPO-DA (GenX; Wang et al. 2017), and HFPO-TA, with 9 carbons and 2 ether oxygens, was more hepatotoxic than PFOA, which has an 8-carbon chain (Sheng et al. 2018). In mice, the bioaccumulation in blood serum and liver increased with chain length for a series of PFPECAs with two to four O-CF2 groups, and only the largest PFAS, with four such groups (PFO4DA), caused increased liver weight at the doses tested (Guo et al. 2019). A recent study (Chen et al. 2021) reported half-lives in male mice of 24 hours for PFO4DA and 43 days for its larger homologue, PFO5DoA after a single intravenous dose. In a 140-day study of male mice, both compounds accumulated in the liver and caused increases in body weight, relative liver weight, and serum glucose, triglycerides and free fatty acids, as well as biochemical changes in the liver consistent with reduced glycolysis (Chen et al. 2021).

Industrial products consisting of mixtures of ClPFPECA congeners of various chain lengths ranging from 8 carbons and 3 ether oxygens to 14 or 17 carbons and 5 ether oxygens caused toxicity to liver, lung, thymus, seminal vesicles, and thyroid in 4-week and/or 13-week rat studies, with some changes persisting after a several-week recovery period (Research Toxicology Centre 2006, 2016). The doses at which hepatic effects occurred were similar to those reported for long chain

PFCAs (for example, PFOA, PFNA; NJDWQI 2015, 2017). The half-lives for five of the congeners (ranging from 8 carbons and 3 ether oxygens to 14 carbons and 5 ether oxygens) were reported as 8–29 days in male rats and 1.6–91 days in female rats. These half-lives are similar to those documented for PFOA (4-6 days) and PFNA (30 days) in male rats (Table 17-7).

Additionally, industrial products consisting of mixtures of another type of PFPECAs, dicarboxylic acid polyether carboxylates (chain lengths not specified), caused toxicity to the liver, lung, thymus, seminal vesicles, and kidneys, with hepatic effects at very low doses, in 4- and/or 13-week studies in rats. As for the ClPFPFECAs, some effects persisted after a several week recovery period. The estimated half-life in male rats after a single dose was 43 days, and the estimated half-lives after repeated dosing were approximately 8 days in males and 11 days in females (Research Toxicology Centre, 2005; Research Toxicology Centre, 2006). In contrast, PFOA and PFNA, with half-lives of 2-4 hours and 1-2 days, respectively, as well as some other PFAS, are much less persistent in female rats (Section 17.2.3; Table 17-7).

PFESAs and PFPESAs

6:2 ClPFESA, the primary component of F53B, and Nafion byproduct 2, also a PFPESA, caused liver toxicity in mice (Zhang et al. 2018; Lang et al. 2020). In a subchronic study of reproductive toxicity of 6:2 ClPFESA in male mice, relative weights of reproductive organs decreased at the highest dose tested. However, at the doses used in the study, there were no histopathological changes in these organs, and hormone levels, sperm counts, fertility, and expression of several testicular genes were not affected (Zhou et al. 2018). After subchronic exposure to mice, 6:2 ClPFESA accumulated in the small and large intestine, damaged the gut barrier, and caused inflammation of the colon (Pan et al. 2019).

Zebrafish Studies

Zebrafish are well accepted as an in vivo model system for human health effects. Zebrafish studies for the ether and polyether PFAS are relevant to evaluation of their potential human health effects and are discussed below.

PFECAs and PFPECAs

The hexafluoropropyl acids—HFPO-DA, HFPO-TA, and HFPO-TeA—caused estrogenic effects in zebrafish (Xin et al. 2019). A suite of PFPECAs of various chain lengths decreased thyroid hormone levels in developing zebrafish embryos, leading to thyroid hormone-dependent malformations of the swim bladder (Wang et al. 2020).

6:2 ClPFECA

A number of studies have reported toxic effects of 6:2 ClPFECA in zebrafish. These include: bioaccumulation in larvae and adults (Wu et al. 2019); hepatoxicity, in adults (Shi et al. 2019; Wu et al. 2019); reproductive toxicity in a two-generation study (Shi et al. 2018); disruption of cardiac development (Shi et al. 2017); and thyroid toxicity from developmental exposures to environmentally relevant concentrations (Deng et al. 2018) and in unexposed offspring after exposure of the parental generation (Shi et al. 2019). Tu et al. (2019) reported that 6:2 ClPFECA was more bioaccumulative and was a more potent disruptor of metabolism than PFOA in zebrafish.

17.2.6.2 Fluorotelomer Alcohols

Fluorotelomer alcohols (FTOHs) are polyfluoroalkyl substances synthesized as intermediates for the manufacture of various fluorosurfactants and fluoropolymers (Dinglasan-Panlilio and Mabury 2006; ECHA 2012). The telomer alcohols are named with the number of fully fluorinated carbon atoms first, followed by the number of partially fluorinated carbon atoms (for example, 8:2 FTOH, 6:2 FTOH). In the environment, FTOHs may degrade to PFCAs with 8:2 FTOH degradation capable of forming PFOA and PFNA (Butt, Muir and Mabury 2014). FTOHs are present in multiple consumer products, with 6:2 FTOH the primary FTOH manufactured for end use. Humans may be exposed by ingestion of FTOH-contaminated food or dust (Yuan et al. 2016). Some FTOHs are volatile, and human exposure may also occur via inhalation (Huang et al. 2019).

The following section summarizes currently available information on the toxicokinetics and adverse health effects of 6:2 and 8:2 fluorotelomer alcohol (6:2 and 8:2 FTOH, respectively) in experimental animals and humans. No peer-reviewed data were identified for other FTOHs.

Toxicokinetics

As polyfluoroalkyl substances, FTOHs are extensively metabolized in rodents and humans. Depending on the specific FTOH, the terminal metabolites include long- and/or short-chain PFCAs, unsaturated fluorotelomer acids (FTUCAs), fluorotelomer acids (FTAs) and glutathione, sulfate, and glucuronide conjugates (Kudo et al. 2005; Fasano et al. 2006, 2009; Himmelstein et al. 2012; ECHA 2012; Nilsson et al. 2013; Kabadi et al. 2018; Huang et al. 2019; Rice et al. 2020).

6:2 FTOH is rapidly absorbed following oral exposure, and undergoes metabolism in rats to form PFBA, PFPeA, PFHxA, PFHpA, certain FTAs, and glutathione, sulfate, and glucuronide conjugates (Russell et al. 2015; Kabadi et al. 2018). In vitro metabolic data from hepatocyte cultures indicate that 6:2 FTOH is likely metabolized similarly in rat, mice, and humans (reviewed in Rice et al. 2020). One of the non-PFCA metabolites, 5:3 FTA, is persistent, having an estimated half-life of ~100 days in male and female rats after repeated dosing (Kabadi et al. 2020). Russell et al. (2015) calculated an apparent geometric mean elimination half-life of 43 days for 5:3 FTA in humans based on occupational data of Nilsson et al. (2010, 2010, 2013). PFHxA and the other terminally stable short-chain PFCAs formed by the metabolism of 6:2 FTOH do not undergo further degradation and are eliminated rapidly in rodents (see Table 17-7). The metabolic pathways, rate determining steps, and elimination half-lives of the parent 6:2 FTOH and other metabolites have not been established.

8:2 FTOH administered orally or by inhalation is also rapidly absorbed and metabolized in rats and mice, with PFOA, 7:3 FTA, 8:2 FTA, PFNA, PFHxA, PFHpA, and glucuronide, glutathione, and other conjugates identified as metabolites (Kudo et al. 2005; Fasano et al. 2006, 2009; Himmelstein et al. 2012; ECHA 2012). In vitro data from rat, mouse, and human hepatocytes indicate that 8:2 FTOH is metabolized to PFOA in rodents and humans, although rodent hepatocytes appear to transform greater amounts of 8:2 FTOH to PFOA than human hepatocytes. Other in vitro metabolites in rodent hepatocytes include 8:2 FTCA, 8:2 FTUCA, and PFNA (ECHA 2012).

Recent data from the NTP (Huang et al. 2019) confirmed that 8:2 FTOH is rapidly absorbed and distributed in male and female rats after a single oral or intravenous (IV) dose. The plasma elimination half-life of the parent compound was 1.1–1.7 hours, and the two primary metabolites were 7:3 FTA and PFOA. The half-life of 7:3 FTA was 2–3 days in both sexes of rats; PFOA's half-life was sex-dependent (approximately 8–15 days in males, and 4.5–6.9 h in females). Nilsson et al. (2010, 2010) measured a mixture of 6:2, 8:2, and 10:2 FTOH and other PFAS in the workplace air of ski wax technicians and subsequently documented the presence of PFOA, PFNA, PFDA, PFDoA, PFTDA, 5:3 FTA, and 7:3 FTA in all samples of the technicians' blood (Nilsson et al. 2013). The metabolites, 8:2 FTUCA and 10:2 FTUCA, were also detected in blood samples from multiple technicians. Although concentrations of 8:2 FTOH were several-fold higher than other PFAS in workplace air, the relative importance of 8:2 FTOH and 10:2 FTOH to the metabolic formation of PFOA, PFNA, other long-chain PFCAs, or the FTAs cannot be determined from these data given that exposures were to multiple PFAS.

Toxicity

6:2 FTOH

Consistent with other data that have demonstrated a lack of genetic toxicity of PFAS (see Section 17.2.5.3), 6:2 FTOH was negative when tested in the Ames bacterial mutagenesis assay. It was not mutagenic in the mouse lymphoma assay and was not clastogenic in a chromosome aberration assay in human lymphocytes. It was found not to be a skin or eye irritant (Serex et al. 2014[2072]).

Given the metabolic transformation of 6:2 FTOH and 8:2 FTOH to several PFCAs, 5:3 FTA (6:2 FTOH metabolite), and multiple additional metabolites of unknown toxicity, it is unclear whether adverse effects associated with exposure of experimental animals to FTOHs (see following) are attributable to the parent FTOH, one or more metabolites, or to combined exposure to multiple compounds. With the exception of the persistent 5:3 FTA metabolite of 6:2 FTOH, for which limited data demonstrating toxicity are available (Rice et al. 2020), the relationship between the adverse effects of FTOHs and their metabolites has not been established.

Rice et al. (2020) synthesized toxicity data on 6:2 FTOH from a 28-day NTP study, a number of peer-reviewed publications (Miyata et al. 2007; Kirkpatrick 2005; O'Connor et al. 2014; Serex et al. 2014; Mukerji et al. 2015), and OECD-compliant studies submitted on behalf of FTOH manufacturers. These studies reported that 6:2 FTOH causes multiple effects in the liver (for example, increased serum liver enzymes, hepatocellular necrosis, and oval cell hyperplasia) and kidney (renal tubular necrosis, mineralization, and degeneration) in rats and mice, as well as decreased thymus weight in rats. Reproductive effects of 6:2 FTOH in rats were observed only when high maternal mortality occurred. In contrast, 6:2 FTOH caused decreased body weight gain during lactation, mammary gland lesions, decreased uterine and ovarian weights, and an increase in anestrus in mice. 6:2 FTOH elicited developmental effects in both rats and mice, including increased pup mortality, delayed skull ossification, decreased pup body weight gain in rats, and decreased pup survival during lactation in mice.

Rice et al. (2020) also summarized the results of a 2-week oral toxicity study of the persistent 6:2 FTOH metabolite 5:3 FTA as reported by the industrial manufacturer. Those data indicate that in rats, 5:3 FTA caused adverse effects on the liver (decrease in total cholesterol, hepatocyte necrosis); kidney (increase in creatinine and urine volume, decrease in total urine protein); thyroid (follicular cell hyperplasia); and thymus (decrease in thymus weight).

There are no publicly available chronic toxicity studies for 6:2 FTOH.

8:2 FTOH

8:2 FTOH was negative when tested in the Ames bacterial mutagenicity study (NTP 2018), and in micronucleus assays reported by the OECD (ECHA 2012).

The liver and kidney were the primary target organs in rats administered 8:2 FTOH orally over a 90-day period (Ladics et al. 2008). 8:2 FTOH caused hepatic necrosis in males, and induced kidney nephropathy in females. Urinary and/or plasma fluorine levels were elevated in animals from all dose groups, an effect attributed to metabolism of the parent compound and an associated increase in fluoride levels. Wang et al. (2019) also documented effects of 8:2 FTOH on the livers of mice, including cellular vacuolation and swelling; swelling of cell nuclei; and immune cell infiltration in animals exposed orally for 28 days. 8:2 FTOH significantly altered mRNA levels of inflammatory cytokines in the thymus and spleen, although it is unclear whether these changes would translate to biologically significant effects on the immune system, as there were no accompanying histological changes in these organs.

Mylchreest et al. (2005) assessed the developmental toxicity of 8:2 FTOH in rats, finding that increased skeletal malformations in pups (delayed pelvic bone ossification and wavy ribs) occurred only at a dose that also elicited maternal toxicity. Mylchreest et al. (2005) also evaluated the reproductive and developmental toxicity of a commercial mixture of FTOH in rats, and observed decreases in litter size, pup weights, and the number of live pups per litter on days 0 and 4 of lactation. Developmental effects were seen only at a dose that also caused maternal toxicity.

There are no publicly available chronic toxicity studies for 8:2 FTOH.

17.2.6.3 Fluorotelomer Sulfonic Acids

Fluorotelomer sulfonic acids (FTSAs) and their salts, the fluorotelomer sulfonates (FTS), are polyfluorinated chemicals that are formed both by direct manufacture and by the degradation of precursors found in certain AFFFs or other industrial products (see Section 2.2.4.1; Field and Seow 2017). Because FTSAs and FTSs exist in anionic form in the body, they are equivalent toxicologically, and the term FTSA is used here to refer to both forms of these chemicals.

4:2 FTSA, 6:2 FTSA, and 8:2 FTSA have been detected in human blood (Lee and Mabury, 2011; Loi et al. 2013; Yeung and Mabry 2016; Eriksson et al. 2017), and 6:2 FTSA and 8:2 FTSA can cross the human placenta (Yang et al. 2016). Humans may potentially be exposed to FTSAs through ingestion of contaminated drinking water or food, or by inhalation of dust (Field and Seow 2017). It is not known if the detection of FTSAs in human blood is due to direct exposure to the parent compounds or to indirect exposure to FTSA or precursors (Field and Seow 2017).

Toxicokinetics

Information on the toxicokinetics of FTSAs is limited. No studies have evaluated the absorption of FTS versus FTSA. Since FTS and FTSA exist in the same anionic form within the body, their toxicokinetics would not differ after absorption. ECHA (2018) provided summary information on a single rodent in vivo study that examined the disposition and metabolism of 6:2 FTSA (species and dose levels not given). Following a single oral dose of 6:2 FTSA, 65–68% of the parent compound was recovered in urine 4 days post-dosing, indicating that metabolism of the majority of the administered dose did not occur. However, because no data were provided on metabolite formation or elimination, many questions remain regarding the metabolism of 6:2 FTSA in animals. In vitro data from ECHA (2018) and Hoke et al. (2015) also suggested that 6:2 FTSA is not extensively metabolized in animals. When 6:2 FTSA was incubated with rat liver microsomal fractions for 2 hours (ECHA 2018) or with rainbow trout hepatocytes for 4 hours (Hoke et al. 2015), no metabolism was detected. FTSA may have the potential to bioaccumulate, in that substantial levels of FTSA were measured in the livers of mice administered FTSA for 28 days (Sheng et al. 2017). The potential of FTSA to bioaccumulate is supported by observations of Yan et al. (2014), who found comparable levels of the bioaccumulative PFOA in the serum and livers of mice exposed under the same experimental conditions used for FTSA by Sheng et al. (2017). In the few human biomonitoring studies that included 6:2 FTSA, it was detected infrequently. For example, the Biomonitoring California Asian/Pacific Islander Community Exposures Project reported no detections of 6:2 FTSA in 2016 (N=96) and FTSA was detected in only 3% of samples analyzed in 2017 (N=99) (LOD=0.05 ng/ml) (CA OEHHA 2020).

Toxicity

6:2 FTSA was not genotoxic in assays of bacterial mutagenesis, or in mammalian cell assays of DNA repair or damage, micronucleus formation, or chromosome aberrations (ECHA 2018).

ECHA (2018) reported the results of unpublished oral range-finding and reproductive toxicity studies in rats. The 14-day range-finding study identified a NOAEL of 10 mg/kg-d based on changes in body and kidney weights and clinical chemistry (creatinine and urea) in one or more dose and gender groups. In the 90-day reproductive toxicity study, 6:2 FTSA did not affect male or female fertility or reproductive performance, and there were no effects on the number of pups, or on pup survival, growth, or sex ratio. The NOAEL for reproductive effects was $\geq$ 45 mg/kg-d.

Adult male mice administered 6:2 FTSA at 5 mg/kg-d over 28 days exhibited increases in liver weight, hepatocellular hypertrophy, hepatocellular necrosis, and biochemical markers associated with liver inflammation. Serum levels of the liver enzyme AST, an indicator of liver damage, and albumin were also elevated, and histological evidence of liver necrosis was observed (Sheng et al. 2017).

17.2.7 PFAS Mixtures

This section provides a brief overview of current toxicity-based approaches for addressing mixtures of PFAS and currently available information on toxicity of PFAS mixtures. This is an active area of research.

17.2.7.1 Proposed Approaches, for Addressing Toxicity of PFAS Mixtures

Total Concentration Approach (Called Simple Additive Approach by Cousins et al. 2020)

In this approach, a single guideline concentration is applied to the total concentration of a specified set of PFAS. This approach is based on the assumption that all of the included PFAS have the same toxic effects and MOA, are equally potent, and their combined toxicity is additive. In the absence of complete information on toxicity and MOA for all of the selected PFAS, this approach has been applied as a conservative public health-protective science-policy strategy.

An example of the total concentration approach is the application of the USEPA Lifetime Health Advisory (LHA) of 70 ng/L in drinking water to PFOA or PFOS individually, and to the total concentration of both. Although PFOA and PFOS do not necessarily share the same MOA, USEPA's rationale for applying the LHA to their combined concentration is that both PFAS cause similar adverse effects in humans and animals, and that the USEPA reference doses for both compounds are numerically identical and are based on similar developmental effects (USEPA 2016).

Additional examples are the drinking water guidelines of 20 ng/L (Vermont) and 70 ng/L (Connecticut) for the total concentration of five long-chain PFAAs (PFOA, PFNA, PFHpA, PFOS, PFHxS) and 20 ng/L (Massachusetts) for the total concentration of six long-chain PFAAs (PFOA, PFNA, PFHpA, PFOS, PFHxS, PFDA) (CT DPH 2016; Vermont DOH 2018; MA DEP 2019), as well as in several other nations (Cousins et al. 2020).

MA DEP (2019) provided a detailed rationale for their approach based on the sum of the six long-chain PFAS. They concluded that this approach is supported by similarities in chemical structures, toxicity values developed by other agencies, toxicological responses, and long serum half-lives for these six PFAS. PFHxA was also considered but was not included, because it has a shorter half-life and causes toxicity at higher doses than the PFAS that were included.

MA DEP (2019) used results of Bayesian benchmark dose (BBMD) modeling of data for thyroid effects (free thyroxine; fT4) and increased liver weight for five of the six PFAS from NTP 28-day rat toxicology studies (NTP 2019). Using PFOA as an index compound with a BBMD of 1, relative BBMDs for fT4 for the other PFAS ranged from 0.5 to 3 on a serum-level basis and 0.8 to 4 on a human equivalent dose (HED) basis. For an increase in liver weight, relative BBMDs based on both serum PFAS levels or HEDs ranged from 0.2 to 2. MA DEP (2019) considered these BBMDs to be sufficiently similar to assume equivalence of the five PFAS.

As discussed by MA DEP (2019), there is a lack of data on toxicological effects, potency, and half-life of PFHpA (the 7-carbon PFAA included in the Connecticut, Vermont, and Massachusetts approaches), and no toxicity values (for example, reference doses) have been developed. Although Massachusetts recognized that PFHpA's half-life is likely shorter than for PFOA, they concluded that there are no data to develop a compound-specific or relative toxicity value for PFHpA, or to conclude that it is toxicologically dissimilar to PFOA. Based on "read-across," (prediction of toxicity based on data from similar compounds) these states consider PFHpA to be equipotent to PFOA.

Hazard Index Approach

Human health risk assessment often uses a hazard index approach, first developed by USEPA (1989), to evaluate the potential cumulative noncancer toxicity from co-exposure to multiple contaminants (USEPA 1989). As discussed in Section 9.1.3.1, calculation of a hazard index is based on the assumption of dose additivity, but it does not necessarily require that the MOA or toxicological endpoint is the same for all components of the mixture.

Health Canada (2018; 2018) has concluded that, although there are no in vivo studies of PFAS mixtures, the similarity in health effects of PFOA and PFOS support an assumption of dose additivity and thus support the use of a hazard index approach to address co-occurrence of PFOA and PFOS in drinking water. ATSDR has also applied the hazard index approach to evaluate potential risk from site-specific exposure to mixtures of several long-chain PFAAs, noting that their approach assumed dose additivity based on “toxicologic similarities” (ATSDR 2020). The application of the USEPA lifetime health advisory (LHA) of 70 ng/L in drinking water to PFOA or PFOS individually and to the total concentration of both (discussed above under Total Concentration Approach) can also be considered an example of an assumption of dose additivity, since both compounds are presumed to be equally potent.

Minnesota Department of Health (undated) uses a health risk index approach—similar to the hazard index approach—to evaluate concurrent exposures to multiple chemicals in groundwater. It is based on grouping chemicals (including PFAS and others) that cause the same general type of adverse health effect (for example, thyroid, endocrine). In the Minnesota health risk index approach, multiple health endpoints may be considered for each individual contaminant.

A recent paper by Mumtaz et al. (2021) provided a “proof of concept” demonstration of the potential use of an ATSDR hazard index approach based on target organ toxicity doses (TTDs) for specific toxicological effects (endocrine, hepatic, reproductive, developmental, and/or immune) to assess the risks of PFOA, PFOS, tetrachlorodibenzo-p-dioxin (TCDD), and polybrominated diphenyl ethers (PBDEs). This approach is intended for use as a screening tool, with a hazard index of >1 for a specific effect indicating the need for further evaluation.

Relative Potency Factor (RPF) Approach

In the RPF approach, each PFAS is assigned an RPF based on its potency compared to an index compound (for example, PFOA), which is assigned a potency factor of 1. The RPFs are applied to the concentration of each PFAS present in the mixture, and the toxicity of the total of the RPF-adjusted concentrations is assumed to be the same as the equivalent concentration of the index compound (for example, PFOA).

The RPF approach is based on dose additivity of the compounds that are included (see discussion in Hazard Index section above). The RPF approach (also known as the toxicity equivalency factor approach) has been adopted for several groups of chemicals known to cause toxicity through a common and well-defined MOA, including cholinesterase-inhibiting pesticides (organophosphates) and dioxins (PCDDs) and dioxin-like compounds (furans [PCDFs]; PCBs) that cause toxicity through activation of the AhR receptor.

The application of the RPF approach for risk assessment of PFAS mixtures is associated with greater uncertainty than for the groups of compounds noted in the preceding paragraph. In contrast to the groups of compounds discussed above, the range of adverse effects of PFAS is not due to a single specific MOA, such as activation of a specific receptor. Furthermore, the MOA may not be the same for all toxicological effects (for example, hepatic toxicity; developmental toxicity) and may vary among PFAS (discussed in this Mixtures section above).

Bil et al. (2021) proposed RPFs for 22 PFAS, with PFOA as the index compound. This is an extension of an earlier proposal of RPFs for 18 PFAS developed by RIVM (Netherlands National Institute for Public Health and the Environment) scientists (Zeilmaker et al. 2018). The RPFs were based on hepatic effects of PFOA and 15 other PFAS in male rats from studies with durations of 40–98 days. Hepatic effects in male rats were selected because these effects are common to many PFAS, and there is a large data set on these effects in male rats. Endpoints evaluated included relative liver weight (all 16 PFAS), absolute liver weight (15 PFAS), and hepatocellular hypertrophy (14 PFAS), and the final RPFs were based on relative liver weight because the data set was most complete. Relative liver weight data for all PFAS (based on external dose) were fit to parallel dose-response curves, which were determined to provide an acceptable fit to the data. BMDs for each PFAS for each effect were developed from the dose-response curves based on a 5% change in absolute or relative liver weight and a 10% change in the incidence of hepatocellular hypertrophy. RPFs were based on the ratio of the BMDs for each PFAS to the BMD for PFOA and ranged from 0.001 (PFBS) to 10 (PFNA). RPF ranges for seven additional PFAS for which no relevant data were available were estimated by read-across/interpolation.

In contrast, Peters and Gonzalez (2011) concluded that it is not appropriate to develop TEFs (similar to RPFs) for PFAS for reasons including differing modes of actions among PFAS. However, Bil et al. (2021) discussed that although the MOA for hepatic effects may differ among PFAS, the similarly shaped dose-response curves for these effects support the assumption of additivity and the application of RPFs for hepatic effects. They also note the need to determine whether the RPFs based on hepatic effects are applicable to other types of toxicity caused by PFAS, such as developmental and immune system effects—an analysis that has not yet been conducted. Goodrum et al. (2021) concluded that the shapes of the dose-response curves for hepatocellular hypertrophy for PFOS and PFHxS in male rats, based on administered dose, differ from the dose-response curves for this effect for other PFAAs. When based on internal dose (serum levels), the shape of the curve for PFHxS differed from the shape of the curves for the other long-chain PFAAs. These results suggest that PFHxS, and possibly PFOS, are not additive with other PFAAs for hepatocellular hypertrophy in male rats; curves for liver weight were not evaluated.

17.2.7.2 Toxicology Studies of Defined PFAS Mixtures

Only a few studies of the toxicity of defined mixtures of PFAS were located; these are summarized below. These include in vitro studies of nuclear receptor activation in cultured cells transfected with the receptor of interest, and toxicity in cultured cells and zebrafish (a model species for human toxicity). Notably, no rodent or primate studies of defined mixtures of PFAS were located.

Receptor Activation

As discussed in Section 17.2.5, an important MOA for many PFAS is activation of cellular receptors, including PPAR-α and others, that regulate expression of genes that control many biological pathways. Wolf et al. (2014) studied PPAR-α activation by PFOA, PFNA, PFHxA, PFOS, and PFHxS singly, and in binary mixtures of PFOA with each of the other four PFAAs using a cultured cell line transfected with the PPAR-α receptor. They concluded that there was additivity for PPAR-α activation in PFAS mixtures at concentrations up to 32 µM. An earlier study from the same research group used this test system with higher concentrations of PFAAs and found that PPAR-α activation in binary mixtures of PFOA, PFOS, PFNA, and PFHxS was antagonistic in the mixture of all four PFAS (Carr et al. 2013).

Activation of the estrogen and androgen receptors by PFOA, PFNA, PFDA, PFUnA, PFDoA, PFHxS, PFOS individually, and an equimolar mixture of all seven PFAAs, was evaluated in cultured cell lines transfected with these receptors (Kjeldsen and Bonefeld-Jorgensen 2013). The results of this study illustrated the complexity of interactions of mixtures of PFAS in regard to receptor activation. PFOA, PFOS, and PFHxS singly, as well as the mixture of the seven PFAAs, were weak agonists of the estrogen receptor and also enhanced activation by the endogenous estrogen, 17-beta estradiol. These three PFAS also inhibited activity of the androgen receptor, and the same three PFAS, as well as PFNA and PFDA, antagonized activation by the endogenous androgen, dihydrotestosterone. In contrast to some of the individual PFAAs, the PFAA mixture did not affect androgen receptor activity in the absence of dihydrotestosterone, but it did antagonize activation of the receptor by dihydrotestosterone. Comparison of the dose-response data for the inhibitory PFAAs and the mixture indicated a synergistic antagonistic effect (greater than additive inhibition) of the PFAAs in the mixture.

Effects in Cultured Hepatocytes

The effects of PFHpA, PFOA, PFNA, PFDA, PFHxS, and PFOS individually, and in 11 binary and 4 ternary mixtures on cell viability of the human liver cell line, HepG2, were evaluated by Ojo et al. (2020). The concentrations that were tested for each PFAS were based on dilutions of the concentration that caused 50% loss of cell viability. Effects of many binary and ternary combinations were synergistic, while other combinations were antagonistic at some concentrations. PFOS was synergistic with the other five PFAS at almost all concentrations, while interactions in mixtures that included PFOA were either synergistic or antagonistic, with synergism predominating at lower concentration levels. In another study of the same cell line, PFOA and PFOS induced and promoted apoptosis, and a mixture of both PFAS showed additivity for this effect (Hu and Hu 2009).

Effects on gene expression of six individual PFAS (PFOA, PFNA, PFDA, PFDoA, PFOS, 8:2 FTOH) and four mixtures (PFOA plus PFOS; three mixtures of all six PFAS in different proportions) were evaluated in primary cultures of hepatocytes from rare minnow (Wei et al. 2009). No clear patterns of response were observed, in those mixtures of PFAS affected the expression of some genes that were not affected by individual PFAS, and vice versa.

Zebrafish Studies

The lethality of PFOA, PFOS, and a mixture of both chemicals was studied in zebrafish embryos (Ding at al. 2013). The interaction between PFOA and PFOS was concentration-dependent, with additive, synergistic, antagonistic, and then synergistic effects observed as the proportion of PFOS was increased.

Behavioral effects in zebrafish embryos were evaluated for PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFBS, PFHxS, PFOS, and 6:2 FTSA individually, and with mixtures of equal concentrations of all nine PFAS (Menger et al. 2020). PFHpA, PFOA, PFNA, PFHxS, PFOS, and 6:2 FTSA alone, as well as the mixture, caused behavioral effects, while PFBA, PFHxA, and PFBS did not. Specific behavioral effects varied among individual PFAS. The mixture of PFAS was less potent than the individual PFAS present in the mixture, suggesting antagonistic interactions among the PFAS in the mixture.

17.2.7.3 Studies of Mixtures of PFAS and Contaminants Other than PFAS

Several additional studies evaluated toxicological interactions of individual PFAS with other environmental contaminants. In male mice, co-exposure to PFOS and PCB126 (a dioxin-like PCB) caused synergistic effects on hepatic expression of genes related to oxidative stress, inflammation, and atherogenesis; levels of a protein that is a biomarker for thrombosis and fibrosis (indicators of cardiovascular disease risk); and hepatic lipid levels. Co-exposure, but not the individual compounds, caused pathological changes indicative of liver injury.

The effects on gene expression in zebrafish embryos of PCB126 alone, PCB126 plus PFOS, PCB126 plus PFHxA, and PCB126 plus both PFOS and PFHxA were evaluated by Blanc et al. (2017). The PFAS were not tested in the absence of PCB126. PCB126 with both PFOS and PFHxA had a greater effect on the expression of several genes than PCB126 alone or PCB126 with PFOS or PFHxA individually. The results suggest synergistic effects of PFOS and PFHxA on the effects of PCB126 in this test system.

17.2.8 Evaluating PFAS Using New Approach Methodologies

In one of its most resource-intensive efforts on PFAS to date, the USEPA developed a screening library containing PFAS compounds. This USEPA-curated list spanned several public-interest lists of PFAS, including those from the USEPA, United States Food and Drug Administration (FDA), Department of Defense (DOD), Agency for Toxic Substances and Disease Registry (ATSDR), Consumer Product Safety Commission (CPSC), and state regulatory agencies. The screening library was developed to support the development of analytical methods, environmental monitoring, and toxicity testing. Further information on the initial list of 430 PFAS compounds is available on USEPA's CompTox Chemicals Dashboard (USEPA 2020), which was developed by the USEPA's Chemical Safety for Sustainability Research Program (USEPA 2020). The purpose of the dashboard, along with related databases and web applications developed by the agency, is to support the USEPA's computational toxicology research efforts to develop new and innovative methods with the goal of incorporating advances in a wide variety of scientific disciplines (biology, biotechnology, chemistry, and computer science) to help identify important biological processes that may be disrupted by chemicals. Using computational toxicology research methods, it is hoped that thousands of chemicals can be rapidly evaluated for potential risk at small cost, and chemicals can be prioritized for further studies based on potential health risk information derived from this initial evaluation (USEPA 2020).

From the initial list of 430 PFAS compounds (discussed above), a subset of 150 PFAS compounds were chosen with the overall goals of maximizing the ability to perform read-across (for example, predicting toxicity of a target PFAS compound by extrapolating such information from a PFAS compound that has been more extensively studied) and capturing structural diversity among PFAS. The USEPA also took into consideration likelihood of exposure or occurrence, and the availability of in vivo (mammalian) or in vitro (for example, cell culture) toxicity data for validation. Because compounds that exist as gases cannot be tested and some PFAS (for example, HFPO-DA [GenX]) rapidly degrade in dimethyl sulfoxide (DMSO), which is used as the vehicle in many of these assays (Liberatore et al. 2020), practical considerations such as the ability to procure in nongaseous form and to solubilize samples in the solvent DMSO without degradation were also considered (Patlewicz et al. 2019; USEPA 2020, 2020).

This group of 150 PFAS compounds is also currently being evaluated at Oregon State University, the University of Pittsburgh, East Carolina University, and other institutions in a USEPA-funded effort to use in vivo and in vitro methods to systematically study PFAS toxicity. The goal of this research is to support the prioritization of PFAS in risk assessment and risk management (USEPA 2019) by using a combination of in vivo toxicity screening assays and transcriptomics (evaluation of changes in RNA expression in specific tissues in response to biologic or environmental cues; these RNA molecules often code for proteins) in the zebrafish model to characterize the toxicity and pharmacokinetics of a range of volatile and nonvolatile PFAS. The subset of 150 PFAS compounds is also being evaluated in in vitro assays intended to be predictive of various endpoints such as hepatotoxicity, developmental toxicity, immunotoxicity, neurotoxicity, mitochondrial toxicity, developmental neurotoxicity, endocrine disruption, and general toxicity (USEPA 2019). Results of these studies will be used to group PFAS compounds by structures and biological activity. As mentioned above, the intent is to capture the structural diversity across the spectrum of PFAS compounds of interest to USEPA and to support determination of the feasibility of read-across within structure-based groupings, an approach in which information from PFAS with extensive in vivo toxicity data could be used to predict toxicity of other PFAS that lack such data.

It is hoped that the results of these high throughput assays will (a) inform PFAS hazard characterization, (b) provide toxicokinetic information that may help predict disposition and excretion of PFAS compounds from the body, and (c) prioritize PFAS for risk assessment and further in vivo mammalian testing that is needed for risk assessment. A further goal of this program is to determine, based on data for PFAS that have been evaluated in both in vitro and mammalian in vivo systems, whether the read-across approach can be used to support in vitro to in vivo extrapolation for estimation of oral equivalent exposures for PFAS compounds (Fenton et al. 2020).

17.2.9 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 PFECAs 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 further develop and validate approaches for addressing groups and mixtures of PFAS, such as those described in Section 17.2.7.

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. The approaches currently under development at USEPA and the National Toxicology

Program (NTP) that are discussed in Section 17.2.8 may prove useful for screening of a large number of PFAS with rapid assays that evaluate parameters related to toxicokinetics and toxicity (USEPA 2018). Additional information is found on the USEPA 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 2018).

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 2021; USEPA 2016; USEPA 2016). 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 (Section 5.2.4). 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 2020; ATSDR 2021; USEPA 2016; USEPA 2016). 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 2016; USEPA 2016), 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 2011) 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 2016; USEPA 2016). 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.

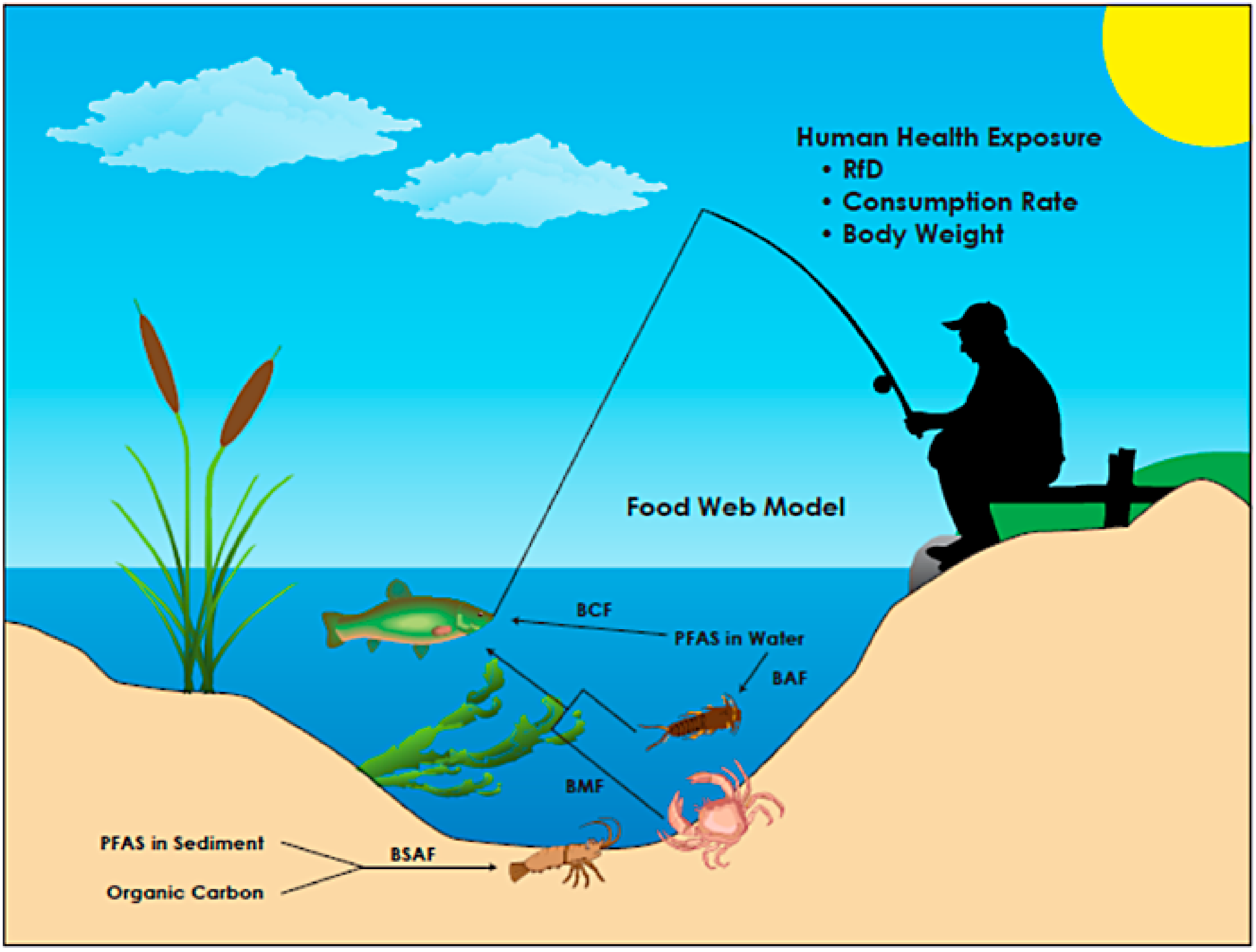

Figure 17-1. Bioaccumulation of PFAS from sediment and surface water. (BAF–bioaccumulation factor; BCF–bioconcentration factor; BSAF–biota-sediment accumulation factor; RfD–reference dose. *(Source: J. Conder, Geosyntec. Used with permission.)*

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 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.

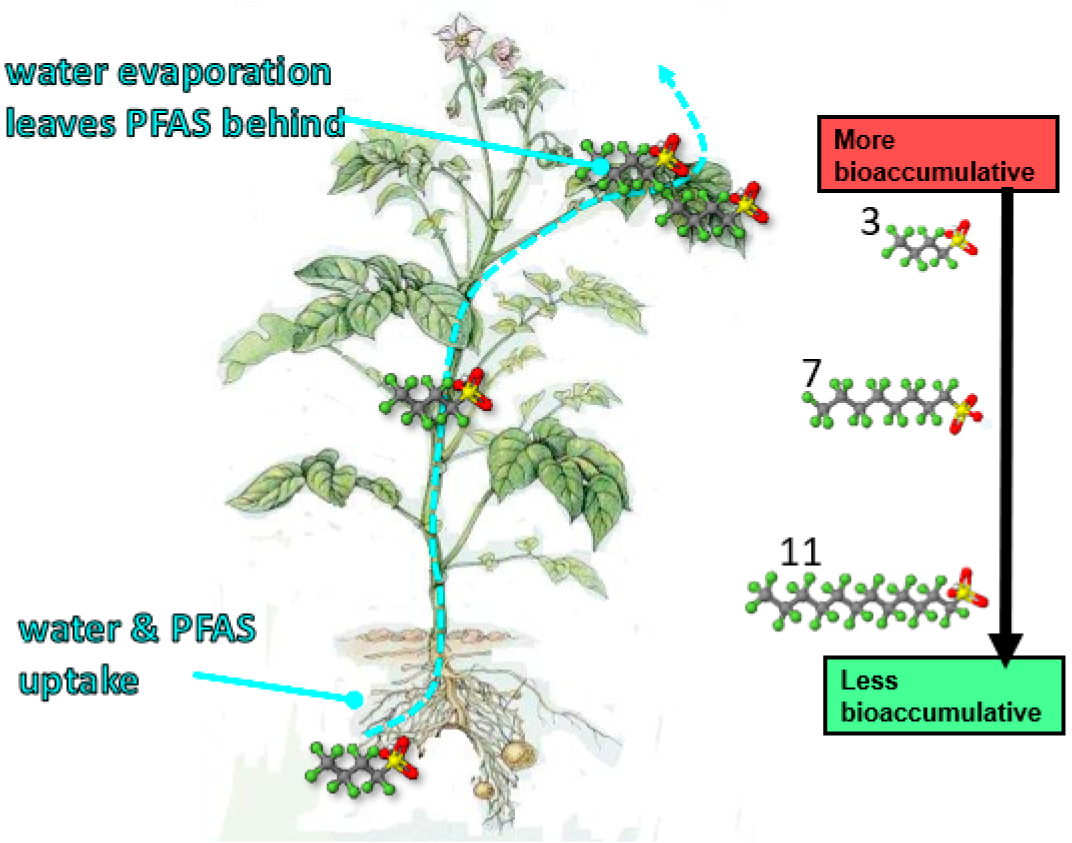

Figure 17-2. Bioaccumulation of PFAS in plants.

Source: J. Conder, Geosyntec. Used with permission.

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 perfluorononanoate
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
AWQC	ambient water quality criteria
BAF	bioaccumulation factor
BARC	bottom antireflective coatings
BBMD	Bayesian benchmark dose
BCF	bioconcentration factor
BERA	baseline ecological risk assessment
BMD	benchmark dose
BMF	biomagnification factor
BMP	best management practices
BOHP	$Bi_3O(OH)(PO_4)_2$
BSAF	biota-sediment accumulation factor
BuFASA	*N*-butyl perfluoroalkane sulfonamide
BuFASE	*N*-butyl perfluoroalkane sulfonamido ethanols
BuFASAA	*N*-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, or corrective 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
CIMS	chemical ionization mass spectrometry
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
DIN EN	Deutsches Institut für Normung, German Institute for Standardization, English
DMSO	dimethyl sulfoxide
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
ELG	effluent limitation guidelines
EPC	exposure point concentration
ERA	ecological risk assessment
ERB	equipment rinse blank
ESS	Environmental Sequence Stratigraphy
ESTCP	Environmental Security Technology Certification Program
EtFASA	*N*-ethyl perfluoroalkane sulfonamide
EtFASE	*N*-ethyl perfluoroalkane sulfonamido ethanol (var: N-ethyl perfluoroalkane sulfonamide ethanol)
EtFASAA	*N*-ethyl perfluoroalkane sulfonamido acetic acid (var: *N*-ethyl perfluoroalkane sulfonamide acetic acid)
ETFE	ethylene tetrafluoroethylene
EtFOSA	*N*-ethyl perfluorooctane sulfonamide
EtFOSE	*N*-ethyl perfluorooctane sulfonamido ethanol (var: *N*-ethyl perfluorooctane sulfonamide ethanol)
EU	European Union

F	fluorine
F-53B	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
FEC	Foam Exposure Committee
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 contex of firefighting foam formulations that contain a fluorinated surfactant)
FRB	field reagent blank
FRM	Federal Reference Method
FSANZ	Food Standards Australia and New Zealand
fT4	free thyroxine
FTA	fire training area
FTCA	fluorotelomer carboxylic acid
FT-ICR	Fourier transform ion cyclotron resonance
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
GC	gas chromatography
GC/MS	Gas chromatography/mass spectrometry
GEF	Global Environment Facility
GenX	trade name for a polymerization processing aid formulation that contains ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoate
GLI	Great Lakes Initiative
GM	geometric mean
GMAV	genus mean acute value
HA	health advisory
HDPE	high-density polyethylene
HFPO-DA	hexafluoropropylene oxide dimer acid

HHRA	human health risk assessment
HI	hazard index
HQ	hazard quotient
HRMS	high-resolution mass spectrometry
IARC	International Agency for Research on Cancer
ICAO	International Civil Aviation Organization
ICV	initial calibration verification
IDA	isotope dilution analysis
IDW	investigation-derived waste
IPEN	International Pollutants Elimination Network
IRIS	Integrated Risk Information System
ITRC	Interstate Technology and Regulatory Council
IX	ion exchange
K_d	bulk partitioning coefficient
K_{oc}	organic carbon partitioning coefficent
K_{ow}	water/octanol coefficient
LC	liquid chromatography
LC/MS/MS	liquid chromatography/mass spectrometry/mass spectrometry
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	*N*-methyl perfluoroalkane sulfonamide
MeFASE	*N*-methyl perfluoroalkane sulfonamido ethanol (var: *N*-methyl perfluoroalkane sulfonamide ethanol)
MeFASAA	*N*-methyl perfluoroalkane sulfonamido acetic acid (var: *N*-methyl perfluoroalkane sulfonamide acetic acid)
MeFOSA	*N*-methyl perfluorooctane sulfonamide
MEP	Multiple Extraction Procedure
ML	method limit
MOA	mode of action
MPCA	Minnesota Pollution Control Agency
MRL	minimum risk level, or minimum reporting limit (laboratory analytical)
MRM	multiple reaction monitoring
MS	mass spectrometry
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
NER	non-extractable residues
NESHAP	National Emissions Standards for Hazardous Air Pollutants
nEtFOSA	N-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	N-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
OC	organic carbon
OECD	Organisation for Economic Co-operation and Development
OEHHA	Office of Environmental Health Hazard Assessment (California)
OH	hydroxide ion, or hydroxyl group (Helmenstine 2018)
ORD	Office of Research and Development (USEPA)
OSB	oriented strand board
PAB	permeable absorptive barrier
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) *Do not use this acronym for any other description including perfluorinated compound or perfluorochemical.*
PFCA	perfluoroalkyl carboxylate, perfluoroalkyl carboxylic acid
PFDA	perfluorodecanoate, perfluorodecanoic acid
PFDoA, or PFDoDA	perfluorododecanoate, perfluorododecanoic acid
PFDoS, or PFDoDS	perfluorododecane sulfonate, perfluorododecane sulfonic acid
PFDS	perfluorodecane sulfonate, perfluorodecane sulfonic acid
PFECA	per- or polyfluoroalkyl 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 PFTS	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/m^3	picogram per cubic meter
pH	negative log of hydrogen ion concentration (measure of acidity)
PHxSF	perfluorohexane sulfonyl fluoride
PICs	products of incomplete combustion
PIGE	partice-induced gamma-ray emission spectroscopy
PIH	pregnancy-induced hypertension
PILI	polymer with ionic liquid coated iron
PNEC	predicted no-effect concentration
POD	porewater observation device
POE	point of exposure
POET	point of entry treatment
polyDADMAC	Polydiallyldimethylammonium chloride
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
PSA	prostate-specific antigen
PTFE	polytetrafluoroethylene
PUF	polyurethane foam
PVDF	polyvinylidene fluoride
PWS	public water system
QAPP	quality assurance project plan
QC	quality control
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
RIVM	Netherlands National Institue for Public Health and the Environment
RL	reporting limit
RML	removal management level
RO	reverse osmosis
RPD	relative percent difference
RPF	relative potency factor
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)
SMAV	species mean acute value
SML	surface micro layer
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
TMDL	total maximum daily loads
TMF	trophic magnification factor
TO	Toxic Organic (method)
TOC	total organic carbon
TOF	time-of-flight
TOP	total oxidizable precursor
TRRP	Texas Risk Reduction Program
TRV	toxicity reference value
TSH	Thyroid-stimulating hormones
TSCA	Toxic Substances and Control Act
TTDs	target organ toxicity doses
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
WV	wildlife value
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 nth 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 carbons 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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⇑

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