Groundwater and PFAS: State of Knowledge and Practice

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The Groundwater Association

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GROUNDWATER AND PFAS: STATE OF KNOWLEDGE AND PRACTICE

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Cover design: The cover design is abstract and not intended to match the molecular structure of PFAS chemicals.

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Groundwater and PFAS: State of Knowledge and Practice

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The Groundwater Association

Groundwater and PFAS: State of Knowledge and Practice

Overview
Section 1

One of eight sections prepared by National Ground Water Association volunteers. Each section was prepared to stand independently, or to be integrated with the other seven sections.

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Overview

INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) are a unique class of emerging drinking water contaminants that have shown widespread occurrence in groundwater and surface water resources, and due to their toxicological characteristics are increasingly the focus of environmental protection agencies worldwide.

For example, the U.S. Environmental Protection Agency (USEPA) recently set drinking water health advisories for perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) at 0.07 micrograms per liter (µg/L). These new parts-per-trillion (ppt) health advisory levels are orders-of-magnitude lower than regulatory levels for most groundwater contaminants and were practically unheard of during conventional hydrogeologic investigations and remediation programs performed since the 1980s. Moreover, PFAS include thousands of individual chemical compounds, each with at least one carbon-fluorine (C-F) bond and most of which are soluble in groundwater. The C-F bond has been called the strongest atomic bond in nature and imparts unique characteristics to PFAS that make them useful to society in a wide variety of applications. But the unique C-F chemistry of PFAS also creates significant challenges in water treatment and remediation.

Additionally, the fate, transport, and chemical transformations of most PFAS in the environment are still unknown and areas of active scientific research. The combination of these factors creates a need for a technical guidance document.

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The National Ground Water Association (NGWA) is publishing this PFAS guidance document to assist members and other groundwater professionals who may be tasked with investigating the transport pathways and extent of PFAS in groundwater and surface water, assessing potential risks to receptors, or designing and constructing engineering controls to manage subsurface PFAS contamination. The main purpose of this document is to summarize the current state of knowledge and practice regarding PFAS fate, transport, remediation, and treatment, recognizing that knowledge in this field is advancing. This document also aims to summarize current technologies, methods, and field procedures being used to characterize sites and test remediation and treatment technologies.

This document is focused on characterization and treatment of PFAS in groundwater and soil. However, other media may need to be considered when conducting due diligence and all appropriate inquiries at potentially impacted properties.

PFAS contamination may be present at some landfills receiving waste since the 1950s and facilities using aqueous film forming foams (AFFF) such as fire training facilities, civilian and military airports, petroleum terminals, and refineries.

Moreover, many raw materials and commercial products may contain PFAS which are not clearly detailed on their packaging, and it is expected that facilities using these products or raw materials may not be aware that PFAS are present. Environmental professionals may use resources such as the USEPA (https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/risk-management and polyfluoroalkyl-substances-pfass) and FluoroCouncil (www.fluorocouncil.com) website to evaluate additional industries potentially utilizing PFAS.

This document is organized as follows. It was

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written so each section could stand alone from the others, if desired:

- Section 1 introduces the problem and summarizes the key takeaways.
- Section 2 provides a glossary of key PFAS-related terminology.
- Section 3 summarizes the chemistry and known human health and ecological impacts of PFAS.
- Section 4 discusses PFAS fate and transport in the environment.
- Section 5 discusses PFAS-specific field sampling technologies, methods, and procedures.
- Section 6 discusses the legal and regulatory status of PFAS in the United States.
- Section 7 discusses PFAS risk communication challenges and solutions.
- Section 8 discusses PFAS remediation and treatment options.

OVERVIEW OF SECTIONS

Section 3: Human and Ecological Impacts

Section 3 describes physical and chemical properties of PFAS that are relevant to investigating and understanding human and ecological impacts, and summarizes the current state of knowledge regarding human exposure, exposure of ecological receptors, and the toxicokinetics and toxicological effects of PFAS. A summary table of screening levels used in the United States is provided. Key findings are summarized as follows:

- Biomonitoring studies have estimated more than 95% of the United States population has been exposed to PFAS and have measurable concentrations in their blood. However, PFOS and PFOA concentrations in humans have demonstrably decreased since 2002.
- Human exposure to PFAS can occur through ingestion, direct contact, inhalation, and occupational exposure.
- The greatest portion of chronic human intake is likely from the ingestion of contaminated foods and drinking water. Small children experience higher exposure due to hand-to-mouth transfer of chemicals from treated carpets and indoor dust.
- Because of the unique properties of many PFAS, they do not preferentially partition to lipids, but instead tend to bind to proteins. In humans, the highest PFAS concentrations have been detected in serum and liver, and to a lesser extent the kidney and other organs.
- PFAS have been detected in the tissues of invertebrates, fish, birds, and mammals around the globe. Of all the PFAS monitored, PFOS is the most frequently detected PFAS, it has generally been measured at the highest concentrations, and it is the dominant PFAS found in all species and locations around the world.
- PFOA and PFOS have been linked to a multiplicity of adverse effects, including hepatic toxicity, reproductive and developmental toxicity, suppression of the immune system, and some types of cancer. The data for PFNA, PFHxS, and PFBS are much more limited, but suggest that these compounds also affect the liver.
- A wide range of regulatory screening levels for water and soil exist throughout the United States and internationally, depending on state or region, and there does not yet appear to be consensus on safe levels for PFAS in soil and water.

Section 4: Fate and Transport

Section 4 discusses the environmental fate and transport of PFAS as a class of compounds, and compares their fate and transport characteristics to other classes of chemical compounds commonly found in groundwater such as hydrocarbons, chlorinated solvents, and polychlorinated biphenyls (PCBs). In addition, Section 4 discusses the environmental fate and transport of the six specific PFAS that USEPA identified in their Third Unregulated Contaminant Monitoring Rule (UCMR3), and focuses on PFOA and PFOS which are often associated with aqueous firefighting foams (AFFFs). Key findings are summarized as follows

- There are multiple potential sources of PFAS to groundwater. Recognized sources of PFAS include (1) storage, transfer, and use of AFFF for firefighting and fire training; (2) disposal/land application of municipal biosolids; (3) discharge of effluent from municipal wastewater treatment systems; (4) release of landfill leachate; and (5) release from a variety of commercial and industrial sources. Some of these release mechanisms differ from typical leaks, drips, spills, and ruptures associated with many other contaminants, and may contribute to broader distribution in the environment and groundwater, rivaling migration

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via advective flow.

- PFAS molecules are miscible in water. They will readily exist in the aqueous phase and will not exist as separate non-aqueous phase liquids (NAPLs) in the subsurface. Therefore, migration of PFAS as pure-phase NAPLs is not expected at sites. However, some PFAS can dissolve into petroleum-based NAPL mixtures and be transported due to capillary phenomenon.
- PFAS molecules are stable and resistant to degradation. PFAS molecules are characterized by a chain (or "tail") comprised of interior carbon atoms bonded to exterior fluorine atoms. The carbon-fluorine bond is very strong and the exterior fluorine atoms form a protective "shell." These characteristics make PFAS molecules especially stable and particularly resistant to degradation by biological or chemical means. PFOS, a type of PFAS molecule, is a terminal degradation product, and may accumulate due to this process.
- The carbon-fluorine tail of PFAS molecules exhibits hydrophobic and lipophobic characteristics. PFAS also exhibit surfactant characteristics that enhance infiltration due to reduction in surface tension and potential for increased mobilization and solubility of separate phase liquid, especially in settings where AFFF and petroleum hydrocarbons are stored, handled, and used in proximity to one another (e.g., fighting petroleum hydrocarbon fires). Surfactant properties of the molecules complicate the interaction between PFAS and hydrophobic/hydrophilic substances.
- PFAS molecules are prone to sorption. When dissolved, some PFAS molecules may exist as anions, some may exist as cations, and some may exist as zwitterions. Consequently, PFAS molecules are prone to sorption via electrostatic attraction to positively charged surfaces. PFAS also sorbs to organic carbon and oil. PFAS molecules exhibit relatively high Koc values compared to other common groundwater contaminants. However, Koc and degree of sorption is site-specific, contingent upon the sorptive medium (e.g., surface charge, mineralogy, and organic carbon content) and solution chemistry, especially ionic strength, pH, and Ca2+ activity.

Section 5: Field Sampling and Analysis

Section 5 discusses the collection and analysis of samples for PFAS. Emphasis is placed on water samples such as drinking water, groundwater, and surface water. Other media including soil, sediment, biota (e.g., fish tissue), and waste are not discussed. Field screening methods are briefly discussed to the extent commercially available in the U.S. Considerations for sampling equipment, sample containers, and collection methods are discussed. Key findings are summarized as follows:

- USEPA Method 537 Rev 1.1 (Method 537) is the only promulgated method for the analysis of PFAS in drinking water. It is a liquid chromatography/tandem mass spectrometry (LC/MS/MS) method.
- There are currently no commercially available field screening methods that are capable of detecting PFAS in water samples at concentrations less than 50 parts per billion (ppb).
- Regulatory agencies are currently interested in PFAS at ppt levels. In conjunction, given the widespread use of PFAS in many consumer, commercial, and industrial products and processes, and very low concentrations to which PFAS are reported, it is critical that the sampling program consider as many sources of PFAS contamination as practicable. This includes the following:
  - Minimize cross contamination during a sampling event.
  - Laboratory-supplied water that has been determined to be PFAS-free should be used to prepare all FRBs and EBs.
  - The quality of the water used for any other purposes should be scrutinized, including public water supplies.
  - The materials of construction of all downhole and surface sampling and monitoring equipment—including pumps, packers, transducers, tubing, liners, valves, and wiring—be free from polytetrafluorethylene (PTFE) or ethylene tetrafluoroethylene (ETFE), to the maximum extent practicable.
  - A wide range of products commonly used in site investigations are known or suspected to contain PFAS.

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Section 6: Legal and Regulatory Issues

Section 6 focuses on the current status of PFAS regulation in the United States. It also discusses the potential liability for water systems and provides an overview of legal theories and case law. Statutory and regulatory authority are both at the state and federal levels and are summarized. Key findings include:

- There are multiple layers of laws and rules that govern PFAS in the environment. At the federal level, a number of laws may apply, including the Toxic Substances Control Act (TSCA) (related to the manufacture and use of PFAS); the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) (related to remediation of contaminated sites); and the Safe Drinking Water Act (SDWA) (related to the presence of contaminants in drinking water). All have a role when PFAS are released into the environment.
- In addition, each state may have analogous standards that can be stricter than their federal counterparts. Currently, 12 U.S. states have their own regulatory standards for PFAS in water. Depending on the jurisdiction, the more stringent standard would apply.
- Different authorities in individual states, including regional water boards and environmental protection agencies, may have drinking water and/or groundwater regulatory standards, health advisories, and/or guidance levels that govern PFAS in state waters.

Section 7: Risk Communication

Section 7 discusses methods for understanding the demographic and socioeconomic makeup of communities and effectively communicating scientifically valid perceptions of risk to all subpopulations. Key findings include:

- Risk communication is the process of informing stakeholders about health or environmental risks, risk assessment results, and proposed risk management strategies. Stakeholders can consist of any organization, group, or individual who takes an interest in a project and can influence project outcomes.
- The overall purpose of risk communication is to assist affected communities in understanding the process 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.
- Potential challenges of performing risk communication include:
  - Uncertainty/variability in regulatory cleanup criteria and policies
  - Misperception of proposed risk management strategies
  - Inability to provide effective risk communication to vulnerable subpopulations
  - Difficulty managing stakeholder expectations.
- Supporting materials to facilitate risk communication are publicly available from a wide range of public health and environmental agencies to assist professionals in communicating potential risks of PFAS exposures to affected parties.
- Development of a comprehensive stakeholder outreach strategy can address and help overcome distrust present between community members and decision-makers (such as regulatory authorities and responsible parties).
- Stakeholder engagement methods, vetted within the social science discipline, can be utilized to address the challenges presented above and facilitate meaningful risk communication.

Section 8: Remediation and Treatment

Section 8 was prepared to allow groundwater professionals with sufficient background and technical information to make informed decisions about treating groundwater impacted with PFAS. It identifies key information that groundwater professionals need to know to properly select, design, construct, implement, and maintain a remedial approach and how to vet a potential treatment technology from concept to full-scale field application. Key findings include:

- PFAS in groundwater present unique challenges with respect to treatment, specifically:
  - Some PFAS are very stable and do not readily degrade.
  - Some PFAS are not effectively treated by conventional remediation technologies or wastewater treatment plants.
  - Treatment of some PFAS may result in PFAS by-products that are more mobile, more toxic, and/or exhibit properties that make them less amenable to treatment.
- Remediation options are limited by the unique physicochemical properties of PFAS.
- Many remediation methods used to address

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hydrocarbon contamination, such as air stripping, air sparging, soil vapor extraction, and bioremediation, are ineffective at treating PFAS due to the low volatility of PFAS and their resistance to microbial degradation.

- Technologies currently being used for remediation of PFAS-contaminated sites include soil incineration, excavation to landfill, and groundwater extraction with PFAS sorption onto activated carbon or resins.
- The effectiveness of GAC for PFAS removal decreases with decreasing chain length of the PFAS.
- Other alternative remedial techniques include soil washing, soil solidification, and the use of in situ permeable reactive barriers or funnel and gate systems.
- Emerging water treatment technologies for PFAS such as photolysis, reductive decomposition, advanced oxidation, and sonolysis require high energy input per unit water volume and long residence times.

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Antioxidants, and Synoxyals,

Section 2

One of eight sections prepared by National Ground Water Association volunteers. Each section was prepared to stand independently, or to be integrated with the other seven sections.

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Abbreviations, Acronyms, Initialisms, and Symbols

Section 2

"Long-chain"	Perfluoroalkyl carboxylic acids (PFCAs) with eight carbons and greater (with seven or more perfluorinated carbons); perfluoroalkyl sulfonates (PFSAs) with six carbons and greater (with six or more perfluorinated carbons)
"Short-chain"	Perfluoroalkyl carboxylic acids (PFCAs) with seven carbons and fewer (with six or fewer perfluorinated carbons); perfluoroalkyl sulfonates (PFSAs) with five carbons and fewer (with five or less perfluorinated carbons)

°C	Degrees Celsius
AFFF	Aqueous film-forming foam
AR-AFFF	Alcohol-resistant aqueous film-forming foam
ASTM	American Society for Testing and Materials
atm	Atmosphere
ATSDR	Agency for Toxic Substances and Disease Registry (United States)
BCF	Bioconcentration factors
BOD	Biochemical oxygen demand
Bunded	A type of secondary containment around storage "where potentially polluting substances are handled, processed, or stored for the purposes of containing any unintended escape of material from that area until such time as remedial action can be taken"
C-F	Carbon-fluorine covalent bond
C6	Carbon chain consisting of six carbons
C8	Carbon chain consisting of eight carbons
Ca^{2+}	Calcium ion
CAA	Clean Air Act
CARs	Canadian Aviation Regulations
CAS	Chemical Abstracts Service
CEPA	Canadian Environmental Protection Act
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFR	Code of Federal Regulations
CIC	Combustion ion chromatography
Class B fire	Fire whose fuel is flammable or combustible liquid or gas (gasoline, diesel fuel, petroleum oil, paint, propane, butane)
CoC	Contaminant of concern
COD	Chemical oxygen demand

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CoPC	Contaminant of potential concern
CSM	Conceptual site model
DND	Department of National Defence (Canada)
DoD	Department of Defense (United States)
DOE	Department of Energy (United States)
DWGV	Drinking Water Guideline Value (Canada)
EC50	Half maximal effective concentration is the concentration of a substance that gives half-maximal response. Used as a measure of the substance's potency.
EFSA	European Food Safety Authority
enHealth	Environmental Health Standing Committee (Australia)
ERL	Environmental risk limit
EQSD	Environmental Quality Standards (Europe)
EU	European Union
Exposure pathway	Pathway through which receptor(s) would be exposed to CoC(s)
FAA	Federal Aviation Administration
FCSAP	Federal Contaminated Sites Action Plan (Canada)
FFFP	Film forming fluoroprotein
FFTA	FirefightingTraining Area
Fluorotelomer	Fluorocarbon-based oligomers, or telomers, synthesized by telomerization
FP	Fluoroprotein foam
Groundwater quality standards	Can be either numeric or narrative. Numeric groundwater standards prescribe maximum allowable contaminant levels that result from human operations or activities, but do not typically apply to naturally occurring contaminants at naturally occurring levels. A narrative standard is descriptive of conditions necessary to support a designated groundwater use or may generally prohibit the discharge of particular types of contaminants. Numeric and narrative standards may be used separately or conjointly. Groundwater quality standards are enforceable standards.
Health advisory	Provides information on contaminants that can cause human health effects and are known or anticipated to occur in drinking water. Health advisories are non-enforceable and nonregulatory and provide technical information to public health officials on health effects, analytical methodologies, and treatment technologies associated with drinking water contamination.
HDPE	High-density polyethylene
Hydrophilic	A compound that is polar and attracted to water
Hydrophobic	A compound that is non-polar and is not attracted to water
IMAC	Interim maximum allowable concentration
kg	Kilogram
Koc	Octanol-carbon partition coefficient
Kow	Octanol-water partition coefficient
L	Liter
LC/MS/MS	Liquid chromatography tandem mass spectrometry

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LC50	Lethal concentration at 50 percent. The lethal concentration required to kill 50 percent of the population (longer-term exposure).
LD50	Lethal dose at 50 percent. The amount of an ingested substance that kills 50 percent of a test sample (short-term exposure).
LNAPL	Light non-aqueous phase liquid
m^3	Cubic meter
MCL	Maximum contaminant level. The highest level of a contaminant that is allowed in drinking water that enters the service network. MCLs are enforceable standards.
MCLG	Maximum contaminant level goal. Represents the level of a contaminant in drinking water below which there is no known or expected risk to health. MCLGs allow for a margin of safety and are nonenforceable public health goals.
mg	Milligram
MIL-SPEC	United States Military Specification MIL-F-24385 (Fire Extinguishing Agent, Aqueous Film-Forming Foam (AFFF), Liquid Concentrate, for Freshwater and Seawater)
mL	Milliliter
mm	Millimeter
MN PCA	Minnesota Pollution Control Agency
MOE	Ministry of Environment (provincial, Canada)
MPC	Maximum permissible concentration
NCSAB	North Carolina Science Advisory Board
NJDEP	New Jersey Department of Environmental Protection
OECD	Organisation for Economic Co-operation and Development
OEHHA	Office of Environmental Health Hazard Assessment (California)
OF	Organic fluorine
Oleophobic	A compound that is repelled from oil
PASF	Perfluoroalkane sulfonyl fluoride
Perfluorinated	The replacement of all hydrogens by fluorine in the aliphatic chain structure
PF	Protein foam
PFAS	Perfluoroalkyl and polyfluoroalkyl substance(s)
PFBA	Perfluorobutanoic acid
PFBS	Perfluorobutane sulfonate
PFCA	Perfluoroalkyl carboxylic acid (e.g., PFOA)
PFCs	Perfluorinated compounds
PFHxA	Perfluorohexanoic acid
PFHxS	Perfluorohexane sulfonic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctanesulfonic acid
pH	Measure of the acidity or basicity of an aqueous solution
PHC	Petroleum hydrocarbons
PIGE	Particle induced gamma-ray emission
PMR	Pacific Market Research
Polyfluorinated	The replacement of most hydrogens by fluorine in the aliphatic chain structure
POP	Persistent organic pollutant
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene difluoride
QA/QC	Quality assurance/quality control
RD	Reference document
Receptor	A human or ecological receptor that would be exposed to the CoC
RFP	Request for proposal
RIVM	National Institute for Public Health and the Environment (Netherlands)

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RM	Risk management
SDS	Safety Data Sheets
SDWA	Safe Drinking Water Act
SMCL	Secondary maximum contaminant level. Under EPA's National Secondary Drinking Water Regulations, EPA established SMCLs that set nonmandatory water quality standards. They are established as guidelines to assist public water systems in managing their drinking water for aesthetic considerations such as taste, color, and odor. These contaminants are not considered to present a risk to human health at the SMCL.
SNUR	Significant New Use Rule
Source	A chemical found at such concentration to be of potential concern (CoC) to human health or the environment
SPSS	Statistical Package for the Social Sciences
Surfactant	A substance that tends to reduce the surface tension of a liquid in which it is dissolved
TC	Transport Canada
TDS	Technical Data Sheets
TGD	Technical Guidance Document
TOP assay	Total oxidizable precursor assay
TRB	Transportation Research Board
TRV	Toxicological reference value
TSCA	Toxic Substances Control Act
UCMR3	Third Unregulated Contaminant Monitoring Rule
µg	Microgram
UK	United Kingdom
UL	Underwriters Laboratories Inc.
UN	United Nations
UNEP	United Nations Environment Programme
USA	United States of America
USEPA	United States Environmental Protection Agency

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Groundwater and PFAS: State of Knowledge and Practice

Human and Ecological Impacts
Section 3

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Human and Ecological Impacts

INTRODUCTION

Poly- and perfluoroalkyl substances—collectively referred to as PFAS—are terms used to describe a large group of organic fluorinated alkanes.[1] In the perfluoroalkyls, all hydrogen atoms attached to carbons in the aliphatic chain have been replaced by fluorines.[2] The polyfluoroalkyls have at least one carbon on the alkane that is not fully fluorinated (Buck et al. 2011).

Over many decades of use, thousands of PFAS have been synthesized and used in a wide range of industrial and consumer applications (Lindstrom et al. 2011; Kirsch 2013). These applications include firefighting foams, metal plating and finishing, textile coatings, paper packaging, and as processing aids in fluoropolymer manufacturing. PFAS enter the environment following industrial releases, use of PFAS-containing firefighting foam, the use and disposal of industrial and consumer articles and the discharge of treated municipal effluent (UNEP 2015).

The six PFAS addressed in this document were selected based on their inclusion in the USEPA's Third Unregulated Contaminant Monitoring Rule (UCMR3), a program conducted under the Safe Drinking Water Act (SDWA) to develop information on the occurrence of unregulated contaminants in public water systems (USEPA 2012a). The six PFAS are categorized as either perfluoroalkyl carboxylic acids(PFCAs) or perfluoroalkyl sulfonic acids (PFSAs).

The PFCAs perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), and perfluoroheptanoic acid (PFHpA) are perfluoroalkl acids that contain a fully fluorinated carbon chain of seven, eight, or six carbons, respectively, and a terminal carboxylic acid functional group.[3] The PFSAs perfluorooctane sulfonate (PFOS), perfluorohexane sulfonate (PFHxS),and perfluorobutane sulfonate (PFBS) contain a perfluorinated alkyl carbon chain of eight, six, and four carbons, respectively, and a terminal sulfonate or sulfonic acid group.

Table 3.1 provides a list of the PFAS addressed in this section: their acronyms, chemical abstract service (CAS) registry numbers, and molecular formulas.

PHYSICAL AND CHEMICAL PROPERTIES

Many of the chemical and physical properties of PFAS that have made them commercially valuable as surfactants also determine their potential for partitioning, persistence, and accumulation in the environment and in biota. The PFAS listed in Table 3.1 have low pKa's[4], and as a result, these PFAS tend to exist in their ionic (charged) forms in environmental and biotic media (Conder et al. 2008; CONCAWE 2016). These characteristics also contribute to their relatively high aqueous solubility. The fluorinated carbon chain of the PFCAs and PFSAs is hydrophobic and lipophobic, and in combination with the carboxylate and

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[1] An alkane is a molecule in which all of the carbon-carbon bonds are single. An alkyl is an alkane where at least one hydrogen has been replaced by a non-hydrogen atom or molecule. An alkyl has the general formula CnH2n+1; the perfluoroalkyls have the basic formula CnF2n+1– (Buck et al. 2011).

[2] Except those hydrogen atoms whose substitution would modify the nature of any functional groups present (Buck et al. 2011).

[3] A carboxylic acid functional group has the molecular formula COOH. A sulfonic acid functional group has the molecular formula SO3H.

[4] The pKa is a measure of the tendency of an acid (in this context, the perfluorocarboxylic and perfluorosulfonic acids) to dissociate in solution (i.e., the aqueous environment). In general, a low pKa indicates that an acid dissociates fairly readily to form the corresponding positively and negatively charged chemical species. For example, PFOA will dissociate to form F(CF2)7COO- and H+.

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Table 3.1. Name, acronyms, and molecular formulas of PFAS.

Name	Acronym	CAS Registry Number	Molecular Formula
Perfluoroalkyl Carboxylic Acids	**PFCAs**		
Perfluoroheptanoic Acid	PFHpA	375-85-9	F(CF2)6COOH
Perfluorooctanoic Acid	PFOA	335-67-1	F(CF2)7COOH
Perfluorononanoic Acid	PFNA	375-95-1	F(CF2)8COOH
Perfluoroalkyl Sulfonates/ Perfluoroalkyl Sulfonic Acids	**PFSAs**		
Perfluorobutane Sulfonate	PFBS	375-73-5	F(CF2)4SO3H
Perfluorohexane Sulfonate	PFHxS	432-50-8	F(CF2)6SO3H
Perfluorooctane Sulfonate	PFOS	1763-23-1	F(CF2)8SO3H

sulfonate functional groups, imparts amphiphilic and surfactant characteristics to these compounds.[5]

Because of the amphiphilic properties of many PFAS, they do not preferentially partition to lipids, but instead tend to bind to proteins. In humans, the highest concentrations have been detected in serum and liver, and to a lesser extent, the kidney and other organs. The carbon-fluorine bond is extremely strong and renders many PFAS resistant to biotic and abiotic degradation (ECHA 2013; CONCAWE 2016). However, PFAS precursors can degrade to terminally stable PFAS such as PFOA and PFOS that are resistant to further degradation (Buck et al. 2011).

Buck et al. (2011) defines PFAS precursors as large functional derivatives and polymers that contain a perfluoroalkyl moiety and degrade in the environment to form PFOS, PFOA, and similar substances that are stable and resistant to further degradation.

Bioaccumulation

Octanol-water partition coefficients (Kow) can be used as a predictor of bioaccumulation, as they provide a measure of the extent to which a chemical partitions between water and lipid. In general, partitioning to lipids is associated with the potential to persist and bioaccumulate, because of the limited metabolic capacity and blood flow of lipid tissue. Given the amphiphilic nature of many PFAS, determination of Kow's is not experimentally feasible. Thus, while Kow's have been calculated for PFAS (see e.g., CONCAWE 2016), it is not clear that they provide a meaningful predictor of the potential of PFAS to accumulate or biomagnify (Conder et al. 2008; ECHA 2013; UNEP 2015; CONCAWE 2016).

The potential for bioaccumulation is typically assessed by empirical measurements of bioconcentration factors (BCFs) bioaccumulation factors (BAFs), biomagnification factors (BMFs), and trophic magnification factors (TMFs). These terms are defined in Appendix 1, which also provides a summary and interpretation of reported values for the PFAS addressed in this section. As can be seen from the range of values shown in that Appendix, the bioaccumulation of PFAS (data are primarily for PFOA and PFOS) depends on whether the organism is aquatic or terrestrial, on the organism's trophic level, and on whether it has lungs or gills (ECHA 2013; CONCAWE 2016).

- PFOS, but not PFOA or PFBS, bioconcentrates in fish.
- PFOS bioaccumulates in fish but not in zooplankton or bivalves.
- PFOA does not bioaccumulate in phytoplankton, bivalves, or fish.
- Both PFOS and PFOA biomagnify in multiple species.
- Trophic magnification of PFOA occurs in air-breathing aquatic species but not in species with gills.

The Stockholm Convention Persistent Organic Pollutants Review Committees for PFOS (OECD 2002) and PFOA (UNEP 2015) considered the weight of evidence sufficient to support conclusions that both PFOS and PFOA are bioaccumulative. Accumulation of PFNA in wildlife is well documented (see section on Exposure of Ecological Receptors). Although there are few empirical data on the potential bioaccumulation of PFBS, PFHpA, and PFHxS, a review of published

[5]An amphiphilic compound has both hydrophilic and lipophilic properties, and as a result, does not fully solubilize in either medium. In biological systems, these compounds tend to partially partition to both aqueous and lipid compartments.

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values indicates that in general, BAFs and BCFs increase with the number of fluorinated carbons (Conder et al. 2008).

HUMAN EXPOSURE

As previously discussed, PFAS, including PFOA and PFOS, are often characterized as persistent since many are extremely resistant to typical environmental degradation processes. They do not hydrolyze, photolyze, or biodegrade under environmental conditions (USEPA 2012b), resulting in widespread human exposure.

Human exposure to these chemicals can occur through the following pathways:

- Ingestion of PFAS-containing food, either directly contaminated (food grown on contaminated soils, fish caught from contaminated waters) or indirectly (food contaminated from PFAS-treated food paper wrappings such as pizza boxes, sandwich wrappers, popcorn bags, etc.)
- Ingestion of PFAS in drinking water
- Occupational exposure
- Direct contact through the use of consumer products containing PFAS
- Personal care products (e.g., dental floss, cosmetics)
- Inhalation of ambient air and dust, or contact with PFAS-contaminated soils.

Currently, the relative importance of the different human routes of exposure, to the general population, to these compounds is not well established.

Due to the ubiquitous use of PFAS in a variety of products and industrial applications, it is estimated that PFAS exposure is widespread throughout the US population. Multiple biomonitoring studies have estimated that greater than 95% of the general population have been exposed to select PFAS (CDC 2009; Olsen et al. 2005, 2007, 2008, 2012; Biomonitoring California 2016).

In 2002, 3M Company, a principal manufacturer of PFOS at that time, discontinued production of PFOS and related chemicals. In 2006, the USEPA launched the PFOA Stewardship Program. The goals of the program for member companies were to commit to a 95% reduction in emissions of PFOA, precursor chemicals, and product content levels and to work toward eliminating these chemicals from emissions and products by 2015. Under the Stewardship Program and through the Toxic Substances Control Act (TSCA), as of 2015 EPA will have removed or restricted approximately 300 distinct PFAS from the market (USEPA 2016a).

Calafat et al. (2007) and Olson et al. (2005, 2007, 2008, 2012) have evaluated the temporal trend of PFAS concentrations in blood plasma. Data from the NHANES study (Calafat et al. 2007) and from Olson and coworkers' evaluation of PFAS serum concentrations of adult American Red Cross blood donors have shown that serum concentrations of PFOS, PFOA, and PFHxS have declined following reduction of PFOS and related chemical production. Olsen et al. (2012) determined the decline in PFOS serum concentrations suggest a population halving time of 4.3 years which is generally consistent with a PFOS excretion half-life of 4.5–7.4 years (Harada et al. 2005).

A discussion of the potential routes of human exposure and the relative importance of each route follows in the discussion below.

Water Use

PFOS and PFOA have been widely detected in surface water including rivers, lakes, and streams (Boulanger et al. 2004, 2005; Kim and Kannan 2007; Nakayama et al. 2007; Lasier et al. 2011), and in groundwater in the United States (USEPA 2017a, NJDWQI 2016; ATSDR 2016a). PFHpA and PFHxS were commonly detected in the few studies that analyzed surface water for these compounds (Kim and Kannan 2007; Nakayama et al. 2007; Simcik and Dorweiler 2005). Reported concentrations of PFAS in surface water samples are generally below 50 nanograms (ng)/L (ATSDR 2015).

Surface water contamination can occur as a result of wastewater discharge from PFAS manufacturing (Davis et al. 2007; USEPA 2008), from municipal wastewater facilities (Boulanger et al. 2005; Sinclair and Kannan 2006), through the use of PFAS containing firefighting foam at military installations and firefighting training facilities (Moody and Field 1999; Moody et al. 2003; ATSDR 2016a), and potentially through the land application of biosolids contaminated with PFAS (Higgins et al. 2005; Lindstrom et al. 2011; Yoo et al. 2009; Washington et al. 2009a, b; USEPA 2011; Yoo e al. 2011; Sepulvado et al. 2011; Venkatesan and Halden 2013; Armstrong et al. 2016).

The USEPA uses the UCMR program to collect data for contaminants suspected to be in drinking

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Table 3.2. Summary of UCMR3 data[1] (January 2017).

Contaminant	MRL (µg/L)	# PWSs with Results > MRL	HA (µg/L)	# PWSs with Results > HA
PFOA	0.02	117/4920	0.07	13
PFOS	0.04	95/4920	0.07	46
PFNA	0.02	14/4920	No Value	Not Applicable
PFHxS	0.03	55/4920	No Value	Not Applicable
PFHpA	0.01	86/4920	No Value	Not Applicable
PFBS	0.09	8/4920	No Value	Not Applicable

[1] January 2017 UCMR3 Data Summary for Chemical Contaminants, USEPA 2017.
MRL = UCMR Minimum Reporting Level; HA = Health Advisory

water, but do not yet have health-based standards set under the Safe Drinking Water Act (SDWA). The USEPA develops a new list of UCMR contaminants every five years. Under the third revision to UCMR (UCMR3), the USEPA began testing public water supplies (PWSs) in 2013 for six PFAS; the agency's data provides the most comprehensive population-based data set of PFAS occurrence in drinking water. Table 3.2 summarizes the UCMR data as of January 2017.

In 1035 samples of raw and finished PWS water in New Jersey, PFOA was the most frequently detected PFAS. It was detected in 65% of 72 public water supplies, with the highest detection in finished water of 100 ng/L, and at least one sample with concentrations exceeding 40 ng/L in 17% of the public water supplies tested (NJDWQI 2016).

One of the most robust studies investigating PFAS exposure due to groundwater contamination is the C8 Health Project which was created, authorized, and funded as part of the settlement agreement reached in the case of *Jack W. Leach et al. v. E.I. du Pont de Nemours & Company* (no. 01-C-608 W.Va., Wood County Circuit Court, filed 10 April 2002). Industrial discharges of PFOA to the atmosphere with subsequent deposition and leaching into groundwater, as well as direct releases into the Ohio River, led to groundwater contamination over six water districts (Frisbee et al. 2009). The C8 Health Project published a series of Probable Link Reports which, based upon the available scientific evidence, linked PFOA exposure to a number of human diseases including diagnosed high cholesterol, testicular and kidney cancer, ulcerative colitis, thyroid disease, and pregnancy-induced hypertension. The C8 Science Panel did not find a link between PFOA exposure and other types of cancers reviewed in the study, birth defects, miscarriage or stillbirth, preterm birth or low birth rates, Type II diabetes, stroke, asthma or chronic obstructive airway disease, neurodevelopmental disorders in children, common infectious or autoimmune disorders, Parkinson's disease, osteoarthritis, liver disease, chronic kidney disease or coronary artery disease (C8 Science Panel 2013; Looker et al. 2014).

Drinking Water

Biomonitoring studies have shown drinking water can be a significant source of exposure among populations whose water is impacted with PFAS contamination (Frisbee et al. 2009; Hoffman et al. 2011; ATSDR 2013; MN DOH 2009; NH DHHS 2016), often resulting in PFAS serum concentrations above those measured in the general population (CDC 2009). Frisbee et al. (2009) and Hoffman et al. (2011) conducted biomonitoring as part of the C8 Health Project. Frisbee and coworkers evaluated data for 66,899 study participants and found that four PFAS (PFHxS, PFOS, PFOA, PFNA) were detectable in >97% of the serum samples. The geometric mean PFOA serum concentrations were approximately 8.5 times higher in the C8 study population as compared to the NHANES study population. Concentrations of PFHxS, PFOS, and PFNA were comparable between the two groups (Frisbee et al. 2009; CDC 2009). In a subset of the C8 Study population, Hoffman and coworkers used a pharmacokinetic model to evaluate the relationship between drinking water and serum PFOA levels. The authors concluded that for each 1 µg/L increase in PFOA water concentration, there was a 141.5 µg/L (95% confidence interval, 134.9–148.1)

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increase in serum concentration. The steady-state serum:drinking water ratio from the pharmacokinetic model was calculated to be 114 (Hoffman et al. 2011).

Less is known however, as to whether drinking water is a significant route of PFAS exposure among the general population. Hurley et al. (2016) determined there was an association between PFOS and PFOA serum concentrations in women and concentrations of these compounds in public drinking water supplies. Study participants were linked to UCMR3 public water drinking supply PFAS results through residential zip code. It was determined that 40% of the combined concentrations of PFOS and PFOA exceeded the USEPA Drinking Water Health Advisory (HA) of 0.07 µg/L (USEPA 2016c, d). The investigators found median serum concentrations of PFOS and PFOA were 29% and 38% higher, respectively, among those with detectable levels of PFOS and PFOA in water compared to those without detectable levels.

Dermal: Studies have shown very limited absorption of PFAS through the skin, and thus routine exposures such as during showering or bathing, or through recreational activities such as swimming or wading will not likely cause significant exposure to PFAS (ATSDR 2016b; MDDOH 2016).

Although there is experimental evidence PFOA is dermally absorbed in experimental animals (Kennedy 1985; O'Malley and Ebbens 1981), it is not expected to be a significant route of exposure (Fasano et al. 2005). Studies measuring the dermal penetration of PFOA in preparations of isolated rat, mouse, and human epidermis have indicated that the rodent skin may be more permeable to PFOA than human skin (Fasano et al. 2005; Franko et al. 2012). Franko et al. (2012) found that approximately 24% of a dermal dose of PFOA (0.5 mg in 1% acetone) was absorbed across isolated full thickness human skin in 24 hours and 45% of the dose was retained in skin, while Fasano et al. (2005) found that following application of the ammonium salt of PFOA to isolated human or rat epidermis (approximately 30 mg ammonium PFOA/cm2), approximately 1.44% was absorbed across rat epidermis, while only 0.048% of the dose was absorbed across human epidermis. Fasano et al. (2005) estimated the dermal penetration coefficient to be 9.49 $x10^{-7}$ cm/hour in the isolated human epidermis and 3.25 $x10^{-5}$ cm/hour in the isolated rat epidermis. There are little to no data available on the dermal absorption of other PFAS but they are expected to be similar to PFOA.

Incidental Ingestion: There is no information regarding exposure to PFAS through incidental ingestion during routine activities such as showering, bathing, or brushing teeth. It has been recommended by various state agencies to avoid ingestion of PFAS-contaminated water during these activities in order to reduce exposure. However, the incidental ingestion of PFAS during showering, bathing, or brushing teeth is not expected to be a significant source of exposure due to the negligible amount of water ingested (NJDOH 2016; AKDHHS 2015; MNDOH 2016; VT ANR DOH 2016). There is no information regarding exposure to PFAS through incidental ingestion during recreational activities such as swimming. However, the incidental ingestion of PFAS during recreational activities such as swimming is not expected to be a significant source of exposure due to the negligible amount of water ingested.

Soil

There is little information regarding background concentrations of PFAS in soil (ATSDR 2015) and the one limited study found concentrations to be very low or below detection limits (Washington et al. 2009a). Soil contamination tends to occur at manufacturing sites of producers and users of PFAS (3M 2007, 2008), where aqueous film forming (AFFF) type firefighting foams have been used or where disposal of treated products has occurred (e.g., landfills) (USEPA 2016c, d), and potentially where biosolids containing PFAS are applied (Washington et al. 2009a, b; Sepulvado et al. 2011; Venkatesan and Halden 2013; Armstrong et al. 2016), or where contaminated groundwater is used for irrigation. Contaminated soils also can be transported offsite via water and wind.

Numerous military installations and firefighting training areas have PFAS contamination due to the use of AFFF-type fire suppression agents (Moody and Field 1999; Moody et al. 2003; ATSDR 2016a, ASTSWMO 2015). Soil contamination with resultant groundwater contamination can occur through direct application or through spray drift.

The use of PFAS-contaminated biosolids as a soil amendment and the use of contaminated groundwater for irrigation may result in the contamination of soils and therefore may also result in the indirect

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contamination of produce and domestic animal feed grown on contaminated soils. PFAS have been detected in biosolids samples (Washington et al. 2009a; Sepulvado et al. 2011; Venkatesan and Halden 2013; Armstrong et al. 2016) as a result of wastewater plants having received PFAS-containing industrial waste (USEPA 2011a; Yoo et al. 2009; Yoo et al. 2011). Concentrations in biosolids are expected to decline because of the phaseout of the use of PFOS and PFOA in manufacturing and industrial processes.

Incidental Ingestion: Incidental ingestion of soils represents a potential exposure route for PFAS

Dermal: As discussed in the previous sections, the dermal absorption of PFOS is slow and not significant. Although there are little to no data on other PFAS, dermal absorption is also expected to be insignificant.

Inhalation of re-suspended soil particulates: There is no information available regarding exposure through the inhalation of re-suspended soil particulates. However, this pathway is not expected to be a relevant exposure pathway to the general population unless located near contaminated soil sites or near agricultural fields where PFAS-contaminated biosolids were applied as a soil amendment.

Ambient air and dust

PFOA and PFOS are not volatile and airborne fractions are primarily bound to aerosol particles (Trudel et al. 2008; USEPA 2016c, d; ATSDR 2015). These compounds can be released into the atmosphere from fluoropolymer manufacturing and industrial and municipal waste incinerators (ATSDR 2015; USEPA 2016c, d). They can be transported long distances through the atmosphere and have been detected globally at low concentrations (Jahnke et al. 2007).

PFOS has been detected in samples collected over the Atlantic Ocean east of southern Africa. Shoeib et al. (2006) detected PFAS concentrations crossing the North Atlantic and the Canadian Arctic Archipelago. However, although air maybe a potential source of exposure, it is considered an insignificant exposure pathway.

PFAS have been measured in indoor dust in residential, commercial, and office settings because of their use in carpets, textiles, paint, furniture, and other consumer products. Strynar and Lindstrom (2008) detected nine PFAS in indoor dust samples collected from homes and daycare centers in Ohio and North Carolina. PFOS and PFOA were the most commonly detected (94.6% and 96.4% of samples, respectively) with maximum detections of 12,100 ng/g for PFOS and 35,700 ng/g for PFOA. Incidental exposure from indoor dust is an important exposure route, particularly for small children because of their hand-to-mouth behaviors (USEPA 2016c, d).

Food

Food is a significant source of exposure to PFAS (Trudel et al. 2008; ATSDR 2015; Lindstrom et al. 2011; Vestergren and Cousins 2009; ASTSWMO 2015), and modeling has indicated that 90% of human exposure to PFOS and PFOA may be through ingestion of contaminated food (Fromme et al. 2009). PFOA has been detected in a variety of foods including snack foods, vegetables, meat, dairy products, human breast milk, and fish. PFOS has been detected in eggs, milk, meat, fish, root vegetables, and human breast milk. Occurrence in food products can result from the use of contaminated water in processing and preparation; growth of food in contaminated soils (e.g., in areas that receive biosolids soil amendments from wastewater treatment plants); direct and indirect exposures of domestic animals to PFAS from drinking water and consumption of feed crops grown in contaminated soil; fish tissue bioaccumulation from contaminated waterways; and food packaging materials containing PFAS (Hag et al. 2011; Lindstrom et al. 2011; Sepulvado et al. 2011; Venkatesan and Halden 2013; Armstrong et al. 2016; ATSDR 2015; Forns et al. 2015; USEPA 2016c, d).

Infants can be exposed to PFAS compounds through the ingestion of breast milk and through the ingestion of formula or cereals made with contaminated drinking water or cross contaminated through migration from packaging and containers (Tao et al. 2008, Hag et al. 2011, Fromme et al. 2010; Liorca et al., 2010). Studies have shown breast milk is a significant exposure route for infants to PFAS. A study of PFAS content in breast milk was conducted by Tao et al. (2008). PFOS and PFOA were the predominant PFAS compounds found in the analysis of 45 breast milk samples, with mean concentrations of 131 pg/mL and 43.8 pg/mL, respectively. Hag et al. (2011) have shown breast milk contributed greater than 94% of total PFOS exposure in 6-month-old infants, and greater than 83% of PFOA exposure. Fromme et al. (2010) determined that the resultant body burden at

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age six months was similar to (PFOS) or higher (PFOA) than that found in adults after evaluating measured PFAS content of maternal blood during pregnancy and six months after delivery, in cord blood, and in blood of infants at six months and nineteen months after birth, as well as in monthly breast milk samples.

Liorca et al. (2010) evaluated commercial formulas and food purchased from a retail store. Six PFAS compounds, including PFOS and PFOA, were detected in all brands of infant milk formulas and baby food cereals analyzed. It was hypothesized that the presence of the PFAS compounds could be associated with possible migration from packaging and containers during processing.

Some studies suggest the consumption of fish from contaminated waters may be a major source of human exposure to PFOS (Trudel et al. 2008; Fromme et al. 2009; Domingo 2012). PFOS has been shown to bioaccumulate readily in fish, appears to have the highest bioaccumulation potential of the PFAS in food webs, and is the predominant PFAS detected in fish tissue (Houde et al. 2011). In a study of PFAS concentrations in fish and surface water in New York State, although PFOA was typically found at higher concentrations in water than PFOS, measured concentrations of PFOS in fish tissue were approximately 9,000-fold greater than the levels detected in surface water (Sinclair et al. 2006). The USEPA national screening study of PFAS in freshwater fish determined 80% of samples of urban river fish tissue samples and 100% of Great Lake fish tissue samples contained some detectable PFAS. PFOS was the most commonly detected PFAS in both fishpopulations; the maximum detected PFOS concentrations were 127 ppb and 80 ppb in river fish and Great Lake fish tissues, respectively (Stahl et al. 2014).

Exposure to PFAS-Containing Products

Consumer Products

Although not a primary exposure route, use of PFAS-containing consumer products may result in potential exposure. Some examples are listed as follows (ATSDR 2015; USEPA 2016c, d).

- Stain/water repellants on clothing, bedding materials, upholstered furniture, carpets, and automobile interiors (Walters and Santillo 2006; Lindstrom et al. 2011). These materials can be a particularly important exposure route for infants and children because of their hand-to-mouth behaviors.
- Cooking surfaces (PFOA)
- Toothpaste and dental floss, shampoos, cosmetics (PFOA)
- Polishes and waxes (PFOA)
- Paints, varnishes, sealants (PFOS, PFOA)
- Food containers and contact paper (PFOA and PFOS are impurities that can be found in some grease-proofing paper coatings [Begley et al. 2005])[6]
- Pesticides (PFOA)
- Textiles and leather (PFOS, PFOA)
- Plumbing tape (PFOA)
- Cleaning products (PFOS, PFOA).

Occupational Exposure

Occupational use of PFAS-containing products may result in potential exposure. Some examples are listed as follows (USEPA 2016c, d).

- Aqueous film forming foams (continuing use; used for firefighting) (PFOS, PFOA)
- Flame retardants (PFOS, PFOA)
- Aviation fluids (continuing use, PFOS)
- Metal plating and finishing (continuing use, PFOS)
- Lubricants/surfactants/emulsifiers (continuing use, PFOA)
- Semiconductor industry (PFOS)
- Oil and mining (PFOS)
- Electronics (PFOA)
- Photograph development (continuing use, PFOS).

Conclusions

As discussed, PFAS have been used in a variety of products and industrial applications, resulting in widespread exposure of the general population. Biomonitoring studies have estimated more than 95% of the U.S. population have been exposed to PFAS and have measurable concentrations in their blood. However, it should be noted these concentrations have been demonstrably decreased since the discontinuation of production of these chemicals in 2002. The greatest portion of chronic intake is likely from the ingestion of contaminated foods and drink-

[6] In January 2016, the Food and Drug Administration amended their food additive regulations to no longer allow for the use of perfluoroalkyl ethyl containing food-contact substances as oil and water repellants for paper and paperboard for use in contact with aqueous and fatty foods (USEPA 2016c, d).

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ing water. Consumer products, recreational activities, ambient air, and soil exposures contribute to a lesser extent to the total chronic intake. Small children, however, experience higher exposure due to hand-to-mouth transfer of chemicals from treated carpets and indoor dust.

EXPOSURE OF ECOLOGICAL RECEPTORS

PFAS have been detected in the tissues of invertebrates, fish, birds, and mammals around the globe (Kelly et al. 2009; Butts et al. 2010; Houde et al. 2011; CONCAWE 2016). Much of the published tissue monitoring data for free-ranging wildlife are for PFCAs and PFSAs in fish-eating Arctic marine mammals (e.g., seals, dolphins, whales) and polar bears. Additionally, PFAS have been measured in multiple fish species from urban freshwater bodies in the U.S. (Delaware River Basin Commission 2009; Delinsky et al. 2011; Xiao et al. 2013), Korea (Lam et al. 2014), Germany (Holzer et al. 2011), Sweden (Ahrens et al. 2015), and numerous other countries. PFOS is the most frequently detected PFAS; has generally been measured at the highest concentrations; and is the dominant PFAS found in all species and locations around the world (Butt et al. 2010; Houde et al. 2011). PFOA, PFHpA, PFNA, and PFHxS have also been detected (Kelly et al. 2009; Houde et al. 2011; CONCAWE 2016). In the Arctic, PFNA (and perfluoroundecanoate) levels are generally second only to PFOS, with elevated levels of other longer-chain PFCAs observed in seabirds (Butt et al. 2010).

PFAS may be released to the aquatic environment from the discharge of effluent from wastewater treatment facilities, spills, commercial operations, or via groundwater seepage and surface water flow; however, the prevalence of PFOS and other PFAS in species such as polar bears, seals, and beluga whales is attributed to precursor volatilization and atmospheric degradation to these terminal stable species, followed by deposition to aquatic and terrestrial environments and food chain transfer (Houde et al. 2011; Government of Canada 2013).[7] The recent review by Houde et al. (2011) noted that PFAS accumulation in wildlife is common; long-chain PFCAs (C7-C12), especially the C8 PFOS and the C9 PFNA, have accumulated in seals, seabirds, and polar bears. These patterns have been observed in wildlife in Europe and Asia as well; in general, lower PFAS levels have been measured in wildlife from the Southern Hemisphere. The direct discharge of PFAS to the ocean from groundwater or surface water is partially mitigated by dilution and dispersion associated with tidal fluctuation, wave action, and currents. Additionally, the salinity of ocean water reduces the solubility of PFAS (USEPA 2014) and promotes its adhesion to sediments (Chen 2012), thus reducing its concentration in marine water. Consequently, emerging surface water criteria for marine waters are typically less stringent than for freshwater.

Wildlife Effects

PFOA wildlife tissue measurements made on samples collected from free-ranging wildlife species have made few correlations between tissue levels and adverse effects. The exceptions to this include Kelly et al. (2009) who calculated nursing beluga whale calves in Hudson Bay were exposed to PFOS via maternal transfer at concentrations ($2.7 \times 10^{-5}/8 \times 10^{-4}$ mg/kg-d) that could be toxicologically significant, and Kannan et al. (2006). The latter established the mean concentrations of PFOA (69 ng/g) and PFOS (65 ng/g) in California sea otters were significantly associated with mortality from disease. Dietary exposures of mallard and quail to PFBS (100–900 mg/kg) had no effect on mortality, organ histology, or reproductive endpoints such as egg production, viability, hatchability, and hatchling success and survival (Newsted et al. 2008). In contrast, PFOS caused mortality when fed to mallards and quail at 50 and 150 mg/kg in the diet, and 10 mg/kg PFOS affected egg hatchability and survival of quail (Newsted et al. 2007). Substantially lower concentrations of PFOS (1 to 5 mg/kg) injected into the eggs of chickens elicited a spectrum of adverse effects including increases in spleen and liver weights, and developmental and immunologic effects such as shorter wings, brain asymmetry, and lowered antibody levels. Average serum PFOS levels (154 ng/g) in these chickens were within levels observed in wild birds, indicating environmental exposures of birds have the potential to cause biologically significant effects.

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Table 3.3. Elimination half-lives for PFAS.

Species	Chemical					
	PFOS	PFOA	PFNA	PFHxS	PFHpA	PFBS
Human	4.5-7.4 years	2.3-10.1 years	2.5-4.3 years (estimated mean)	8.5 years	—	27.7 days
Primates	110-170 days	20.1-32.6 days	—	87-141 days	—	8-95.2 hours
Mice	731-1027 hours	408-456 hours	619-1653 hours	597-732 hours	—	—
Rats	179-1992 hours	1.9-322 hours	58.6-1128 hours	39-688 hours	—	0.64-7.42 hours

Source: PFNA data from Tatum-Gibbs et al. (2011); Ohmori et al. (2003); and NJDWQI (2015). All other values from ATSDR 2015 except for estimated elimination half-life of PFOA in mice (Lau 2015).

TOXICOKINETICS

For the general population, ingestion is likely the primary route by which humans are exposed to PFOA and PFOS (Trudel et al. 2008; Fromme et al. 2009); oral exposure may also be a significant exposure route for PFHpA, PFHxS, PFBS, and PFNA, but this has not been unequivocally established.

Following oral exposure, PFOA, PFOS, PFHxS, and PFBS are absorbed across the gastrointestinal tract and bind to albumin and other serum proteins. PFOA and PFOS are known to distribute from serum to organs via the action of several different classes of transporter proteins. The distribution of these transporter proteins—and thus the distribution of PFAS—varies between organs. The liver typically accumulates the greatest concentrations of PFAS, with lesser amounts in the kidneys and other organs (ATSDR 2015; Lau 2015; USEPA 2016f, g).

Due to the strength and stability of the carbon-fluorine bond, terminally stable PFAS are not metabolized. Their elimination varies with PFAS carbon chain length, species, and gender, with the longest half-lives for PFSAs > C4 and PFCAs > C6 in humans. Primates eliminate PFAS relatively slowly, and rodents tend to clear PFAS more quickly (Table 3.3). In general, males eliminate PFAS more slowly than females. PFAS are eliminated in the urine, with minor amounts also eliminated in the bile. Significant reabsorption from the kidney occurs in humans and primates, and to a much more limited extent in rodents, and is thought to be a key factor in the species-specific differences in elimination half-lives (ATSDR 2015; Lau 2015; USEPA 2016f, g).

TOXICOLOGICAL EFFECTS OF PFAS

PFOA and PFOS have been linked to a multiplicity of adverse effects including hepatic toxicity, reproductive and developmental toxicity, suppression of the immune system, and cancer. The majority of these findings come from animal studies, with supporting epidemiologic evidence for certain endpoints. The data for PFNA, PFHxS, and PFBS are much more limited, but suggest these compounds also affect the liver. PFNA caused developmental toxicity that was qualitatively similar to that associated with PFOS and PFOA; available data indicate PFBS and PFHxS do not cause reproductive or developmental effects. PFCAs and PFSAs do not appear to be genotoxic or mutagenic (USEPA 2016f, g; Butenhoff et al. 2014).

Reproductive and Developmental Effects

PFAS cross the placenta of humans and animals, and can also be transferred to offspring during lactation (Karrman et al. 2007; Fenton et al. 2009; Gutzcow et al. 2012).

PFOA. PFOA is one of the PFAS known to cross the mammalian placenta, and exposures during gestation have been tied to a range of reproductive and developmental effects (USEPA 2016e). Epidemiological studies of individuals exposed to PFOA-contaminated drinking water from industrial discharges ("highly exposed populations") have demonstrated an association between PFOA and pregnancy-induced hypertension (Darrow et al. 2013; USEPA 2016f). Although PFOA has not been linked to low birth weight in these highly exposed populations, there is some evidence associating PFOA exposure in the general population with documented small decreases in birth weight

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(Verner et al. 2015), decreases in fecundity (Velez et al. 2015) and fertility (Fei et al. 2009). In mice, PFOA has a significantly longer half-life than in rats—a fact that likely contributes to the greater sensitivity of mice to the reproductive and developmental effects of PFOA (Lau 2015). In mice, PFOA (≥1 mg/kg administered dose) has caused decreases in pup body weight and decreased neonatal survival, whereas higher doses (> 5 mg/kg) increased litter resorption and numbers of still births. Rats also experience developmental effects of PFOA, albeit at larger doses than mice. Decreased body weight gain, delayed sexual maturity, and decreased viability were observed in rat offspring after gestational exposure to 30 mg/kg (Butenhoff et al. 2004). The USEPA identified reduced ossification of the fore- and hindlimbs in male and female mouse pups, and accelerated puberty in male mice pups administered 1 mg/kg PFOA as the critical endpoints used to derive the reference dose (RfD) (USEPA 2016e).

PFOS. In human populations, fetal PFOS exposure has been linked with lower average birth weights and with low infant body weight. Elevated serum PFOS levels have also been associated with decreased fertility and fecundity, manifested as greater time to pregnancy (USEPA 2016f). Several studies have shown effects of PFOS on semen quality, although the majority of studies that examined sperm parameters have not found a significant effect (USEPA 2016f). Additional evidence has linked serum PFOS with pre-gestational diabetes, and pregnancy-induced hypertension (USEPA 2016f). In rodents, PFOS has caused increased pup mortality, decreased body weight, and developmental delays. Exposure of rodents during gestation and lactation has been associated with abnormal glucose regulation in the offspring at maturity (USEPA 2016f). The EPA identified decreased body weights in newborn rats as the most sensitive endpoint observed from toxicity studies, and used the no observed adverse effect level (NOAEL) of 0.1 mg/kg-d as the basis of the RfD (USEPA 2016f).

PFNA. In mice, PFNA caused qualitatively similar developmental toxicity to PFOA and PFOS, with oral PFNA exposure causing dose-related effects in the number of live pups at birth and survival to weaning (Wolf et al. 2010) and neonatal mortality (Das et al. 2015). Surviving pups (1, 3, and 5 mg/kg) exhibited delayed eye opening and a delay in the onset of puberty (Das et al. 2015).

Other PFAS. Limited data indicate neither PFHxS nor PFBS are reproductive or developmental toxins, in that orally administered PFBS (30–1000 mg/kg) did not affect fertility, reproduction, or multiple indices of developmental toxicity in rats including litter size, mean pup birth weight, or pup survival (Lieder et al. 2009a). Similarly, PFHxS did not cause reproductive or developmental effects in rats given 0.3 to 10 mg/kg prior to mating, and during gestation and lactation (Butenhoff et al. 2009). However, increasing serum concentrations of PFHxS have been correlated to small decrements in human fecundity (Velez et al. 2015). There are no data on the reproductive or developmental effects of PFHpA.

Liver and Lipoproteins

PFOA. In PFOA-exposed workers and nearby "highly exposed" community members exposed via drinking water, multiple epidemiology studies have linked elevated PFOA serum concentrations with increases in total cholesterol and low-density lipoproteins (serum PFOA levels of 0.4 to 12 micrograms per milliliter [µg/mL] in workers, and an average of 0.08 µg/mL in community members). PFOA serum levels of 0.002 to 0.007 µg/mL were associated with elevated levels of triglycerides (USEPA 2016e). In animals, PFOA (and PFOS) tend to lower levels of total cholesterol, triglycerides, and lipoproteins (USEPA 2016e).

Epidemiology studies of PFOA-exposed workers and residents of communities affected by industrial discharges of PFOA have consistently shown a relationship between serum PFOA levels and the liver enzymes alanine aminotransferase and gamma-glutamyl transaminase. These results notwithstanding, epidemiology data have not provided evidence of PFOA-induced liver damage. Rodents exposed to PFOA frequently exhibit increased liver weight and hepatocellular hypertrophy. Unless there is concomitant necrosis or cellular degeneration however, these effects are generally not considered biologically significant as they tend to be reversible once exposure ends (USEPA 2016e).

PFOS. Data from epidemiology studies have demonstrated an association between serum PFOS levels (0.0084 µg/mL to 0.022 µg/mL) and increases in total cholesterol (USEPA 2016f). Multiple species of animals exposed to PFOS (0.098 to 1.56 mg/kg) have

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exhibited a similar spectrum of hepatic effects to those induced by PFOA, including cellular hypertrophy, increased liver weight, and vacuolation (USEPA 2016).

Other PFAS. Limited data indicate the liver is also a target for PFNA, PFBS, and PFHxS, with hepatocellular hypertrophy, increased liver weight, and decreased lipoprotein synthesis observed. PFBS exposure elicited increased liver weight and adaptive hepatic hypertrophy in rats following doses of 300–1000 mg/kg (Lieder et al. 2009a). PFHxS caused increased liver weight and hypertrophy in rats (0.3–10 mg/kg); decreased triglyceride levels (rats, 3–10 mg/kg; mice, 30 mg/kg), and decreased levels of cholesterol and various lipoproteins in mice (6 mg/kg) were also features of PFHxS exposure (Butenhoff et al. 2009; Bijland et al. 2011). While PFBS exposure (30 mg/kg) has also been associated with impaired lipoprotein synthesis, the effects were limited to triglycerides (Bijland et al. 2011).

There are no data on the potential effects of PFHpA on the liver.

Immune System

PFOA and PFOS. Evidence from both human and animal studies indicate PFOA and PFOS adversely affect multiple components of the immune system and as a result, can alter immune function (National Toxicology Program [NTP] 2016). Both PFOA and PFOS suppressed the antibody response and increased hypersensitivity-related outcomes in humans and animals. In humans, there is also evidence PFOA decreased resistance to infectious disease and increased autoimmune disease (NTP 2016). Animal data also indicate PFOS suppresses disease resistance and natural killer (NK) cell activity (NTP 2016).

Other PFAS. PFNA was cytotoxic to the spleen and thymus of mice (key organs of the immune system), reducing populations of splenic T cells, impairing cell replication in the thymus, and impairing the production of cell-signaling molecules (Fang et al. 2008).

There are no data on the effects of PFHpA, PFBS, or PFHxS to the immune system.

Carcinogenicity

PFOA and PFOS. Available data indicate neither PFOA nor PFOS are genotoxic or mutagenic (USEPA 2016e, f). However, both PFOA and PFOS induce liver tumors in rodents after long-term high-level exposure; and PFOA also induces testicular and pancreatic tumors. Mechanistic data indicate that the rodent liver tumors develop following PFOA- or PFOS-induced activation of the peroxisome proliferator activated receptor alpha (PPARα), a mode of action that may also be relevant to rodent testicular and pancreatic tumors. PPARα-mediated hepatic tumors are generally not considered biologically relevant to humans given differences in both endogenous levels and responses of PPARα between humans and rodents (Corton et al. 2014; Kennedy and Symons 2015). The relevance of PFAS-induced rodent testicular and pancreatic tumors to humans is unclear.

The USEPA Office of Water determined that there is "suggestive evidence of carcinogenic potential" for PFOA (USEPA 2016c) and PFOS (USEPA 2016d). The International Agency for Research on Cancer (IARC 2016) found PFOA to be "possibly carcinogenic." Neither agency nor independent scientists have evaluated the genotoxicity, mutagenicity, or carcinogenicity of other PFAS.

Epidemiology studies from highly exposed populations exposed to PFOA in drinking water found associations between PFOA serum levels and kidney and testicular cancers (C8 Science Panel 2013). In rats, PFOA exposure led to liver, testicular, and pancreatic tumors (reviewed in USEPA 2016e). Based on the rat testicular data for PFOA, the USEPA (2016e) derived a cancer slope factor (CSF) of 0.07 (mg/kg-d-1).

The evidence regarding the potential carcinogenicity of PFOS is more limited than for PFOA, and consists of somewhat equivocal epidemiologic evidence linking human exposure to PFOS to bladder and prostate cancer. Animal data support an association between PFOS exposure and an increased incidence of several tumor types, with the strongest evidence for liver tumors (USEPA 2016f). The USEPA (2016f) found the PFOS tumor data insufficient to derive a CSF.

Other PFAS. The carcinogenicity of PFNA, PFHpA, PFBS, and PFHxS has not been evaluated.

Conclusions

Terminally stable PFAS are not metabolized; their elimination depends on carbon chain length, species, and gender. In humans, the longest half lives have been observed for PFSAs > C4 and PFCAs > C6.

Animal and/or epidemiologic data have linked

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PFOA and PFOS to a range of adverse effects including hepatic, reproductive, developmental, and immune system toxicity. The data for PFNA, PFHxS, and PFBS are much more limited, but suggest that these compounds also affect the liver. PFNA, but not PFBS or PFHxS, appear to cause developmental effects in animals. PFCAs and PFSAs are not considered genotoxic or mutagenic. The USEPA considers that there is suggestive evidence of carcinogenicity of PFOA and PFOS.

For ecological species, bioaccumulation of PFAS is a key issue; the extent of bioaccumulation depends on whether the organism is aquatic or terrestrial; on the organism's trophic level; and on whether it has lungs or gills. A number of PFCAs and PFSAs are ubiquitous in the tissues of terrestrial and aquatic species of wildlife worldwide. Based on measured concentrations and the frequency of detection, PFOS is the dominant PFAS in wildlife, with PFNA and other PFCAs also common.

RISK ASSESSMENT OF PFAS

Many PFAS are environmentally persistent, bioaccumulate in living organisms, and have demonstrated toxicity in laboratory animals and humans.

The C8 Health Project, one of the most robust studies of PFOA exposure, provided data on approximately 70,000 exposed Ohio and West Virginia residents.

Drinking water exposure to PFOA was linked to serum PFOA concentrations and a range of specific adverse health outcomes. Additionally, national biomonitoring studies have shown that the majority of the U.S. population has been exposed to PFAS. It is therefore prudent to assess and potentially mitigate human and/or environmental exposures.

Available Toxicity Criteria and Screening Levels

Toxicity Criteria

Non-Cancer RfD: USEPA developed updated oral Reference Doses of 2E-05 mg/kg/day, applicable to both PFOS and PFOA. The RfDs were derived from developmental toxicity studies in mice (PFOA) (USEPA 2016e) and rats (PFOS) (USEPA 2016f). The RfD is an estimated daily exposure level for the human population (including sensitive subpopulations) that is likely to be without an appreciable risk of deleterious effects during a lifetime (USEPA 1989). USEPA recommends this value for both short-term (sub-chronic) and chronic (lifetime) exposures.

PFOA: The RfD for PFOA is based upon the Lau et al. (2006) study that evaluated six groups of timed-pregnant CD-1 mice that were given 1 to 40 mg/kg PFOA by oral gavage from gestational day 1 to 17, while controls received water. After 17 days, some dams were sacrificed for maternal and fetal exams, while the rest were dosed until birth. The study demonstrated a lowest observable adverse effect level (LOAEL) of 1 mg/kg/day for reduced ossification of the proximal phalanges (of the forelimb and hindlimb) and accelerated puberty in male pups (4 days earlier than controls). A human equivalent dose (HED) was calculated from the LOAEL using a volume of distribution (Vd) of 0.17 L/kg bw calculated by Thompson et al. (2010) and the half-life (t1/2) in humans of 2.3 years based upon Bartell et al. (2010) determination of a decline in serum levels among the general population exposed to drinking water near the DuPont Works plant in Washington, West Virginia. A total uncertainty factor of 300 (10 –variability within the human population, 3 – extrapolation from animal to human, and 10 – LOAEL to NOAEL extrapolation) was applied to the HED to obtain the RfD of 2E-05 (USEPA 2016e).

PFOS: The RfD for PFOS is based upon the Luebker et al. (2005) two-generation study. The parental (F0) generation were dosed 0.1 to 3.2 mg/kg PFOS by oral gavage for 6 weeks prior to and during mating. Females were treated throughout gestation, parturition, and lactation. Controls received water. The F1 generation pup viability was significantly reduced at the two highest groups, therefore only the 0.1 and 0.4 mg/kg/day dose groups were carried into the second generation. Dosing began at weaning and continued until sacrifice. All first (F1) generation females were allowed to deliver and were sacrificed on lactation day 21. The study demonstrated a NOAEL of 0.1 mg/kg/day for reduced pup body weight in the second generation off-spring. A HED was calculated from the LOAEL using a volume of distribution (Vd) of 0.23 L/kg bw calculated by Thompson et al. (2010) and the t1/2 in humans of 5.4 years based upon Olsen et al. (2007) determination of a decline in serum levels among a retired worker population followed for 5 years. A total uncertainty factor of 30 (10 –variability within the human population, and 3 – extrapolation from animal to human) was applied to the HED to obtain the RfD of 2E-05 (USEPA 2016e).

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Other PFAS: USEPA has derived a provisional sub-chronic RfD (0.2 mg/kg/day) and a provisional chronic RfD (0.02 mg/kg/day) for perfluorobutane sulfonate (PFBS) based upon a sub-chronic and reproductive study in rats (USEPA 2014b). Lieder et al. (2009b) identified a NOAEL of 200 mg/kg/day in a sub-chronic duration study in rats based on histopathological findings in the kidney. Three groups of rats were dosed 60 to 600 mg/kg/day with potassium PFBS (K+PFBS) by gavage for 90 days. Controls received water. A HED for the study was calculated using a body weight scaling to the ¾ power (BW ¾) approach as a default method to extrapolate toxicologically equivalent oral doses in laboratory animals to humans for the purpose of deriving a RfD when there is no chemical specific data to calculate based upon toxicokinetic modeling (USEPA 2014b). A total uncertainty factor of 100 (10 –variability within the human population, 3 – extrapolation from animal to human, 3 – limited study database) was applied to the HED to obtain the RfD of 2E-01 (USEPA 2014b) for the provisional sub-chronic RfD.

In a two–generation reproductive study in rats, Lieder et al. (2009a) identified a NOAEL of 100 mg/kg-day in F0 and F1 generation animals based on increased incidence and severity of histopathological kidney changes in both sexes. Four groups of rats were dosed 30–1000 mg/kg/day K+PFBS by gavage, controls received water. The F0 generation received daily doses beginning at six weeks of age and lasting until at least 70 days prior to cohabitation. The F1 rats received the same dosing regimen as their respective sires and dams beginning at lactation day 22. A HED for the study was calculated using the BW ¾ approach (USEPA 2014b). A total uncertainty factor of 1000 (10 –variability within the human population, 3 – extrapolation from animal to human, 3 – limited study database and 10-to extrapolate from less than chronic duration exposure) was applied to the HED to obtain the RfD of 2E-02 (USEPA 2014b) for the provisional chronic RfD.

Non-Cancer RfC: At this time, there are insufficient data available to calculate an inhalation Reference Concentration (RfC) for PFOS and PFOA (USEPA 2016e, f).

Cancer Slope Factor: PFOA and PFOS have been classified as having Suggestive Evidence of Carcinogenic Potential in humans by USEPA (USEPA 2016e, f), while PFOA has also been classified as a Group 2B carcinogen (possibly carcinogenic to humans) by the International Agency for Research on Cancer (IARC) (IARC 2016). An oral cancer slope factor of 0.07 (mg/kg/day^{-1}) has been developed for PFOA by USEPA, based upon testicular cancer (Leydig Cell tumors) in rodents (USEPA 2016e). An oral cancer slope factor has not been calculated for PFOS since the available tumor data were determined to be inadequate for quantitative assessment (USEPA 2016f). PFBS is provisionally classified as "Inadequate Information to Assess Carcinogenic Potential" (USEPA 2014b). Cancer slope factors provide an upper-bound estimate of the probability of a response (i.e., cancer) per unit intake of a chemical over a lifetime (USEPA 1989).

Drinking Water Health Advisory

Currently there are no federal regulations under the SDWA or national recommended ambient water quality criteria under the Clean Water Act (CWA) for PFAS. In 2009, USEPA developed interim, provisional HAs for short-term exposure to PFOS and PFOA of 0.2 and 0.4 µg/L, respectively (USEPA 2009). HAs identify the concentration of a contaminant in drinking water at which adverse health effects are not anticipated to occur over specific exposure durations (e.g., 1 day, 10 days, a lifetime). HAs serve as informal technical guidance to assist federal, state, and local officials and managers of public or community water systems in protecting public health when emergency spills or other contamination situations occur (USEPA 2016c, d).

As of May 2016, the lifetime drinking water HA for PFOA and PFOS is 0.07 µg/L, which is applicable to either chemical individually or collectively. The HA is based upon the RfD of 2E-05 mg/kg discussed previously. Since the HA was developed based upon sensitive developmental effects, it is also protective of adverse effects seen in adults (liver and kidney toxicity). Because the HA is lower than the concentration derived for carcinogenic effects of PFOA, it is also protective of carcinogenic effects for the general population (USEPA 2016c, d).

Screening Levels

A summary of screening levels for PFOS and PFOA are provided in Tables 3.4 (Soil), 3.5 (Drinking Water/Groundwater), 3.6 (Recreational Sediment and Surface Water), and 3.7 (Fish Tissue). Note, these tables are not meant to be all inclusive and are provided to show some of the screening levels available for these compounds. Additional screening levels for PFBS and

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Table 3.4. Soil screening levels for PFOS and PFOA (mg/kg).

Entity	Resident		Industrial Worker		Recreational User		Outdoor Commercial Worker		Excavation or Construction Worker	
	PFOS	PFOA	PFOS	PFOA	PFOS	PFOA	PFOS	PFOA	PFOS	PFOA
USEPA (USEPA 2016g)	1.26	1.26	16.4	16.4	NE	NE	18.2[1]	18.2[1]	NE	NE
Maine (ME DEH 2014)	11	0.80	NE	NE	18	1.3	82	6.2	19	1.4
US Navy (NAVFAC 2013)	4.9	12	49	123	NE	NE	NE	NE	NE	NE
Delaware (DNREC 2016)	6	16	NE	NE	NE	NE	NE	NE	NE	NE
Iowa (IDNR 2016)	1.8	1.2	NE	NE	NE	NE	NE	NE	NE	NE
Minnesota (MPCA 2009)	2.1	2.1	14	13	2.6	2.5	NE	NE	NE	NE
Texas (TRRP 2016)	1.5/1.5[2]	0.6/0.49[2]	15/14[2]	2.4/1.4[2]	NE	NE	NE	NE	NE	NE

NE = Not Established [1] Calculated with USEPA's RSL Calculator

[2] Total Soil Combined Protective Concentration Level for 0.5-acre/30-acre source area

Table 3.5. Drinking water/groundwater screening levels (µg/L) for PFOS and PFOA.

Entity	PFOS	PFOA
USEPA (USEPA 2016g). States that adopted USEPA HA: Alabama (ADEM 2016), Arizona (Liberty Utilities 2016), Colorado (CO DPHE 2016), Connecticut (CT DPH 2016), Delaware (DNREC 2016), Iowa (IDNR 2016), Massachusetts (MA DEP 2016), Maine (ME DEP 2016), New Hampshire (NHDES 2016), New York (NYS DOH 2016), West Virginia (WV DHHR 2016)	0.07	0.07
Alaska (AKDNC 2016)	0.4	0.4
Illinois (ASTSWMO 2015); Kentucky (NKWD 2016)	0.2	0.4
Michigan (MI DEQ 2016)	0.011	0.42
Minnesota (MN DOH 2017)	0.027	0.035
New Jersey (NJDEP 2007)	NE	0.04
North Carolina (NC DENR 2013)	NE	2
Texas (TRRP 2016)	0.56	0.29
Vermont (VT DOH 2016)	0.02 (combined) (a)	0.02 (combined) (a)
INTERNATIONAL		
Australia (AU DOH 2017)	0.07 (a)	0.56 (a)
Canada (Health Canada 2016)	0.6 (a)	0.2 (a)
Denmark (Danish MOE 2015)	0.1 (a,b)	0.1 (a,b)
Germany (Germany MOH 2006)	0.1 (combined) (a)	0.1 (combined) (a)
Italy (Valsecchi, et al. 2017)	NE	0.5 (a)
Netherlands (RIVM 2011)	NE	0.0053 (a)
Sweden (C0ncawe 2016)	0.09 (a)	0.09 (a)
U.K. (U.K. DWI 2009)	0.3 (a)	0.3 (a)

NE = Not Established (a) Drinking water value (b) Risk-based groundwater value

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Table 3.6. Recreational sediment and surface water screening levels for PFOS and PFOA.

Entity	Recreational Sediment (mg/kg)		Recreational Surface Water (µg/L)	
	PFOS	PFOA	PFOS	PFOA
USEPA (USEPA 2016f)	NE	NE	NE	NE
Maine (ME DEH 2014)	20	1.5	1.2	0.05
Michigan (MI DEQ 2016)	NE	NE	0.012	12

NE = Not Established

Table 3.7. Fish Tissue screening levels for PFOS and PFOA.

Entity	Fish Tissue (ug/kg)	
	PFOS	PFOA
USEPA (USEPA 2017b)	32.7 - 334 (a)	32.7 – 334 (a)
Maine (ME DEH 2014)	175	13
Michigan (MI 2016)	< 9 (b)	NE
Alabama (ADPH 2017); Minnesota (MN DOH 2008)	<40 (c)	NE
Oregon (OR HA 2013)	0.2	0.2

NE = Not Established

(a) EPA RSL for fish tissue. Calculated using range of mean statewide survey intake levels of freshwater recreational fish intake using RSL calculator. Intake ranges 5–51 g/day (EFH 2011b, Table 10-5). USEPA recommends using site-specific fish ingestion levels when using the RSL calculator for fish tissue RSL calculations.

(b) Fish Consumption Advisory Level - 16 meals/month

(c) Fish Consumption Advisory Level - Unrestricted meal frequency

a number of other PFAS are available from USEPA (USEPA 2016g) and from other state agencies including Delaware (DNREC 2016), Indiana (IDEM 2016), Minnesota (MPCA 2009; MN 2016), New Jersey (NJDEP 2015, 2016), Nevada (NDEP 2015), North Carolina (NC DENR 2016), and Texas (TRRP 2016).

Relative Source Contribution in the Derivation of PFAS Risk-Based Criteria

A Relative Source Contribution (RSC) factor takes into account drinking water and non-drinking water exposures to a contaminant including food, soil, air, water, and consumer product use. The RSC is applied in the USEPA HA calculation to ensure an individual's total exposure from a contaminant (i.e., PFOA) does not exceed the RfD. The RSC accounts for the portion of the RfD attributed to drinking water (directly or indirectly in beverages like coffee, tea, or soup); the remainder of the RfD is allocated to other potential exposure sources. In the case of PFOA, other potential sources include ambient air, foods, incidental soil/dust ingestion and consumer products.

The USEPA's default RSC value is 20%, which means 20% of the total exposure is assumed to come from drinking water and 80% from non-drinking water sources. The USEPA determined there were insufficient data to develop a chemical-specific RSC for PFOA and PFAS, and therefore the default value of 20% was used to calculate the HA (USEPA 2016c, d).

Unique Receptors and/or Exposure Factors Used in the Derivation of PFAS Risk-Based Criteria

The lifetime HAs for PFOS and PFOA were calculated using drinking water intake and body weight parameters for lactating women in order to be protective of this critical exposure period for infants. Studies have shown significant exposure to infants through the ingestion of breast milk (Hag et al. 2011; Forns et al. 2015); consistent with this fact, studies have also shown breast feeding to be a potential excretion route for mothers (Mondal et al. 2014). The lactating woman provides the more protective scenario over the pregnant woman, given an increased

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water intake is needed to support milk production. The use of these exposure factors to calculate the lifetime HA are specific to the most sensitive population and therefore are protective of pregnant and lactating women as well as the general population (USEPA 2016c, d).

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APPENDIX 1

PFAS Bioaccumulation Potential

Factor	Definition	Reported Values	Interpretation	References
Bioconcentration factor (BCF)	Ratio of chemical concentration in an organism to the concentration in water (at steady-state). Values > 2000 indicate bioconcentration	PFOA 1.8-27 (fish)	PFOA. Does not bioconcentrate in fish	ECHA 2013; CONCAWE 2016
		PFOS 830-26,000 (fish)	PFOS. Bioconcentrates in fish	
		PFBS <1 (fish)	PFBS. Does not bioconcentrate in fish	
Bioaccumulation factors (BAFs)	Ratio of chemical concentration in an organism to the concentration from all sources (water, diet, soil, air). Values > 2000 indicate bioaccumulation	PFOA. 0.9-292 (fish, mussels, phytoplankton)	PFOA. Does not bioaccumulate in fish, mussels, phytoplankton	ECHA 2013; CONCAWE 2016
		PFOS 240 (zooplankton); 1200 (mussels); 16,000-95,000 (fish)	PFOS. Bioaccumulates in fish	
Biomagnification factors (BMFs)	Ratio of chemical concentration in an organism to the concentration in the diet. Values >1 indicate biomagnification	PFOA. 0.02-7.2 (fish); 1.8-125 (dolphins, polar bears); 0.1-2.7 (whales, seals); 0.9-11 (wolves, caribou)	PFOA. Biomagnifies in multiple species	ECHA 2013; CONCAWE 2016
		PFOS. 4.6-8.7 (fish); 2.0-9.1 (caribou); 0.8-4.5 (wolves); 0.9 (dolphins); 4.0-8.4 (whales).	PFOS. Biomagnifies in fish, caribou, dolphins, whales	
Trophic magnification factors (TMFs)	The increase in chemical concentration in an organism with an increase of one trophic level. Values >1 indicate trophic magnification	PFOA 0.37-0.53 (fish); 1.2-13 (seals, dolphins); 0.3-2.64 (whales); 1.1-1.3 (wolves, caribou)	PFOA. Trophic magnification occurs in air- breathing aquatic mammals, not in gill-breathers	ECHA 2013

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Groundwater and PFAS: State of Knowledge and Practice

Fate and Transport
Section 4

One of eight sections prepared by National Ground Water Association volunteers. Each section was prepared to stand independently, or to be integrated with the other seven sections.

NGWA Press
The Groundwater Association

Fate and Transport

INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) are a unique class of organic compounds that include thousands of individual chemical compounds, each with at least one carbon-fluorine (C-F) bond, and each with its own unique physicochemical properties governing environmental fate and transport. These compounds do not occur naturally. The synthesis and commercialization of PFAS arose from a branch of chemistry called fluorochemistry, which concerns itself with the unique characteristics of the C-F bond. The C-F bond is the strongest known carbon single bond, and imparts unique characteristics to PFAS that make them useful to society in a wide variety of applications. Hundreds of commercial PFAS products have been created for waterproofing of materials, non-stick surfaces on cooking utensils and food packaging, stain-resistant coatings on carpets and fabrics, and fireproofing coatings of materials among other uses. Chief among the commercial PFAS-containing products are aqueous film-forming foams (AFFFs) which have seen widespread use because of their effectiveness in extinguishing large and complex industrial fires.

This section presents relevant properties of PFAS including chemistry, sources, mobility, fate and mass balance, distribution in the subsurface, and exposure points. Although typical environmental occurrences may include hundreds to thousands of individual PFAS compounds, this section focuses on the six UCMR3 PFAS analytes. This list is selected due to wider regulatory interest and availability of information on these compounds.

Disclaimer: This publication is a collaborative effort to try to set forth best suggested practices on this topic but science is always evolving, and individual situations and local conditions may vary, so members and others utilizing this publication are free to adopt differing standards and approaches as they see fit based on an independent analysis of such factors. This publication is provided for informational purposes only, so members and others utilizing this publication are encouraged, as appropriate, to conduct an independent analysis of these issues. The NGWA does not purport to have conducted a definitive analysis on the topic described in this publication, and it assumes no duty, liability or responsibility for the contents or use of the publication.

Key Takeaways of This Section

- There are multiple potential sources of PFAS to groundwater. Recognized sources of PFAS include (a) storage, transfer, and use of AFFF for firefighting and fire training; (b) release from a variety of commercial and industrial sources; (c) disposal/land application of municipal biosolids; (d) discharge of effluent from municipal wastewater treatment systems; and (e) release of landfill leachate. Some of these release mechanisms differ from typical leaks, drips, spills, and ruptures associated with many other contaminants, and may contribute to broader distribution in the environment and groundwater, rivaling migration via advective flow.
- PFAS exhibit hydrophobic, lipophobic, and surfactant properties[1]. These factors combine to confer unique transport considerations.
- PFAS molecules are miscible in water. They will readily exist in the aqueous phase and will not exist as separate non-aqueous phase liquids (NAPLs) in the subsurface. PFAS surfactant characteristics enhance infiltration due to reduction in surface tension.
- The polar "head" of many PFAS, particularly PFAAs, tends to ionize in aqueous environments. Consequently, certain PFAS molecules are prone to sorption via electrostatic attraction to charged surfaces.
- PFAS also sorb to organic carbon owing to their hydrophobic and lipophilic C-F "tail." PFAS molecules exhibit relatively high Koc values compared to other common groundwater contaminants. However, Koc and degree of sorption is site-specific, contingent upon the sorptive medium

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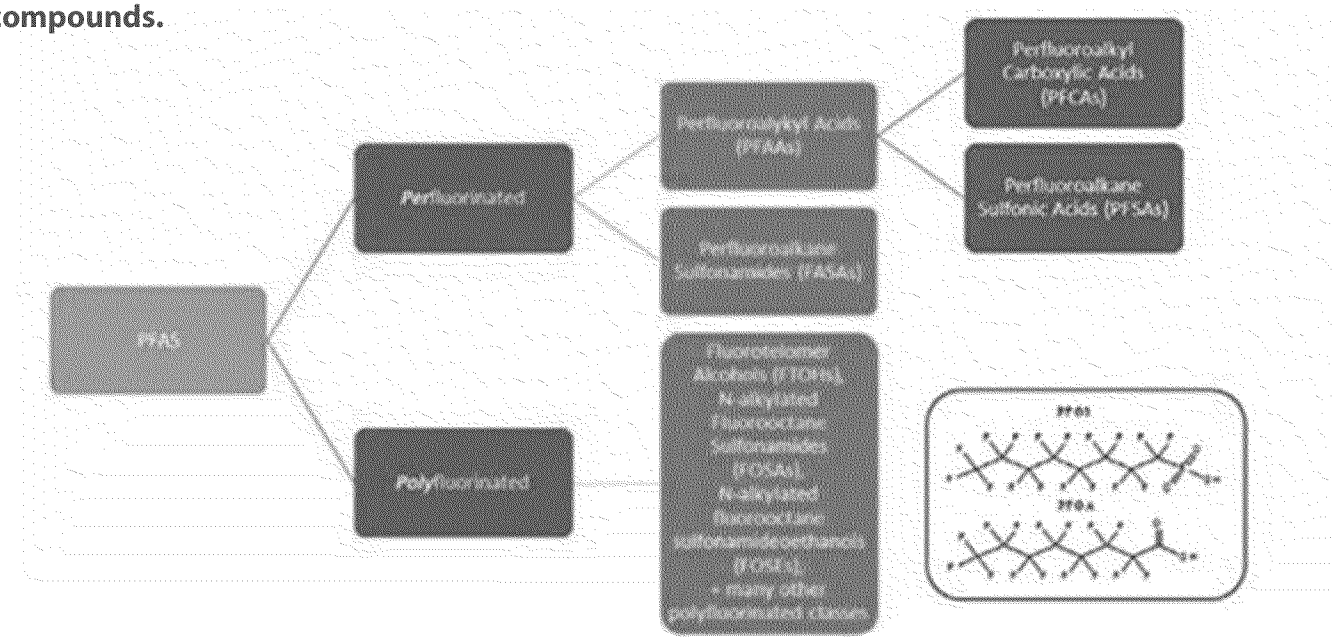
Figure 4.1. Simplified depiction of PFAS compounds grouped as per– and polyfluorinated compounds.



Source: S. Suthersan et al./ *Groundwater Monitoring & Remediation* 36, no. 3/Summer 2016 NGWA.org

(e.g., surface charge, mineralogy, and organic carbon content) and solution chemistry, especially ionic strength, pH, and calcium ion activity. Petroleum-based NAPL that may be present as a co-contaminant can lead to accumulation of PFAS at the oil-water interface due to the strong hydrophobic nature of the carbon-fluorine tail.

- PFAS molecules—especially polyfluorinated PFAS—may biotransform to stable, perfluorinated end products, with no further natural defluorination. The carbon-fluorine bond is very strong and the exterior fluorine atoms form a protective "shell." These characteristics make PFAS molecules especially stable and particularly resistant to degradationn by biological or chemical means. PFOS and PFOA can be present in the environment due to their creation via biotransformation of other PFAS (i.e., precursors), as well as because of their use in consumer and industrial products.

UNIQUE CHEMISTRY OF PFAS

The term PFAS includes both **poly**fluorinated alkyl substances, in which only some of the carbons in the alkyl chain have fluorines bound to them, and **per**-fluorinated alkyl substances, in which the alkyl-chain is fluorine-saturated (Buck et al. 2011). Figure 4.1 is a simplified depiction of poly- and perfluorinated alkyl substances. A substantial reason for the unique chemistry of PFAS is that the carbon-fluorine (C-F) bond is the strongest known carbon single bond (Table 4.1). Fluorine atoms on a PFAS molecule act as a shell that protects the C-C bonds and other bonds and renders the PFAS molecule resistant to cleavage. The combination of (1) strong C-F bond; and (2) protective shell of F atoms renders some PFAS especially stable and particularly resistant to degradation by biological or chemical means.

Table 4.1. Bond energy and bond length for selected elements singly bonded to carbon. (TAMU 2017)

Bond	Bond Dissociation Energy (kilojoules/mole)	Bond Length (picometers)
Carbon-Nitrogen	305	147
Carbon-Silicon	318	185
Carbon-Chlorine	327	177
Carbon-Carbon	346	154
Carbon-Oxygen	358	143
Carbon-Hydrogen	411	109
Carbon-Fluorine	485	135

[1] PFAS may behave as surfactants (literally "surface-active-agents") owing to their ability to lower the surface tension of a liquid, or the interfacial tension between two liquids, or between a liquid and a solid. In contrast to traditional surfactants (i.e., compounds possessing hydrophobic and hydrophilic moieties), PFAS surfactant properties may persist at very low concentrations (Buck et al. 2011).

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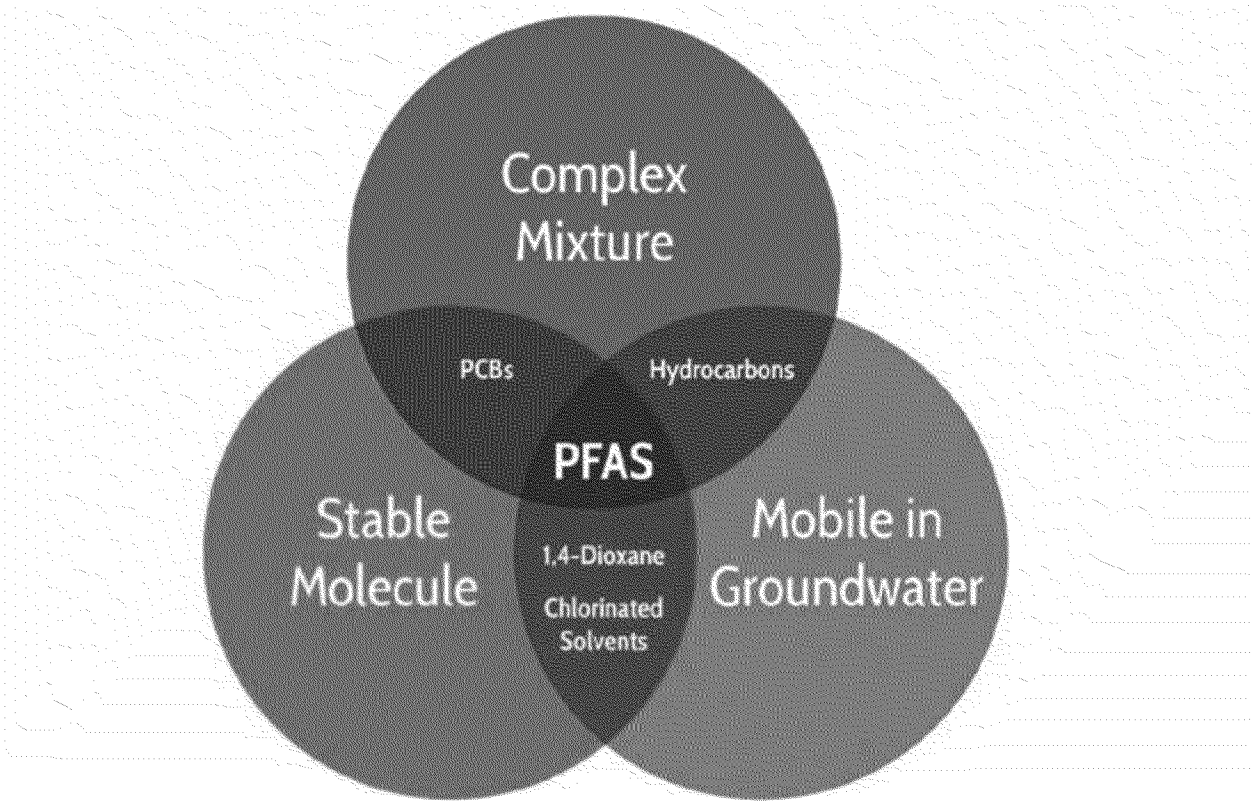
Figure 4.2. PFAS comparison to other contaminant classes.



Some PFAS exist in natural waters as anions, some as cations, and some as both:

- Anions are negatively charged.
- Cations are positively charged.
- Zwitterions have anionic and cationic portions.

Certain properties of many PFAS are similar to better-understood contaminants such as PCBs, chlorinated solvents, and hydrocarbons (Figure 4.2). For example, PFAS (especially originating from AFFF) tend to be present in complex mixtures, as is typical of hydrocarbons and PCBs. However, PFAS are much more soluble than PCBs, and are therefore more prone to forming dissolved-phase plumes. Unlike hydrocarbons and chlorinated solvents, the PFAS molecules are not considered biodegradable; precursors may be transformed via biodegradation into other PFAS species, but the total quantity of PFAS molecules is typically preserved. Some PFAS have similarities to chlorinated solvents in terms of mobility via advection and dispersion in groundwater, although there are limitations to this comparison. Chlorinated solvents and PFAS are both known to produce contaminant plumes of extended lengths. However, in situ biodegradation is a commonly applied remedy for chlorinated solvents but, to date, has not been shown to be effective for PFAS. In terms of recalcitrance, PCBs are a more apt comparison to PFAS; PCB congeners may biologically transform, but the number of PCB molecules can remain unchanged.

UCMR3 List, and PFOS and PFOA Chemistry

Six PFAS were listed on USEPA's UCMR3. A summary of their physicochemical properties is provided in Table 4.2.

The general properties of PFAS affecting fate and transport may be exemplified through consideration of two of the more common species: PFOS and PFOA. The molecular structures of PFOS and PFOA (perfluorinated alkyl substances) are presented in Figure 4.3, which illustrates some of their unique characteristics that affect fate and transport in groundwater. It should be noted AFFF formulations may contain dozens to hundreds of individual PFAS molecules; the discussion herein focuses on PFOA and PFOS because (1) they are the only PFAS molecules for which Health Advisory Levels have been published by the EPA; and (2) the most information is available for these

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Table 4.2. Chemical and physical properties of PFAS listed on USEPA UCMR3.

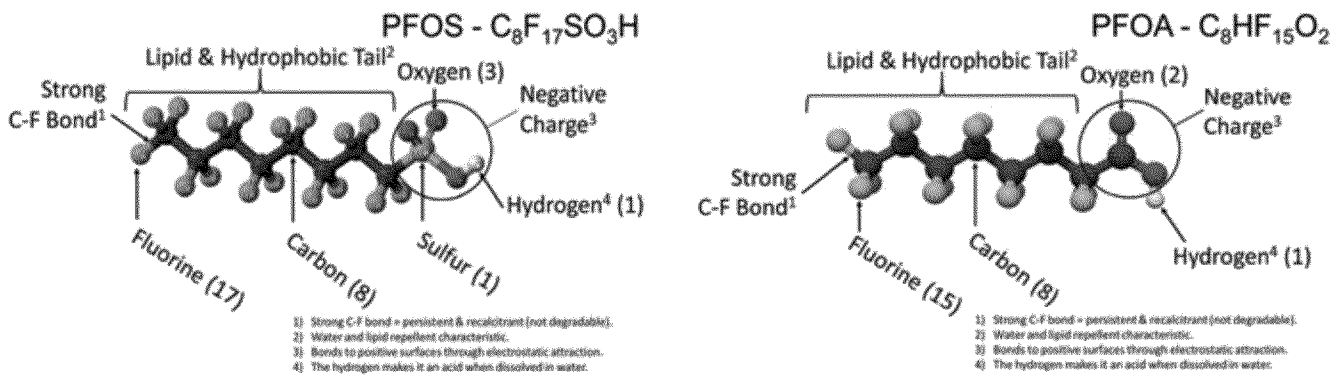
PFAS Listed in UCMR3	CAS RN	Chemical Formula	MW g/mol	pKa at 25°C (USNLM 2017)	Solubility, g/L at 25°C (Concawe 2016)	Log Kow (Concawe 2016)	Log Koc (USNLM 2017)	USEPA Health Advisory Level for drinking water
Perfluorooctane-sulfonic Acid (PFOS)	1763-23-1	$CF_3(CF_2)_7SO_3H$	500	<1.0	0.52 – 0.57	6.43	2.4 – 4.7	Individual or Combined 70 ng/L*
Perfluorooctanoic Acid (PFOA)	335-67-1	$CF_3(CF_2)_6COOH$	414	-0.5 – 4.2	3.4 – 9.5	5.30	1.92 – 2.59	
Perfluorononanoic Acid (PFNA)	375-95-1	$CF_3(CF_2)_7COOH$	464	-0.21	9.5	5.92	5.08	No Standard
Perfluorobutane-sulfonic Acid (PFBS)	375-73-5	$CF_3(CF_2)_3SO_3H$	300	-3.31	46.2 – 56.6	3.90	2.26	
Perfluoroheptanoic Acid (PFHpA)	375-85-9	$CF_3(CF_2)_5CO_2H$	364	-2.29	4.2	4.67	1.52 – 2.82	
Perfluorohexane-sulfonic Acid (PFHxS)	355-46-4	$CF_3(CF_2)_5SO_3H$	400	-6 – -5	2.3	5.17	1.78	

CAS RN = Chemical Abstracts Registry Number
MW = molecular weight
ng/L = nanograms per liter
g/L = grams per liter
g/mol = grams per mole
Kow = octanol/water partition coefficient
Koc = organic carbon partition coefficient
*The USEPA Health Advisory Level for drinking water is 70 ng/L for PFOS and PFOA as individual analytes, but EPA guidance recommends application of the 70 ng/L level to the combined concentrations.

compounds. Practitioners interested in the other PFAS described above can use this description as a general guide, but should look at the most current research for particular compounds.

As illustrated in Figure 4.3, PFOS has a sulfonate end ("head") comprised of three oxygens, a sulfur, and a hydrogen. PFOA exhibits a similar "head" comprised of two oxygens and a hydrogen with no sulfur. The hydrogen dissociates in aqueous systems, making PFOS and PFOA acids. When the hydrogen dissociates in water, the "head" of these compounds take on a negative charge, which contributes to

Figure 4.3. Ball-and-stick representation of PFOS and PFOA molecular structure. Carbon is black, fluorine is green, oxygen is red, hydrogen is white, and sulfur is yellow.



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Source of Figure 4.3

https://www.google.com/imgres?imgurl=https%3A%2F%2Fupload.wikimedia.org%2Fwikipedia%2 commons%2Fe%2Fe1%2FPerfluorooctanesulfonic-acid-3D-balls.png&imgrefurl=https%3A%2F%2Fcommons.wikimedia.org%2Fwiki%2FFile%3APerfluorooctanesulfonic-acid-3D-balls.png&docid=d-gU759J3hzAZpM&tbnid=SgQphTV_c0QkuM%3A&vet=10ahUKEwjw47Sy3bPWAhXoz1QKHUGKCQAQMwgoKAwAg.i&w=2895&h=1000&bih=674&biw=1366&q=pfos%20molecule%20image&ved=0ahUKEwjw47Sy3bPWAhXoz1QKHUGKCQAQMwgoKAIwAg&iact=mrc&uact=8

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Table 4.3. Comparison of PFOA and PFOS properties to other organic compounds.

Property	PFOS	PFOA	Benzene	PCE	1,4-Dioxane
Water Solubility (mg/L)	370[a] (freshwater) 550 to 570[a] (purified water)	9,500[a] (purified water)	1,780.5[f]	162[f]	Miscible[j]
Vapor Pressure @20°C (mm Hg)	2.48×10^{-6} [a]	0.017 [a]	105[g]	25[g]	38.1 (at 25°C)[j]
Koc (L/Kg)	229 to 6310[b] 580[c] 480[d]	203[c] 130[d]	58[f]	300[f]	17[j]
Half-life (years)	>41[a]	>92[a]	2[f]	23[f]	1.0[f]
Drinking Water Criteria (µg/L)	0.07[e]	0.07[e]	5[h]	5[h]	200[j]
	a USEPA 2014 [b] Franz et al. 201. [c] Ferrey and Wilson 2009 [d] Higgins and Luthy 2006 [e] USEPA 2016 (applies to individual or combined concentrations of PFOS and PFOA) [f] 25 Pa. Code Chapter 250, Table 5–Physical and Toxicological Properties, A. Organic Regulated Substances [g] Engineering ToolBox 2017 [h] USEPA Maximum Contaminant Level (MCL) [i] State action level (multiple states) [j] USEPA Technical Fact Sheet: 1,4-Dioxane. January 2014				

sorption by electrostatic attraction. Properties of PFOS and PFOA compared to other common groundwater contaminants are compared in Table 4.3.

Key takeaways about PFAS chemistry include:

- These PFAS are soluble in water, which means they will readily exist in the aqueous phase and will not exist as separate NAPLs in the subsurface. Therefore, migration of PFAS as pure-phase NAPLs is not expected at sites. However, as discussed below, some PFAS can dissolve into petroleum-based NAPL mixtures and be transported due to capillary phenomenon.
- Koc values for these PFAS may vary over several orders of magnitude depending on the site-specific geochemistry; therefore, characterizing sorption and retardation of PFAS may require a higher level of geochemical analysis. This facet of PFAS fate and transport also has implications in terms of remediation and treatment. Water chemistry matters when it comes to characterizing PFAS transport.
- This discussion has focused on PFOA and PFOS, although many other PFAS compounds are likely to be encountered in typical field scenarios. Other PFAS compounds may vary in all of the physical/chemical properties discussed herein, but are similar in terms of including the highly stable carbon-fluorinebond.

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ENVIRONMENTAL SOURCES

AFFF Composition, Release, Emplacement, and Migration

The presence of PFOA and PFOS in drinking water has emerged as a widespread concern. A recent survey estimated the EPA Health Advisory values are exceeded in drinking water supplies for 6 million people as of 2013 to 2015 (Hu et al. 2016). Much of the PFOA and PFOS contamination in drinking water originates from groundwater that has been affected by environmental releases. There are 290 military fire training areas (US DoD 2014) and 533 civilian airports (US FAA 2015) certified for the use of aqueous film-forming foam (AFFF) throughout the United States. The presence of military fire training areas was shown to be positively correlated to aqueous concentrations of PFOA and PFOS in the environment, but civilian airports were not positively correlated (Hu et al. 2016). This study was limited by only correlating PFOA and PFOS occurrences with GIS (geographic information system) locations with no consideration of hydrogeologic conditions or other possible PFAS sources (metal plating, PFTE manufacture, paints, food contact packaging, landfills, wastewater, etc.)

Formulations of PFAS used in AFFF have changed substantially, with variable manufacturing methods employed by different suppliers and at different times. The dominant PFAS-producing process prior to 2001 was electrochemical fluorination, which resulted in PFOS as a prevalent component of firefighting foams. This process was largely replaced by fluorotelomerization that produces fluorotelomers as molecular components of firefighting foams (Concawe 2016). Fluorotelomers are polymers of limited length (2 to 5 polymerizations). Fluorotelomer sulfonates (FtSs) are identified by the ratio of the perfluorinated to non-perfluorinated carbons in the molecule's chain length. For example, 6:2 FtS is a fluorotelomer sulfonate with 8 total carbons, 6 of which are perfluorinated. Fluorotelomer chains typically contain 8, 10, or 12 carbons (e.g., 6:2 FtS, 8:2, FtS, and 10:2 FtS). According to the Western Australia Department of Environment Regulation (2017), "Legacy AFFF …contains PFOS and PFOA; [these have been replaced by] newer AFFF formulations [which] contain fluorotelomers such as 6:2 FtS to 10:2 FtS. Longer-chain fluorotelomers (C8 and above) may degrade in the environment to produce [PFAAs such as] PFOA and perfluorohexanoic acid (PFHA)." Although fluorotelomer-based AFFF has recently displaced formulations containing PFOA and PFOS, fluorotelomer-based AFFFs have been on the market since the 1970s. Studies have reported that FtS are not the dominant fluorotelomers in telomerized AFFF, but rather are only present in small concentraitons and fluorotelomer thiamido sulfonates are more prevalent (Backe et al, 2013). The shorter-chain C6 fluorotelomers (6:2 FtS) cannot degrade to PFOS or PFOA (Concawe 2016); however, shorter-chain PFAS including end products still require consideration. More work is needed to assess the toxicological effects of shorter-chain PFAS and to guide the possible health advisory limits or regulations.

Discharge of AFFF, containing PFAS, differs from typical mechanisms of contaminant release to the environment, such as inadvertent drips, leaks, and spills. Mechanisms of AFFF release to the environment include: (1) low volume spills of foam concentrate during storage or transfer more likely to be present at areas where AFFF is stored, such as around above-ground storage tanks containing flammable liquids; (2) one-off, high-volume, broadcast application of foam solution for firefighting—typical at a site where a plane crash or significant fire occurred; (3) periodic, moderate to high volume, broadcast application of foam solution for apparatus testing or training—this release mechanism is especially relevant at firefighting training areas; and (4) incomplete treatment of effluent containing foam residues, which may impact surface water and sediments downstream of a wastewater treatment plant receiving influent with foam residues. AFFF is applied by mixing foam concentrate and water to make foam solution that is aerated when sprayed from a nozzle to produce finished foam. Thousands of gallons of foam solution may be applied for a fire or training event. Foam solution drains from the finished foam as an aqueous film with low surface tension that floats on fuel (Guzzi 2011; Vyas and Patel 2013). Depending on the ionic structure of the PFAS in the foam and the soil geochemistry, the foam solution may vertically infiltrate through soil to groundwater, potentially interacting with subsurface NAPL. In many FFTAs, NAPLs are used as fuel for the training exercises; in this case, PFAS may be present alongside the NAPL. Surfactant properties of many PFAAs can reduce interfacial ten-

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sion and result in adsorption at the fluid-fluid interface, potentially affecting the mobility and solubility of petroleum hydrocarbon NAPL. In addition to subsurface transport, AFFF may be prone to aerial dispersion and redeposition prior to infiltration (Guzzi 2011).

Depending on the release history and groundwater flow conditions, PFAS extent and distribution in groundwater associated with AFFF use may predominantly be associated with runoff and infiltration of foam solution around the time of the release, as opposed to subsequent horizontal migration in groundwater via advection and dispersion of dissolved PFAS (Hale 2016). This may be attributed to AFFF application over a broad area resulting in the runoff and infiltration (facilitated by low surface tension) of a high volume of foam solution; however, recalcitrance also plays a role. Advective transport of PFAS in groundwater can be inhibited by sorption and slower seepage velocities than surface water runoff.

Considering PFOS as an indicator constituent, higher PFOS concentrations (e.g., > 10 µg/L) may occur beneath fire training and AFFF bulk storage areas. Lesser PFOS concentrations (e.g., 500 ng/L to 10 µg/L) in groundwater may occur beneath satellite AFFF storage areas, historic fire locations, apparatus testing locations, and where infiltration of distal runoff occurs (Hale 2016).

In some instances, concentrations of PFAS in shallow soil correlate to underlying shallow groundwater concentrations by location. In these instances, shallow soil concentrations represent a residual fingerprint (perimeter and internal spatial concentration pattern) of past infiltration to groundwater that has been impacted by the direct infiltration of foam solution or foam concentrate (Hale 2016). As such, shallow soil analytical results may be used to guide intrusive groundwater investigation activities. If PFAS-impacted soil was excavated and placed above unimpacted groundwater, or if groundwater remediation occurred without soil remediation, leaching of residual PFAS from soil could exacerbate groundwater conditions. Treatment of co-contaminants, such as NAPL, can result in the biotransformation of precursor compounds to perfluoroalkyl acids (PFAAs). PFAA refers to a category of PFAS that describes perfluoroalkyl sulfonic acids (PFSAs) such as PFOS and PFHxS, and perfluoroalkyl carboxylic acids (PFCAs) such as PFOA and PFHpA.

Biosolids

PFAS have been widely detected in municipal biosolids (Venkatesan 2013). In one nationwide survey of biosolids, PFOS and PFOA were the most prevalent of the 13 PFAS measured, and were detected at an average of 403 and 34 ng/g respectively. Although Venkatesan and Halden (2013) demonstrated a significant presence of PFAS in biosolids, their work was done on biosolids from a 2001 inventory. PFOS and PFOA have been largely phased out since 2001, suggesting that biosolids might currently have lower PFOS and PFOA content; however, one more recent study (Armstrong et al. 2016) measured 12 PFAS in biosolids from 2005 to 2013 and reported no significant decrease in concentration with time of the 7 PFAS detected. In this study, PFOA, PFOS, and PFNA were all detected at an average of 22-25 ng/g. Approximately 50% of biosolids produced in the U.S. are applied to agricultural land as fertilizer (Sepulvado et al. 2011), providing a potential pathway for contamination of soil and groundwater.

Sepulvado et al. (2011) report that PFAAs can transport to groundwater via leaching, and leaching rates decrease with increasing chain length. This finding is consistent with reported Koc values, which increase with chain length for C5-C10 PFAS. This suggests that shorter-chain PFAAs might be more mobile in biosolid-affected groundwater.

Industrial biosolids, especially those associated with the manufacturing or processing of PFOA and PFOS, are also a pathway of these PFAS to groundwater. Lindstrom et al. (2011a) describe the impact of more than 34,000 dry metric tons of land-applied biosolids originating from local industries engaged in the production or handling of PFAS-containing materials. Although the concentrations of PFAS in the biosolids are not known, PFOS and PFOA were detected in the soil at concentrations of 30–410 and 5–320 ng/g, respectively.

Regardless of the concentration of PFAS in the applied biosolids, transport principles are consistent. Long- and short-chain PFCAs exhibit some differences in that longer-chain PFCAs are more strongly correlated with total biosolid mass applied while shorter-chain PFCAs are more subject to attenuation

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as the time since application increases (Washington et al. 2010). This demonstrates the effect of chain length and leaching potential on the transport of some PFAS in biosolids to groundwater and soils.

Landfill Leachate

The reported PFAS concentrations measured in landfill leachates range from below the reporting limit to 36 µg/L (Allred et al. 2015; Beskin et al. 2012; Ahrens et al. 2011). Although results reflect the selected analytes (there are many PFAS while only a small portion are individually quantifiable), referenced studies reported similar quantities of PFAS analytes. Typically landfill leachate is either recirculated through the landfill or treated. If treated, typically a municipal wastewater treatment plant (WWTP) receives the leachate and may be ill-equipped to remove or treat PFAS (see Wastewater Treatment Systems below). The estimated 8.5–25 kg/year of PFAS (Beskin 2012) leaving a landfill via leachate has the potential to impact WWTPs and surface water bodies that receive WWTP effluent. This may also be a significant source of PFAS to biosolids. If leachate recirculation is employed, there is a risk of contaminating the surface water and an increased likelihood of leachate leaking into the aquifer due to the increase in leachate head.

Possible contributions of PFAS in groundwater via landfills should be considered on a site-by-site basis. There are many characteristics that would alter a landfill's likelihood of PFAS release (leachate handling, liner integrity, etc.) making the risk each landfill poses unique.

Wastewater Treatment Systems

Wastewater treatment systems can transport PFAS via effluent and biosolids. Biosolids containing PFAS have the potential to impact soil, groundwater, and surface water when used as soil amendments (as discussed above). WWTPs that do not employ treatment steps that possibly remove PFAS (specifically, reverse osmosis, ion exchange, or granulated activated carbon) can be a significant source of PFAS to surface water. These treatment technologies are rarely used in conventional WWTPs, making WWTP effluent a potential source of PFAS to surface water.

Houtz et al. (2016) explore PFAS concentrations in six WWTP effluents. Sampling demonstrated decreases in PFOA and PFOS concentrations from 2009 and 2014 (32 to 21 ng/L and 24 to 13 ng/L, respectively) while there were increases in the concentrations of shorter-chain PFAS such as PFBA and PFPeA (7.4 to 16 ng/L and 6.7 to 12 ng/L, respectively). The changes in effluent composition may result from the shift of fluorotelomer manufacture away from C8 PFAS (PFOA and PFOS) and toward shorter-chain PFAS.

It has also been shown that concentrations of PFOS and PFOA can increase from inflow to the outflow of a WWTP (Schultz et al. 2006; Sinclair et al. 2006). This is likely due to the biodegradation of precursor PFAS to stable end products (PFOS and PFOA, among others) during secondary treatment.

Onsite wastewater treatment systems, specifically septic systems, can be a source of PFAS to groundwater and domestic drinking water wells. In one study, 20 domestic water wells were sampled and some PFAS were detected in more than 50% of the wells (PFOS, PFHxS, PFBS, and PFHxA) (Schaider et al. 2016). Using the co-occurrence of nitrate, which also can leach from a septic tank to a domestic water supply well, it was determined the source of PFAS in most of the impacted wells was the septic system. There was also some evidence a nearby landfill may have impacted two wells. In domestic areas utilizing onsite wastewater treatment systems, it is important to consider the transport of organic wastewater compounds into the aquifer.

As the composition of PFAS in consumer products and industrial uses shift, and as impacts from historical releases decrease, the composition of WWTP effluent will likely continue to shift in the future.

Air Deposition

Air deposition can be an important source of PFAS for areas directly surrounding a production facility that produces, manipulates, or applies fluorinated coatings or products. Polytetrafluoroethylene (PTFE) coatings, which are ubiquitous in consumer goods, are prepared from colloidal aqueous dispersions of PTFE particles, stabilized with appropriate surfactants. Historically, PFOA and PFOS were used as surfactants in PTFE dispersions. The surfactants were removed in a drying process, in many cases leading to widespread atmospheric deposition of PFOA and PFOS from drying stack emissions. The potential impact of air deposition should be evaluated if production facilities are nearby.

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Figure 4.3.

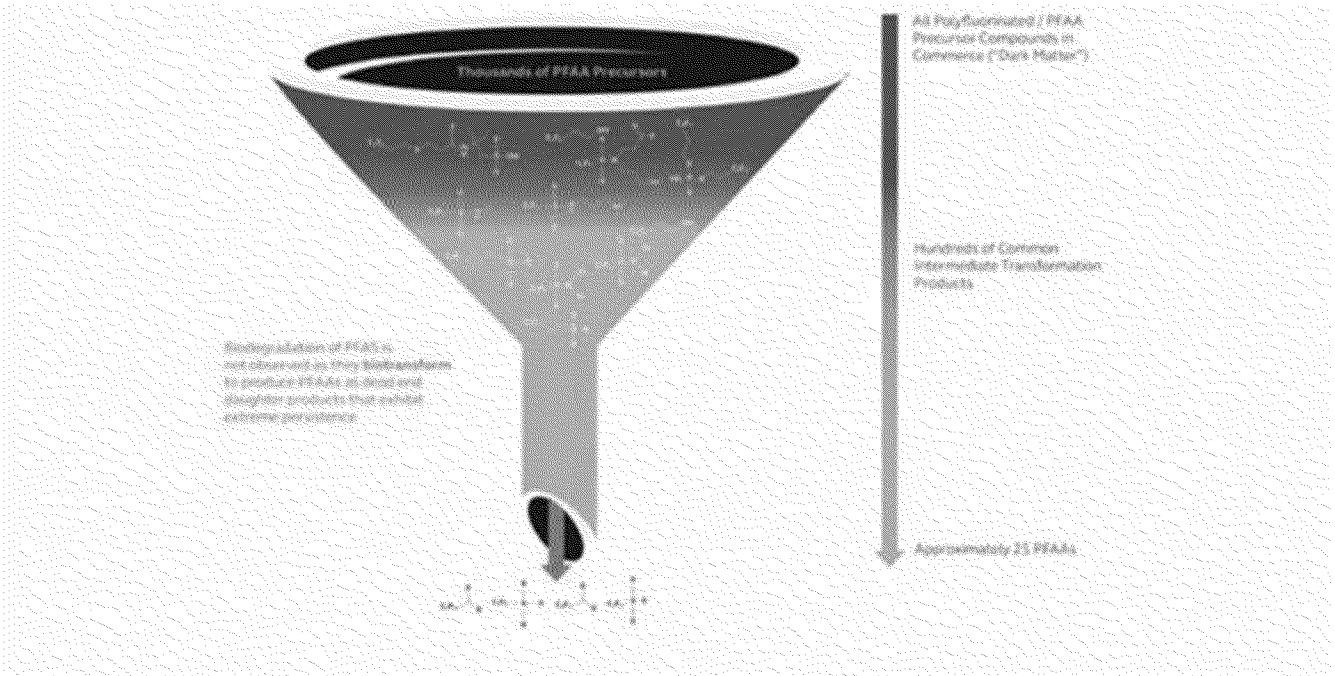

Figure 3. Aerobic biotransformation funnel: There are potentially thousands of PFAA precursors, which can biotransform under aerobic conditions to make hundreds of common polyfluorinated intermediate products. The terminal aerobic biotransformation products of all of these PFAA precursors are the perfluorinated acids. The terminal acids produced through aerobic biotransformation contain the same number or fewer of fluorinated carbons as the original PFAA precursor structure. Some PFAA precursors, such as many fluorotelomer compounds, will partially defluorinate in the aerobic biotransformation process.

Suthersan et al. 2016 (NGWA copyrighted)

PFAS have also been widely detected in precipitation in the form of rain and snow (Codling et al. 2014). Studies have shown urban regions which are strongly affected by wintertime snowfall are impacted by atmospheric deposition of PFAS.

MOBILITY

PFOA and PFAS are far less volatile and may be more prone to sorption than other common contaminants (e.g., benzene, PCE, MtBE), based on comparison of organic carbon partition coefficients (Koc) and vapor pressure. As an example, values of Koc for PFOS range from 229 to 6310 (Franz et al. 2013). The sorption of PFOS and its Koc vary depending on site-specific factors (Higgins and Luthy 2006; Chen et al. 2009; Tang et al. 2010; Chen et al. 2012; Wang and Shih 2012).

Generally, shorter-chain PFAS are more mobile in groundwater and will leach from soil to groundwater at a faster rate (Sepulvado et al. 2011). This results in shorter-chain PFAS at the leading edge of a groundwater plume. Other factors affecting PFAS sorption in the subsurface include:

- The presence of other PFAS compounds competing for sorption sites.
- The solution chemistry of the water in which PFAS is dissolved.
- Characteristics of the sorptive/aquifer matrix (e.g., organic carbon content and surface charge), particularly at AFFF-impacted sites (Guelfo and Higgins 2013).
- Co-contaminant interference at sorption sites.
- NAPL as a sorbent.
- Hydrocarbon surfactant-enhanced PFAS solubility.
- Increased sorption of hydrocarbon surfactant–PFAS mixed hemi-micelles.

PFAS can sorb to organic carbon, positively charged mineral surfaces, and oil by hydrophobic and electrostatic interactions. Low pH (increased hydrogen ion activity) and high calcium ion activity tend to promote sorption. Anions in solution may compete with PFOS for electrostatic adsorption to positive surfaces (i.e., the electrical double layer effect); however, anions in solution may also reduce repulsion of

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PFOS molecules, forcing them to pack together on weakly charged surfaces.

PFOS tends to exist as dissolved species in low salinity water, i.e., freshwater, but sorbs to sediment in high salinity water, e.g., seawater (Weiss et al. 2015).

MASS BALANCE

The chemical bond between carbon and fluorine is short, strong, and difficult to break thermally, chemically, or biologically. The enzymes produced by environmental bacteria can attack the longer, weaker bonds between carbon and other elements in polyfluorinated precursors, leaving stable perfluorinated chemicals in the environment, particularly the longer-chained PFOA, PFOS, and PFNS, but also PFBS, PFHxS, and PFHpA. Suthersan et al. (2016) call the stable perfluorinated chemicals formed from PFAS precursor degradation "dead-end daughter products." Suthersan et al. (2016) call this transformation of a wider range of PFAS species into a smaller number of dead-end daughter products "biological funneling" (Figure 4.4).

Our 21st century identification of PFAS as an emerging contaminant is analogous to polychlorinated biphenyls (PCBs) in the 20th century. Both classes of compounds were highly valued for their chemical stability, which directly translated to environmental stability and persistence. Biological degradation is the predominant natural attenuation process in soil and groundwater. Biodegradation intermediates typically partition differently between soil and groundwater than their parent chemicals. PCB biotransformation generates chemical intermediates (commonly referred to as "daughter products") that are less chlorinated, more water-soluble, more mobile, and more easily biodegraded. In contrast, although polyfluorinated precursors have moieties that can biotransform, they can be less water-soluble and less mobile than their dead-end perfluorinated daughter products (Bhhatarai and Gramatica 2011).

To date, evidence suggests PFAS are in general very resistant to biotransformation. In situ, anaerobic, reductive defluorination mechanisms have not yet been established. Aerobic processes can partially defluorinate PFAS precursor compounds, but their perfluorinated daughter products are persistent (Suthersan et al. 2016). Petroleum hydrocarbon co-contaminants in firefighting training areas that have high concentrations of PFAS from AFFFs typically consume groundwater oxygen, generating anaerobic PFAS plumes. In situ chemical oxidation (ISCO) remediation of co-contaminants in groundwater contaminated with PFAS can generate dead-end perfluorinated daughter products, including PFOA (McKenzie et al. 2016). Understanding mass discharge at PFAS-contaminated sites is essential to site evaluation geared toward developing remediation plans that will give priority to both water resource protection and cost-effective site restoration.

Many factors complicate the estimation of a mass balance at PFAS sites, including:

- The large universe of PFAS, and the fact that a significant portion of the total environmental PFAS is currently unidentified (Richardson and Kimura 2016).
- The difficulty detecting and quantifying many classes of PFAS.
- Biotransformation of polyfluorinated precursor compounds to perfluorinated compounds.

These factors need to be considered when evaluating PFAS sites, as they can lead to underestimates of contaminant nature and extent and consequently misspent remediation dollars. Difficult-to-detect polyfluorinated compounds can be carried by advection with groundwater flow (Houtz et al. 2013). As these compounds enter the biodegradation "funnel" (Figure 4.3), they can transform to persistent perfluorinated end products, leading to increased downgradient abundance of persistent PFAS. Section 5, Field Sampling and Analyses, discusses specialty analytical methods for soil and groundwater that can be used to quantify the bulk amount of precursors in the funnel. These analyses, along with laboratory methods for quantifying individual compounds, can be used to estimate the mass balance at a site.

In one sense, the generation of persistent, bioaccumulative PFAS downgradient from the source is akin to the generation of vinyl chloride from PCE and TCE. However, a key distinction is that with chlorinated solvents, the parent compounds are relatively easily measured and the degradation pathways are well understood, leading to a comprehensible mass balance. The enormous variety of PFAS parent compounds and precursors—that critically can be difficult to detect and quantify—and degradation pathways complicates mass balance estimation significantly. Additionally, unlike PCE and TCE, atmospheric

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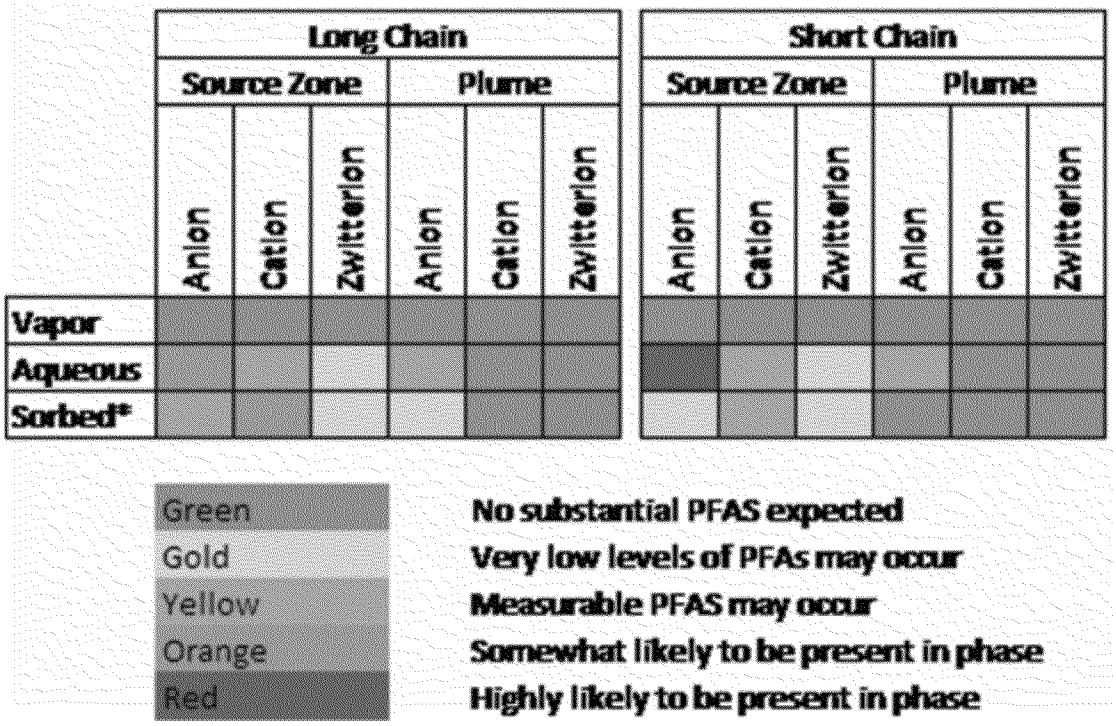
Figure 4.4. Modified 14-compartment model set up for long-chain PFAS (e.g., PFHpA, PFOA, PFOS, PFNA) and short-chain PFAS (e.g., PFBS, PFHxA).



*Sorption of PFAS is highly dependent on site-specific parameters, including mineralogy and organic carbon (as discussed previously in the Mobility section). Color-shading reflects general values.

deposition of PFAS can be a non-point source input to the mass balance that is unrelated to a site-specific discharge or source. PFAS surfactants used to prepare fluorinated polymers can travel great distances from their source before they enter ground- and surface waters (Stemmler and Lammel 2010; Taniyasu et al. 2013; Wang et al. 2014).

DISTRIBUTION IN THE SUBSURFACE

Previous sections have illustrated that PFAS in the subsurface can originate from diverse environmental sources. The nature of the resulting PFAS distribution in the subsurface greatly depends on the method of release and subsequent transport. As noted previously, post-release surface transport of AFFF can result in a widely dispersed initial footprint. Although PFAS extent and distribution in groundwater associated with AFFF use may predominantly be associated with runoff and infiltration of foam solution around the time of the release, subsequent transport in groundwater can also be significant, and has resulted in plumes extending downgradient for extended distances at many documented sites.

When considering the distribution of PFAS in the subsurface, the "source" can encompass the footprint of the original release, including post-release surface transport; the "plume" can refer to the area downgradient of the release that has only been impacted due to groundwater transport. The source/plume relationship may be different for PFAS than other organic contaminants such as chlorinated solvents or hydrocarbons. In source areas, chlorinated solvents and hydrocarbons may be present as non-aqueous phase liquids (NAPLs), whereas PFAS may comprise a different chemical signature in the source zone than in the plume. Soil sampling can be helpful in resolving the source footprint and differentiating it from the advective plume. In general (depending on the age of the site and co-contamination), unless groundwater flow is particularly rapid, the source zone is more likely to be affected by a relatively higher concentration of precursors while the plume is likely to be enriched in the dead-end products, which include PFOA, PFOS, and the other UCMR3 PFAS. Vertical transport and transformation processes may also play a role in source zone PFAS distribution.

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Substantial knowledge gaps exist in terms of our general understanding of the subsurface distribution of PFAS. Three primary factors behind the knowledge gaps include (a) the complex mixture of compounds comprising PFAS, (b) the lack of simple analytical methods to identify specific compounds, and (c) the combined hydrophobic/hydrophilic nature of the PFAS molecules that strongly affects sorption and mobility. Specific knowledge gaps include:

- Limited data on transport-related properties of PFAS other than PFOA and PFOS, including precursors and other dead-end products.
- Limited understanding of sorption mechanisms; e.g., conditions under which a linear organic-carbon sorption model is applicable, and recommendations for alternative sorption models.
- The surfactant properties of PFAS (the combined hydrophobic/hydrophilic nature) can lead to partitioning at the interfaces of environmental media, such as soil/water, water/air, and water/non-aqueous phase co-contaminants. In sufficient concentrations, PFAS may form hemimicelles at the air/water interface. It is not clearly understood when partitioning to interface is or is not probable in the subsurface at PFAS-impacted sites.
- The role of precursors in maintaining a contaminant plume is also not well understood. Precursor identification and quantification has largely been limited to academic studies to date.
- The potential effects of non-aqueous phase liquid co-contaminants (such as hydrocarbon NAPL at a fire training area) for PFAS distribution in the subsurface is also not well understood. The surfactant properties of the compounds complicate the interaction between PFAS and NAPLs.

As a means to present the relative importance of subsurface PFAS distribution in different environmental media, a 14-compartment model adapted from ITRC (2011) was utilized. The "NAPL" phase was removed from the standard 14-compartment model, as PFAS are unlikely to be present as a non-aqueous phase liquid. However, it is noted that in multi-phase systems where a NAPL phase is present (e.g., chlorinated solvent or petroleum), fluid interfaces may play an important role in PFAS distribution and partitioning. Partitioning of PFAS into a NAPL phase is a complicated process that is beyond the scope of this discussion. For this discussion, the model compartments were further subdivided into the various ionic species of PFAS: anions, cations, and zwitterions (molecules that contain both positively and negatively charged groups).

All six of the UCMR3 PFAS compounds, and the dead-end products discussed previously, are anions. Specifically, these compounds are acids that dissociate into anionic form at near-neutral pH values. The compartmental model is shown in Figure 4.4 for both short-chain PFCAs and long-chain PFCAs (long-chain PFAS are classified as PFCAs with seven or more perfluoroalkyl carbons and PFSAs with six or more perfluoroalkyl carbons). Color-coded ratings are assigned to each compartment with the intent of illustrating PFAS distribution at a typical site. The color-coding presented herein is based on expected behavior under hypothetical circumstances; actual presence and distribution of the PFAS compounds is highly site-specific, depending on factors such as geochemistry, co-contaminants, and source strength.

EXPOSURE POINTS

Non-occupational human exposure to per- and polyfluorinated compounds typically occurs through food, drinking water, and air. Food accounts for 90% of non-occupational exposure (Fromme 2009). If an individual's water supply has been impacted by PFAS, drinking water can become the dominant exposure pathway rather than food (Weiss et al. 2015). Infants may be exposed to PFOA and PFOS through breastfeeding as breastmilk will contain higher levels of PFAS than the impacted water consumed by the mother (Mogensen et al. 2015). Even if not used for drinking water, groundwater contaminated with PFAS can be discharged to surface water. Surface water has additional exposure points including drinking water, recreational use, and fish consumption.

Due to the bio-accumulative properties of PFAS, fish from impacted surface water bodies are dominant exposure to PFOS and other long-chain PFAS (Haug 2010).

The prevalence of PFAS in drinking water was surveyed as part of the USEPA Unregulated Contaminant Monitoring Rule (UCMR3), which found 66 public water supplies that contain PFOA and PFOS concentrations greater than the current health advisory of a combined PFOS and PFOA concentra-

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tion of 70 ppt (Hu 2016). Hurley et al. (2016) correlate higher levels of PFOS and PFOA in the blood of people residing in Californian zip codes with PFOA/PFOS detections than in the blood of people residing in zip codes with no PFOA/PFOS detections. Despite the low concentrations of PFAS relative to other studied emerging contaminants in public water supplies, the USEPA health advisory concentrations indicate that water with very small amounts of PFOA and PFOS can be a health concern for sensitive populations when exposed over a lifetime.

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Groundwater and PFAS: State of Knowledge and Practice

Field Sampling and Analyses
Section 5

One of eight sections prepared by National Ground Water Association volunteers. Each section was prepared to stand independently, or to be integrated with the other seven sections.

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Field Sampling and Analyses

INTRODUCTION AND SCOPE

This section presents and discusses the current best practices for the collection and analysis of environmental samples for PFAS. Emphasis is placed on water samples (e.g., drinking water, groundwater, and surface water); other media [soil, sediment, biota (e.g., fish tissue), and waste] are not discussed. Emphasis is also placed on laboratory analysis using USEPA Method 537 Revision 1.1, as subsequently clarified in a Technical Advisory issued by USEPA (referred to simply as USEPA Method 537 in this section) (USEPA, 2009, 2016a); other laboratory analytical methods and field screening methods are briefly discussed to the extent they are commercially available in the U.S.

Some sources of PFAS, such as aqueous film-forming foams (AFFFs), include many fluorinated compounds, many of which are difficult to quantitate using promulgated analytical methods and commercial laboratories. However, some polyfluorinated compounds can degrade in the environment to perfluorinated compounds that are of regulatory interest. It is for this reason that some specialty analytical methods are briefly discussed in this section.

USEPA Method 537 is a laboratory analytical method that was promulgated in September 2009 for the quantification of 14 PFAS. In May 2012, USEPA promulgated the third Unregulated Contaminant Monitoring Rule (UCMR3), which required all large public water suppliers and a subset of smaller water suppliers to test for the following six PFAS (USEPA 2012):

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

This discussion is generally focused on the six UCMR3 PFAS.

Disclaimer: This publication is a collaborative effort to try to set forth best suggested practices on this topic but science is always evolving, and individual situations and local conditions may vary, so members and others utilizing this publication are free to adopt differing standards and approaches as they see fit based on an independent analysis of such factors. This publication is provided for informational purposes only, so members and others utilizing this publication are encouraged, as appropriate, to conduct an independent analysis of these issues. The NGWA does not purport to have conducted a definitive analysis on the topic described in this publication, and it assumes no duty, liability or responsibility for the contents or use of the publication.

Sampling and Analysis Program Considerations

When formulating a sampling and analysis program, it is important to develop appropriate data quality objectives (DQOs) that consider how the resultant data will be used and by whom. For example, if sampling a public water supply, USEPA Method 537 should be used for analysis since the method is specific to drinking water samples. When conducting a site investigation, such as a remedial investigation at a Superfund site, a different method might be more appropriate. The level of rigor required for the sampling and analysis, such as the collection of quality assurance/quality control (QA/QC) samples and validation of analytical data packages, may also vary depending on the project objectives and the potential consequences of the results.

Although this document is focused on the six UCMR3 PFAS, some sampling and analysis programs may only need to focus on PFOA and PFOS, for which USEPA or State agencies have issued lifetime health advisories for drinking water. For other programs, it may be prudent to analyze more than the six UCMR3 PFAS. USEPA Method 537 was promulgated for 14 PFAS, and some commercial laboratories have modified the method to analyze additional PFAS.

The matrix(ces) to be analyzed can impact many

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aspects of the sampling and analysis program, including the analytical method and choice of laboratory.

Any sampling and analysis program for PFAS must also consider the potential for sample contamination due to well materials, sampling equipment, and the clothing, personal protective equipment (PPE), and/or personal care products in use by the field personnel at the time of sample collection. This is important due to the pervasive use of PFAS in commercial products, the single-digit ppt detection limits, and the ppt concentrations of regulatory interest. The potential for cross contamination is discussed later in this section.

LABORATORY ANALYSES AND FIELD SCREENING METHODS

Standard Laboratory Analytical Methods

USEPA Method 537 (USEPA 2009)

USEPA Method 537 is currently the only promulgated method for the analysis of PFAS. It is a liquid chromatography/tandem mass spectrometry (LC/MS/MS) method. There are laboratories that follow this method as written, especially for the six UCMR3 PFAS in drinking water. However, most laboratories have their own modified version of Method 537 based on their expertise and improvements in available equipment/calibration standards, to analyze for selected PFAS in additional matrices (groundwater, surface water, soil, sediment, tissue, etc.), and to achieve lower method detection and reporting limits than presented in the published method. In addition, there are linear and branched isomers of some PFAS, and Method 537 specifically addresses including the branched isomers when quantitating for PFOS and PFHxS. In September 2016, USEPA issued a Technical Advisory recommending that laboratories also quantify linear and branched isomers for PFOA (USEPA 2016a). Since the Technical Advisory is a recommendation, it is important to discuss the project objectives with the laboratory when setting up the analytical program, particularly with regards to quantitating for linear and branched isomers.

The typical turnaround times for data from the laboratories using USEPA Method 537 (with or without modification) ranges from two to six weeks depending on the sample matrix, the requested PFAS analyte list, number of samples submitted, and the data deliverables requested [e.g., results only data package; sample results with QA/QC results (USEPA Level II); sample results with QA/QC results and raw data (USEPA Level IV); and/or an electronic data deliverable (EDD)].

NGWA does not endorse or recommend vendors, and it is up to the user to select a laboratory based on the specific needs of a project. In response to increased market demand, there are now many commercial laboratories providing Method 537 analyses throughout the U.S. Information about these laboratories is available online. Although not comprehensive, useful starting points include the following:

- The list of laboratories provided by USEPA in conjunction with UCMR3 (https://www.epa.gov/dwucmr/list-laboratories-approved-epa-third-unregulated-contaminant-monitoring-rule-ucmr-3 or https://www.epa.gov/sites/production/files/2016-10/documents/ucmr3-lab-approval.pdf).
- The searchable database of laboratories accredited by the U.S. Department of Defense (DOD) to perform Method 537 analyses for its projects (http://denix.osd.mil/edqw/accreditation/accreditedlabs/). Note, however, that only a few of the laboratories that perform these analyses are currently accredited by U.S. DOD.
- The environmental, health and/or laboratory-certification agency for the state in which the sampling is being performed. In addition to USEPA requirements and approvals, individual State certifications and approvals should be considered when selecting a laboratory.

ASTM D7979-16 (ASTM, D7979-16)

While less common than USEPA Method 537, which can be modified for the analysis of liquid samples apart from drinking water, ASTM Method D7979-16 can be used for a wide variety of matrices including groundwater, surface water, wastewater, and sludge. Concentrations are determined through a combination of liquid chromatography followed by tandem mass spectrometry (LC/MS/MS).

USEPA SW-846 Method 8321B (SW-846, 2007)

USEPA SW-846 Method 8321B was a precursor to USEPA Method 537, but is still available as a means for analyzing nonvolatile compounds such as PFAS. Concentrations are determined through a combination of high performance liquid chromatography and thermospray mass spectrometry (HPLC-TS-MS).

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Specialty Analytical Methods

As discussed earlier in this section, some sources of PFAS (e.g., AFFFs) include many fluorinated compounds, many of which are difficult to quantitate using promulgated analytical methods and commercial laboratories. Moreover, some of the polyfluorinated compounds that may be present are precursors, meaning they can transform in the environment to the perfluorinated compounds which are currently of regulatory interest. Three specialty analytical methods are briefly discussed below that can be used to evaluate the importance of polyfluorinated compounds to the fate and transport of perfluorinated compounds.

Particle Induced Gamma-Ray Emission (PIGE) Analysis (Schaider 2017)

The PIGE spectroscopy method was developed by Dr. Graham Peaslee and his research group at the University of Notre Dame to screen groundwater and soil samples for total fluorine [similar to how total petroleum hydrocarbons (TPH) can be analyzed at hydrocarbon-impacted sites]. This method can reportedly be performed at a much lower cost compared to standard LC/MS/MS, and can achieve detection limits in the single- to low double-digit parts per billion (ppb) range as fluorine. The resulting total fluorine results can be used to guide characterization locations and delineate the footprint of PFAS-contaminated sites before more extensive analysis for individual PFAS.

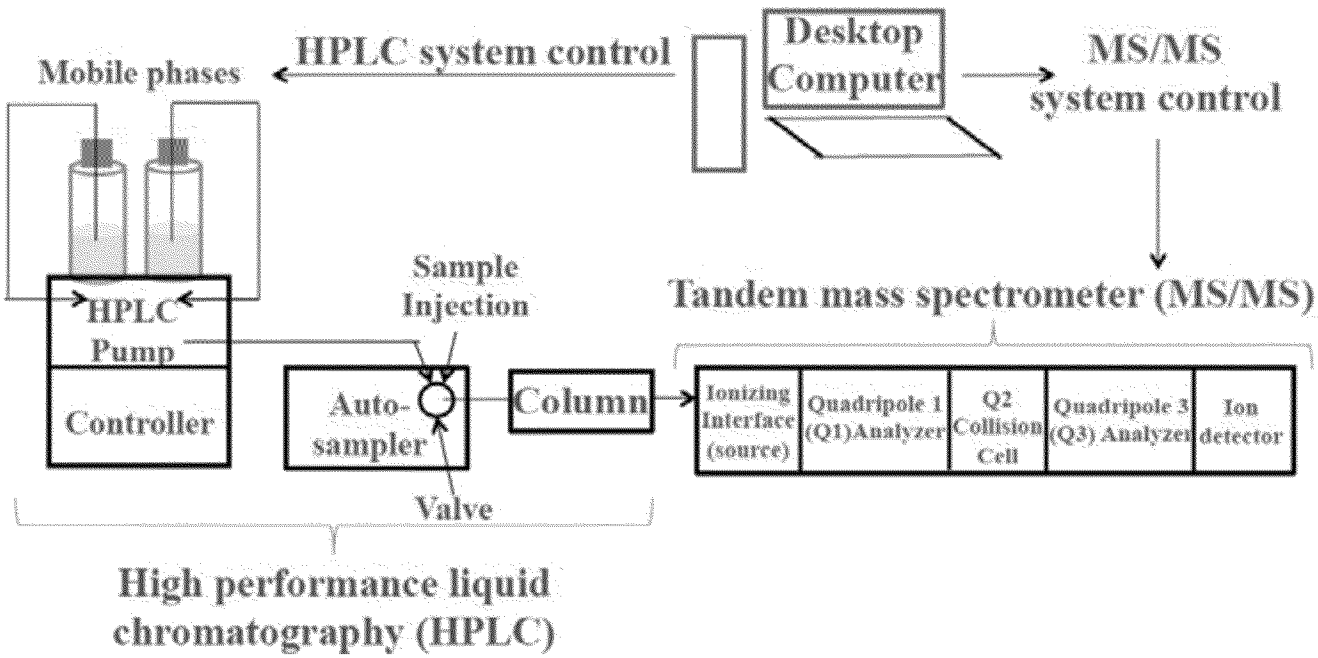
Total Oxidizable Precursor (TOP) Assay

TOP assay involves the use of USEPA Method 537 twice on two identical samples (the second collected similar to a duplicate sample). One sample is analyzed by USEPA Method 537. The other sample is heated and chemically oxidized and then analyzed using USEPA Method 537. The results for the various PFAS are then compared and the difference represents that portion of the precursor pool that can degrade to the perfluorinated compounds that are quantitated by EPA Method 537 (Houtz and Sedlak 2012). It is important to note, however, that the chemical oxidation of the sample is unlikely to completely transform all the fluorinated compounds that may be present in the sample to the perfluorinated compounds being analyzed.

Adsorbable Organic Fluorine (AOF) Analysis

AOF analysis uses combustion ion chromatography (CIC) to provide a total fluorine value (similar to how TPH can be analyzed at hydrocarbon-impacted

Figure 5.1. Liquid chromatography tandem mass spectometry LC/MS/MS



Source: Guelfo, Jennifer. Analysis of Per and PolyFluoroalkyl Substances (PFAS), Brown University Superfund Research Program, August 2016.

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sites). PFAS and other organic constituents are sorbed to an activated carbon matrix. The matrix is then combusted, and the resultant fluoride is measured via ion chromatography (Wagner et al. 2013), with fluorine detection limits in the single-digit ppb range.

Advances in Mobile Laboratory Technology

Site characterization programs for PFAS often involve well drilling, borehole geophysical logging, packer testing, groundwater sampling, and multi-level monitoring well completions. The time-critical nature of these integrated field activities has resulted in the development of at least one mobile laboratory that utilizes LC/MS/MS to provide scientifically defensible water quality analyses (using modified EPA Method 537) in the field, at single-digit ppt detection levels. Another mobile laboratory is reportedly being developed that uses a different analytical method to provide field screening capabilities at the ppb level. The availability of these and possibly other real-time field screening and analysis methods is expected to grow significantly over time. State agency regulatory acceptability and certification of mobile laboratories should also be considered.

Other Considerations for Laboratory Analyses

Components of Analytical Equipment

While there are several laboratory analytical methods as described above, the standard methods each analyze a water matrix using liquid chromatography (LC) to separate the various compounds and tandem mass spectrometry (MS/MS) to detect and quantify. As PFAS can be present in materials used to store, filter, and prepare samples for analysis, some laboratories have modified their methodology to reduce the potential for laboratory-related cross contamination that could appear in the sample results.

Cost

The cost to analyze a sample for PFAS varies quite widely due to a number of factors, including: the analytical method; number of PFAS to be quantified; required turnaround time; requested deliverable(s); number and timing of samples (volume discount, available capacity); and the laboratory. However, PFAS analyses are generally more expensive than routine organic analyses, such as volatiles, semi-volatiles, pesticides, and polychlorinated biphenyls.

Analytical Expectations and Data Validation

The method detection limits for laboratory PFAS analyses are currently in the single digit ppt range. Moreover, PFAS have been used for many purposes for several decades and are environmentally persistent. As a result, there is a likelihood that some PFAS will be reported as being present in environmental samples regardless of where the samples are collected or the analytical method employed. This potential for PFAS to be reported in samples should be expected, and communicated to stakeholders, before the sampling is performed. It is important that the project team understand the analytical acceptance criteria and evaluate whether those are acceptable for the project DQOs. It is also important to discuss with the laboratory and understand the potential effects of the presence of analytes in sample matrix, and if so, are there corrective measures or alternative analytical techniques that may be used.

The lack of standards, guidance values, or health advisories for many PFAS is an additional complication which must be considered. The consequence of detections should be considered in advance and data assessment should include explanations for low-level PFAS concentrations reported in samples. This can include discussion of the QA/QC process and results to evaluate whether the reported concentrations are a potential artifact of field or laboratory sample handling, and discussion of the concentrations with regards to what might be expected given the persistent nature of PFAS, concentrations in the source zone, and the sample location relative to the source zone.

Data validation may be especially important for PFAS sample analysis, due to the low concentration of regulatory interest and the potential for cross contamination, as discussed previously. Although it increases the cost of the project, data validation should also be considered. Validation consists of the detailed review of the analytical results and the supporting QA/QC information to help determine if the data are of sufficient quality to meet the project's data quality objectives and to identify potential issues with the analyses and/or the results. To support data validation, the required QA/QC samples must be collected for analysis, and a complete Level IV analytical package must be obtained from the laboratory. If data validation will be performed, it is important

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to coordinate with the laboratory and ensure the laboratory is aware and can meet any project-specific analysis requirements that the data validator will be using.

USEPA does not currently have data validation guidelines specific to PFAS. As a result, data validators are using USEPA's general guidelines for validating organic data (USEPA 2016b) along with the method description/requirements (e.g., USEPA Method 537) https://www.epa.gov/sites/production/files/2016-09/documents/national_functional_guidelines_for_superfund_organic_methods_data_review_0.pdf). In addition, U.S. DOD and U.S. DOE provide quality control requirements for PFAS analyses in Table B-15 of their Consolidated Quality Systems Manual (QSM) (version 5.1, January 2017), which may also be useful for data validation.

Field Screening Methods

The development of field tests for PFAS is currently in a relatively immature phase. There are currently no commercially available field screening methods that are capable of detecting PFAS at concentrations less than 50 ppb; therefore, the field tests that are currently available are mainly for use in source areas with concentrations that are orders of magnitude higher than drinking water criteria (DiGuiseppi 2017). Field screening methods described include:

- **Foam height** analysis in which a water sample is placed in a small bottle, shaken, and the presence and height of any resulting foam is measured (NEWMOA 2016). This method is useful for determining the potential presence of PFAS only at parts per million (ppm) levels, and is not specific to PFAS (i.e., many surfactants do not contain PFAS).
- **Methylene blue active substance (MBAS)** measurement kits are commercially available (see, for example, Chemetrics 2016). These kits detect surfactant concentrations in the range of 50 ppb, and are not specific to PFAS. The detection level can be decreased by concentrating the samples, but that process is more difficult to perform in the field.
- An **anionic surfactant detection kit (astkCARE™)** was commercially available from CRC Care (http://www.crccare.com/products-and-services/technologies/astkcare). However, this has reportedly been taken off the North American market recently for product improvements and may be re-introduced (DiGuiseppi 2017).
- **Ion-Selective Electrodes (ISEs)** with fluorous anion-exchanger membranes have been developed for the detection of perfluorooctanoate (PFO-) and perfluorooctanesulfonate (PFOS-). Detection limits of PFO- and PFOS- are approximately 1.0 ppb and 0.43 ppb, respectively. Measurements with ISEs can be performed in-situ, are less costly, and avoid lengthy sample preconcentration. Though not commercially available currently, the research team has demonstrated a real-life application of these electrodes, with results that were consistent with those from an earlier LC-MS study (Chen et al. 2013).

FIELD SAMPLING PROCEDURES

Sample Containers and Preservatives

It is recommended that the user verify the current sampling container requirements with the selected laboratory prior to sampling for PFAS, and ensure that the sample containers do not contain the analytes of interest. The current standard is for samples to be submitted in containers (including caps/liners) made of polypropylene or high-density polyethylene (HDPE). Glass sample containers should be avoided due to potential loss of analyte through adsorption to glass. Field filtering of samples should also be avoided to minimize the potential for cross contamination. The laboratory generally needs a minimum volume of 250 milliliters (mL) to perform analysis. Check with the laboratory regarding sample containers for other environmental media (e.g., soil, sediment).

For drinking water that has free/residual chlorine, Trizma® (or similar) may need to be used as a sample preservative. Consult with the laboratory and, if needed, have the laboratory add the appropriate amount of Trizma (or similar) to the sample container(s) that are shipped to the site.

Samples for PFAS analysis should be chilled to <6°C (4+2°C) using ice that is double-bagged in polyethylene plastic; chemical or gel-based cooling products should not be used. Samples should be transported to the laboratory, or shipped overnight, to ensure delivery of the samples at the sample preservative temperature of <6°C.

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Quality Assurance/Quality Control (QA/QC) Samples

Although the collection and analysis of QA/QC samples adds cost to the sampling and analysis program, these additional samples are used to provide information on the quality of the laboratory results for the samples collected at the site, namely the potential for contamination of those samples by other factors (e.g., false positives resulting from field or laboratory sample collection or handling procedures). QA/QC samples can be especially important for PFAS analyses because of the widespread use of these compounds and the very low (single-digit ppt) concentrations being analyzed. Field-related quality control samples should be included in a project-specific Sampling and Analysis Plan (SAP). At a minimum, the following should be considered in the SAP.

Field Reagent Blanks

A field reagent blank (FRB) should be collected during the sampling event to evaluate potential contamination from the overall sample collection and handling process such as the water used by the laboratory for its method blanks, the sample containers, and exposure of the samples to the environment at the sampling locations, including the air, PPE, and the clothing and personal care products of the sampling personnel.

For FRBs, two appropriate containers (one containing PFAS-free water and the other empty) are supplied by the laboratory. During the sampling event, field staff transfer the preserved PFAS-free water from one container into the other container, screw on the laboratory supplied caps, and place the sample containers into the cooler for submittal with the day's sampling set (typically one per day).

Equipment Blanks

Equipment blanks (EBs) are used to assess the potential contamination of samples by the equipment used at the site to collect those samples. To collect an EB, PFAS-free water provided by the laboratory is poured over, in or through a particular piece of sampling equipment (for example, a new, disposable bailer, or a pump that has been decontaminated after its prior use) and collected in a sample container. The collection of equipment blanks should be considered for each sampling program based on the site-specific objectives and requirements, and should focus on the equipment and/or materials that have the potential to come into contact with (a) the media being sampled and (b) the containers being used to collect the samples while those containers are open (e.g., sampling gloves).

Field Duplicate Samples

Field duplicates are recommended at a rate of 1 per 20 samples. A second "blind" field sample is collected at the same location as the primary sample and often has a generic naming convention not known by the laboratory (i.e., avoid using a name like "Dup"). The results are used to check the repeatability of the laboratory analytical results; the documentation for the analytical method that is employed should be consulted for the appropriate relative percent difference (RPD) criteria (e.g., 30% for USEPA Method 537).

Matrix Spike and Matrix Spike Duplicate Samples

Matrix spike and matrix spike duplicate (MS/MSD) samples are field-collected samples into which the laboratory adds known amounts of specific PFAS after receipt, but prior to analysis. Essentially, collecting a MS/MSD sample pair is the same as collecting two field duplicate samples at a certain sampling location; these containers are identified as MS and MSD samples and are not "blind." Laboratories add known amounts of analytes (typically concentrations at/near the middle of the calibration range) when they perform MS/MSD analyses, so it is beneficial to use locations that are known or believed to be clean or have relatively low concentrations for collecting the MS/MSD samples.

Chain of Custody and Sample Shipment

Chain-of-custody (COC) procedures should generally be used to document possession of the samples from collection at the site to receipt by the laboratory. Standard COC procedures are appropriate/adequate for PFAS samples. Make sure that packing and shipping materials do not present the potential for cross contamination during shipment.

It is important to coordinate with the laboratory regarding receipt of the samples. Generally, sampling on the day before the weekend (Friday) or before a holiday should be avoided unless the samples are being transported to the laboratory on the same day, or arrangements have been made with the laboratory to receive the samples and then place in a secure, refrigerated space.

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Holding Times

Aqueous samples, if preserved properly (i.e., stored at <6°C without being frozen), must be extracted within 14 days of sample collection and the extracts must be held at room temperature, and analyzed within 28 days of extraction. There is no specific information for holding times for other matrices, but some laboratories recommend 28 days for soil samples. Until studies are performed on holding times for other matrices, it may be prudent to use the more stringent aqueous sample holding time criteria suggested in USEPA Method 537.

General Field Sampling Considerations

As for any sampling program, best practices should be employed in the field to maintain sample integrity and minimize data variability and cross contamination while providing the highest level of data quality and defensibility. This includes maintaining consistency of approach during sample collection.

Regulatory agencies are currently interested in PFAS at ppt levels (e.g., USEPA issued a lifetime health advisory for drinking water at 70 ppt for PFOA and PFOS, individually and combined). In conjunction, given the widespread use of PFAS in many consumer, commercial, and industrial products and processes, and very low concentrations to which PFAS are reported, it is critical that the sampling program consider as many sources of PFAS contamination as practicable. This includes the following:

- To minimize cross contamination during a sampling event, it is recommended that the sampling be performed during any specific event/day from the anticipated "cleanest" (or lowest concentration) to "dirtiest" (or highest concentration) sample locations. If no PFAS data are currently available, then this order should be based on the conceptual model of the site/contamination [e.g., source(s), environmental media, migration pathways/directions, receptor locations].
- Laboratory-supplied water that has been determined to be PFAS-free should be used to prepare all FRBs and EBs.
- The quality of the water used for any other purposes (e.g., equipment decontamination) should be scrutinized, including public water supplies. Many public water supplies have been analyzed for PFAS pursuant to UCMR3, and those results are available from USEPA's database (https://www.epa.gov/dwucmr/occurrence-data-unregulated-contaminant-monitoring-rule#3) or from the water provider. Even if data are available from the public water supply, sampling the water used during a PFAS investigation should be considered. If data are not available, the water supply should be analyzed for the PFAS of interest prior to use, and the results should be reviewed to determine if the water quality is suitable based on the objectives of the specific sampling program.
- The materials of construction of all downhole and surface sampling and monitoring equipment—including pumps, packers, transducers, tubing, liners, valves, and wiring—should be free from polytetrafluorethylene (PTFE) or ethylene tetrafluoroethylene (ETFE) to the maximum extent practicable. In addition, well drilling procedures and completion materials should avoid the use of fluorocarbon-based lubricants, O-rings and pipe thread pastes, tapes and sealants. If possible, a confirmation letter with analytical testing results should be obtained from a manufacturer or service provider certifying that the equipment (or supplies) are free of any PFAS.
- Reusable sampling equipment should be properly decontaminated. New and disposable equipment can also be decontaminated if any materials of construction are not known to be PFAS-free. EBs can be collected and analyzed to obtain the data needed to evaluate the potential for cross contamination of the samples by fieldequipment.

Sources of Potential Sample Bias and Contamination

A wide range of products commonly used in site investigations are known or suspected to contain PFAS. Due to the combination of low detection limits and potential contamination from PFAS source in sampling equipment and materials such as pumps and tubing (DiGuiseppi et al. 2014), field sampling for PFAS requires special precautions be taken to minimize the potential for sample contamination from materials used by samplers. Field sampling procedures from a variety of sources (AMEC 2016; Western Australia DER 2016; U.S. Navy 2015a; U.S. Navy 2015b, USACE 2016) generally indicate that extensive precautions should be followed to limit the potential for sample

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bias. Therefore, the precautions in Table 5.1 (personal protective equipment, clothing, and hygiene products) and Table 5.2 (sampling equipment) are intended to provide a conservative approach to sample bias prevention. However, the risk of sample bias due to PFAS-containing materials is the subject of ongoing research. A large study is currently underway by Dr. Graham Peaslee of the University of Notre Dame and Dr. Jennifer Field of Oregon State University to determine potential sample bias from over 150 common sampling materials and objects; the results of this study were anticipated to be published in 2018 (DiGuiseppi 2017).

Table 5.1. Personal Protective Equipment, Clothing, and Hygiene Products

PPE, Clothing, or Hygiene Product	PFAS Concerns	Approved Alternative
Steel-toed boots	Boots may not contain Gore-Tex™. Many waterproof boots are lined with Gore-Tex and are prohibited.	Steel-toed boots made with polyurethane and polyvinyl chloride (PVC)
Clothing	Water resistant, waterproof, or stain-treated clothing should be avoided. (EDQW 2016)	Clothing made of synthetic or natural fibers should be worn. Cotton is preferred. Field gear should be laundered a minimum of six times prior to use, avoiding use of fabric softeners. Cotton overalls may be provided for use.
Rain gear	Most rain gear is coated with a Gore-Tex™ lining and contains fluoropolymers.	Rain gear made from polyurethane and wax-coated materials may be worn (U.S. Navy 2015; EDWQ 2016).
Gloves	Nitrile gloves are specified for use in EPA Method 537.	Only nitrile gloves should be used. These should be changed often as outlined in EDQW 2016. Recommended powderless nitrile gloves.
Protective clothing	Fluoropolymer linings are used on Tyvek™, Nomex™, and Viton™ materials (U.S. Navy 2015; EDWQ 2016)	Avoid these materials. Select alternative protective clothing that does not contain fluoropolymers.
Sunblock and insect repellant	Many manufactured sunblocks and repellants contain PFAS.	Avoid use. If necessary, use of a 100% natural ingredient product may be used upon approval.
Cosmetics, moisturizers, hand creams, etc.	Many of these products contain surfactants and represent a potential source for PFAS.	Use of these products should be avoided prior to a sampling event.
Food and drink	Food packaging often contains PFAS as a protectant from water and grease.	No food or drink shall be brought on-site, except for bottled water and hydration drinks. No blue ice packs should be used. Additionally, hands should be thoroughly washed following consumption of any wrapped fast food or pizza.

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Table 5.2. General Sampling Equipment and Field Supplies

Avoid Use	Approved Alternatives
General Sampling Equipment	
Standard decontamination water or municipal water	Water from a known source that has been analyzed for PFAS and has been determined to be acceptable for the specific sampling program
Decon 90™ detergent	Alconox™ and Liquinox™ are the only detergents approved for decontamination (EDQW 2016)
Glass or Teflon™-lined sampling bottles and lids	Polypropylene or high-density polyethylene (HDPE) sample bottles with an unlined polypropylene HDPE screw cap
Fluoropolymer tubing, valves, and other parts in pumps	HDPE and silicon materials (EDQW 2016)
Teflon™ tubing, bailers, tape, and plumbing paste	HDPE and silicon materials or disposable equipment
Pumps, packers, transducers, tubing, liners, valves, and wiring with polytetrafluorethylene or ethylene tetrafluoroethylene	Alternative materials
LDPE HydraSleeves™	HDPE HydraSleeves™ (EDQW 2016)
Aluminum foil	Thin HDPE sheeting
Field Supplies	
Markers and waterproof pens	Non-waterproof pens (EDQW 2016)
Rite-in-the-rain paper, binders, and plastic clipboards	All field paperwork should be printed on standard paper and placed in a non-water-resistant folder or aluminum clipboard (EDQW 2016)
Sticky notes	No Post-It Notes should be brought to the site
Chemical (blue) ice packs	Only regular ice should be used for refrigeration on site (EDQW 2016)

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Groundwater and PFAS: State of Knowledge and Practice

Legal and Regulatory Framework
Section 6

One of eight sections prepared by National Ground Water Association volunteers. Each section was prepared to stand independently, or to be integrated with the other seven sections.

NGWA Press
The Groundwater Association

Legal and Regulatory Framework

TERMINOLOGY

Groundwater quality standards

Groundwater quality standards can be either numeric or narrative. Numeric groundwater standards prescribe maximum allowable contaminant levels that result from human operations or activities, but do not typically apply to naturally occurring contaminants at naturally occurring levels. A narrative standard is descriptive of conditions necessary to support a designated groundwater use or may generally prohibit the discharge of particular types of contaminants. Numeric and narrative standards may be used separately or conjointly. Groundwater quality standards are enforceable standards.

Health advisories

Health advisories provide information on contaminants that can cause human health effects and are known or anticipated to occur in drinking water. Health advisories are nonenforceable and nonregulatory and provide technical information to public health officials on health effects, analytical methodologies, and treatment technologies associated with drinking water contamination.

Maximum contaminant level (MCL)

MCLs represent the highest level of a contaminant that is allowed in drinking water that enters the service network. MCLs are enforceable standards.

Disclaimer: This publication is a collaborative effort to try to set forth best suggested practices on this topic but science is always evolving, and individual situations and local conditions may vary, so members and others utilizing this publication are free to adopt differing standards and approaches as they see fit based on an independent analysis of such factors. This publication is provided for informational purposes only, so members and others utilizing this publication are encouraged, as appropriate, to conduct an independent analysis of these issues. The NGWA does not purport to have conducted a definitive analysis on the topic described in this publication, and it assumes no duty, liability or responsibility for the contents or use of the publication.

Maximum contaminant level goal (MCLG)

MCLGs represent the level of a contaminant in drinking water below which there is no known or expected risk to health. MCLGs allow for a margin of safety and are nonenforceable public health goals.

Secondary maximum contaminant level (SMCL)

Under its National Secondary Drinking Water Regulations, EPA established SMCLs that set nonmandatory water quality standards. They are established as guidelines to assist public water systems in managing their drinking water for aesthetic considerations such as taste, color, and odor. These contaminants are not considered to present a risk to human health at the SMCL.

STATUTORY AND REGULATORY AUTHORITY

There are multiple layers of laws and rules that govern PFAS in the environment. At the federal level, a number of laws may apply, including the Toxic Substances Control Act (TSCA) related to the manufacture and use of PFAS; the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) related to remediation of contaminated sites; and the Safe Drinking Water Act (SDWA) related to the presence of contaminants in drinking water. All have a role when PFAS are released into the environment. In addition, each state may have analogous standards that can be stricter than their federal counterparts. Depending on the jurisdiction, the more stringent standard would apply. Different authorities in individual states, including regional water boards and environmental protection agencies, may have drinking water and/or groundwater regulatory standards, health advisories, and/or guidance levels that govern PFAS in state waters.

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The following subsections summarize the general regulatory authorities governing PFAS in drinking water and groundwater.

Federal System

TSCA

In 2002, EPA issued two Significant New Use Rules (SNURs) under TSCA that restricted the use of 88 PFOS-related chemicals.[1] The SNURs allowed only three specific uses of PFOS: photographic and imaging industries, semiconductor manufacturing, and aviation uses. In 2007, EPA expanded the SNURs to include 183 PFAS chemicals with exceptions allowed for use as an etchant and metal plating and finishing uses.[2] EPA proposed to amend these SNURs in 2015 to remove certain exemptions for importation of certain PFAS chemicals.[3]

CERCLA

In January 2009, after the EPA Office of Water issued the provisional health advisory (PHA) for PFOA and PFOS, the EPA Office of Solid Waste and Emergency Response issued a memorandum: "The Toxicity of PFOA and PFOS." In that memorandum, subchronic reference doses were developed for use in the Superfund program's risk-based equations to derive removal action levels and/or screening levels for soil and water.[4]

SDWA

The Unregulated Contaminant Monitoring Rule (UCMR) was developed by EPA to evaluate constituents that are likely to be present in drinking water but do not have health-based standards set under the SDWA. EPA establishes a new list of no more than 30 UCMR constituents every five years, primarily based on the Contaminant Candidate List (CCL). The CCL is developed by an agency and state working group using a stepwise prioritization process. First, a broad set of constituents are identified that are potentially present in drinking water. These constituents are further evaluated based on their potential to cause adverse health effects (potency and severity) and their occurrence (prevalence and magnitude). EPA uses the information obtained from this monitoring as the primary source of occurrence and exposure information to establish potential future regulatory actions for the protection of public health.

The third Unregulated Contaminant Monitoring Rule (UCMR3) was published on May 2, 2012, and required monitoring for 30 contaminants (28 chemicals and two viruses) between 2013 and 2015. The UCMR3 list included six PFAS: perfluorooctanesulfonic acid (PFOS), perfluorooctanoic acid (PFOA), perfluorobutanesulfonic acid (PFBS), perfluorohexanesulfonic acid (PFHxS), perfluoroheptanoic acid (PFHpA), and perfluorononanoic acid (PFNA).

For the contaminants on the assessment monitoring list, which include the PFAS, all systems serving more than 10,000 people and a representative sample of 800 public water systems serving 10,000 or fewer people were also selected for monitoring and are required to test for UCMR contaminants. UCMR3 data are available on EPA's website at *www.epa.gov/dwucmr/occurrence-data-unregulated-contaminant-monitoring-rule#3*.

In 2008, EPA conducted testing of agricultural sites in Alabama where sewage sludge was applied from a wastewater treatment plant that received wastewater from industrial sources, including facilities that manufactured and used PFOA. EPA expanded its testing to include sampling of public drinking water systems. In response to the data it collected, the EPA Office of Water issued a provisional health advisory (PHA) for PFOA of 0.4 parts per billion (ppb) and PFOS of 0.2 ppb.[5] In May 2016, EPA replaced the 2009 PHA with a new lifetime health advisory (HA) of 70 parts per trillion (ppt) for PFOA and PFOS, applicable to either chemical individually or in combination.[6] EPA's health advisories provide technical information to state agencies and other public health officials on health effects, analytical methodologies, and treatment technologies associated with drinking water contamination. As noted in the previous definitions, health advisories are informational only and do not represent enforceable regulatory decisions by the EPA or states.

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[1] https://www.gpo.gov/fdsys/pkg/FR-2002-03-11/pdf/02-5746.pdf; https://www.gpo.gov/fdsys/pkg/FR-2002-12-09/pdf/02-31011.pdf

[2] https://www.gpo.gov/fdsys/pkg/FR-2007-10-09/pdf/E7-19828.pdf

[3] https://www.federalregister.gov/documents/2015/01/21/2015-00636/long-chain-perfluoroalkyl-carboxylate-and-perfluoroalkyl-sulfonate-chemical-substances-significant

[4] *See* Perfluorinated Chemicals (PFCs): Perfluorooctanoic Acid (PFOA) & Perfluorooctane Sulfonate (PFOS) - Information Paper, August 2015, page 9 (https://clu-in.org/download/contaminantfocus/pops/POPs-ASTSWMO-PFCs-2015.pdf).

[5] https://www.epa.gov/sites/production/files/2015-09/documents/pfoa-pfos-provisional.pdf

[6] https://www.epa.gov/sites/production/files/2016-06/documents/drinkingwaterhealthadvisories_pfoa_pfos_updated_5.31.16.pdf

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State System

In the absence of national regulatory standards, some states have developed their own state-specific regulations and guidelines relative to PFAS in drinking water and groundwater. New Jersey was one of the first states to take any action on PFAS contamination. In 2007, in response to a request by Penns Grove Water Supply Co., the NJDEP Office of Science and Research issued a lifetime health-based guidance level for PFOA of 0.04 ppb, and is now 0.014 ppb.[7] Since then, states have issued groundwater remediation levels, drinking water source limits, and drinking water guidance levels. Some states, Minnesota for example, have also issued fish-consumption advisories.[8]

Drinking Water MCL

The most common method states use to regulate drinking water quality is to adopt federal MCLs or to promulgate more stringent state-specific MCLs. These are enforceable standards that define the highest concentration of a contaminant that is allowed in drinking water. These concentrations are generally based on consideration of health risks, technical feasibility of treatment, and cost-benefit analysis that are designed to protect the public against consump- tion of drinking water contaminants that present a risk to human health.

Groundwater Quality Standards

Some states have approached regulation of PFAS through regulation of groundwater quality standards, which may be different than drinking water MCLs.

New Hampshire, for example, established an ambient groundwater quality standard (AGQS) for PFOA and PFOS at EPA's health advisory level, 70 ppt. The AGQS provides the state with the authority to direct site remediation activities related to PFOS and PFOA and also requires public water systems to comply with these standards if the chemicals are found in their sources of drinking water.[9]

Other Approaches

Some states have issued health advisories for fish. Michigan, for example, has issued a "do not eat" advisory for all fish taken from Clarks Marsh and a recommendation that "resident" fish taken from the lower Au Sable River not be eaten due to the presence of perfluorinated chemicals.[10]

State Regulatory Summary

Table 6.1 summarizes the status of some state regulation of PFOS and PFOA as of November 1, 2017.[11]

WATER SYSTEM LIABILITY ISSUES

Liability Theories

In general, the two primary tort theories of liability are negligence and products liability. Negligence is generally defined as the failure to exercise due care toward others, which a reasonable person would do in the circumstances. There are four basic elements to a negligence claim: duty, breach, causation, and harm. Products liability claims are made against a manufacturer or seller of a defective good or product that causes harm. Products liability claims can also be based on a failure to warn of a hazard that the manufacturer knew or should have known about. This section summarizes some of the cases that discuss these liability theories in the context of contaminated drinking water. In addition, some of the defenses that apply to water systems are discussed.

Because tort law is a mix of statute and judicial opinions, the applicability of any statute or court decision may be limited to a particular state or federal district. There are also a limited number of cases involving water system liability for contaminants in the water system, so trends in this area of law can be difficult to discern. This is not intended to be a comprehensive summary of all the cases that de- scribe the liability of water suppliers. Instead, it is a sampling of the reasoning applied by various courts when applying these legal theories.

Examples of negligence approach

In Green v. Ashland Water Co. (Wisconsin 1898), the water company was sued for damages arising out of a death caused by typhoid fever that originated in the water system. The Wisconsin court decided that the applicable rule is *caveat emptor* or "let the buyer beware." Given the age of the case and the develop-

[7] http://www.state.nj.us/dep/dsr/pfoa_doc.pdf; http://www.nj.gov/dep/watersupply/pdf/pfoa_dwguidance.pdf

[8] http://www.health.state.mn.us/divs/eh/fish/eating/mealadvicetables.pdf

[9] http://des.nh.gov/media/pr/2016/20160531-pfoa-standard.htm

[10] https://www.michigan.gov/documents/mdhhs/General_Questions_from_March_2016_Public_Meeting_Posted_527011_7.pdf

[11] The regulatory limits in Table 6.1 should be used for guidance only. Please consult with current law to determine what standards apply in your state.

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Table 6.1. Examples of State Water Criteria

State	PFOS (µg/L)	PFOA (µg/L)	BASIS
AK	0.4	0.4	Groundwater cleanup levels in effect under amendments for 18 AAC 75 — effective January 2017
DE	0.07 (combined)		July 2016 Guidance for Notification under Division of Waste and Hazardous Substances
IA	0.07 (combined)		2016 Statewide Standards for Protected Groundwater Source
ME	0.56	0.13	Augusta, 2016 Health-Based Groundwater Screening Levels for Resident, MeCDC
MI	0.011	0.42	October 2016 Rule 57 Water Quality Rule—Human Noncancer Values for Drinking Water. Also have groundwater-surface water interface protection criteria.
MN	0.027	0.035	May 2017 MDH Groundwater HRLs published in 2009, and revised HBVs published 2017, also have fish criteria and criteria for PFBS, PFBA.
NC	—	2	2006 Interim Maximum Allowable Concentration (IMAC) in groundwater of 2 µg/L developed for PFOA by DENR. July 2017 Health goal for perfluoro-2-propoxypropanoic acid (GenX) of 0.014 ug/L published in July 2017.
NH	0.07 (combined)		May 2016 Ambient GW Quality Standards and Public Water System DW — Emergency Rule
NJ	—	0.014	November 2017 health-based MCL for PFOA established. Groundwater and drinking water criteria also available for PFNA.
NV	0.667	0.667	2015 DEP Basic Comparison Level for cleanup-residential water. BCL also published for PFBS (667 ug/L)
OR	300	24	2011 Oregon Department of Health Initiation Levels for POPs-NPDES and water pollution control facilities. It pertains to facilities with one million gallons a day or more. They are required to sample effluent for various POPs,including PFASs, and if they exceed, they have to implement a reduction plan.
VT	0.02 (combined)		2016 Vermont Health Advisory published . Also adopted as Interim Groundwater Quality Standard.
TX	0.56	0.29	March 2016 Protective Concentration Levels (PCLs) for Texas Risk Reduction cleanup program. Criteria available for 14 other PFASs — March 2016

ment of products liability and negligence law that has developed since this case, while it is interesting, it may not have much substantive value as precedent.

In another case involving typhoid fever, *Hayes v. Torrington Water Co.* (Connecticut 1914), the plaintiff contracted typhoid fever from the water supply. Although the court noted that the supplier of water is not a guarantor of the purity of its water, it is bound to use reasonable care in ascertaining whether there is a reasonable probability that its water supply may be infected. If the exercise of such care would have disclosed a reasonable probability of disease, then it becomes the duty of a water company to adopt whatever approved precautionary measures are, under the circumstances, reasonably proper and necessary to protect the community it serves from the risk of infection. Thus, the Connecticut court took a much different view of the duty of a water system than did the Wisconsin court. Again, this too is a very old case and may ultimately not hold much precedential value in Connecticut.

The court in *Coast Laundry Inc. v. Lincoln City* (Oregon 1972) took a view similar to the Connecticut court. The plaintiff was a laundry business that claimed it suffered damage because the city supplied water that contained particles of tar. The Connecticut court said that the municipality, which supplied water for a charge to its inhabitants, is not an insurer or guarantor of quality water. As such, it is not liable for injuries resulting from impure water unless it knew or ought to have known of the impurity, but it will be held liable for illness or epidemic resulting from negligent-

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ly permitting its water supply to become contaminated or polluted. As such, the water system has a duty to exercise reasonable care and diligence in furnishing an adequate supply of water.

Products Liability

In *Adel v. Greensprings of VT* (363 F.Supp.2d 692, D. VT 2005), the plaintiff was diagnosed as suffering from Legionnaires' disease resulting from consuming water at a condominium. The defendant was a privately owned water system regulated by the state of Vermont as a public system. The plaintiff's lawsuit sought to hold the water system strictly liable under a theory of a breach of the warranty of merchantability. This is a claim that is brought when a product—or "good"—has a hidden defect and does not meet the standards for that product. The water system argued it provided a service and did not sell a product.

The *Adel* court considered decisions in other jurisdictions and concluded that the water suppliers were "sellers" of "goods" consistent with the majority of other courts. The court also found that water suppliers could be held liable for a breach of the warranty of merchantability, although the court noted that courts around the country are split on that issue.

Defenses to Liability

Governmental immunity

Governmental immunity is distinct from sovereign immunity, which applies to states and state agencies but does not extend to municipalities. When applying governmental immunity, courts have recognized that municipal corporations possess a dual capacity, sometimes acting in a governmental capacity, which is protected by governmental immunity, and other times in a private, corporate, or proprietary capacity, which is not protected. Most states have passed tort-claim statutes that replace general common-law governmental immunity with a list of specific immunities, some of which continue to differentiate on the basis of governmental vs. proprietary action.

Safe harbor statutes

Although uncommon, some states have passed statutes that expressly provide water systems with safe harbors from tort liability if the supplier is not in significant noncompliance with drinking water standards. In Ohio, for example, a water supplier that operates a public water system is not liable for injury, death, or loss to person or property if:

- During the period of time the water supplier supplies water to the person, the water supplied by the water supplier meets all applicable drinking water standards.
- The water supplier has not been found to be in significant noncompliance with drinking water standards.
- The injury, death, or loss to person or property is alleged to be caused by a substance for which drinking water standards have been established. (O.R.S.A. Title 61 §6109.35)

In Arizona, the legislature enacted a statute that set the legal standard for water that is "reasonably safe and fit for consumption" if it complies with the more stringent maximum contaminant levels that are established under federal or Arizona's drinking water acts. (Arizona Rev. Stat. Ann. § 12-820.08)

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Groundwater and PFAS: State of Knowledge and Practice

Risk Communication
Section 7

One of eight sections prepared by National Ground Water Association volunteers. Each section was prepared to stand independently, or to be integrated with the other seven sections.

NGWA Press
The Groundwater Association

Risk Communication

WHY IS RISK COMMUNICATION IMPORTANT?

According to United States Environmental Protection Agency (USEPA)'s Risk Communication Guidance, 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* (USEPA 2007).

Risk is the relationship between the probability of harm associated with an activity and vulnerability of people or the environment (Slovic 1987, 2003; UN-ISDR 2002). Risk communication is the process of informing stakeholders about health or environmental risks, risk assessment results, and proposed risk management strategies. Stakeholders can consist of any organization, group, or individual who takes an interest in a project and can influence project outcomes (Cundy et al. 2013). In the context of PFAS sites, stakeholders primarily include regulators, impacted water users, and responsible parties. Risk communication should be performed as a two-way conversation in which all stakeholders are informed of each other's needs and project objectives are identified to meet them (Cundy et al. 2013; USEPA 2007).

When performing risk communication, it is important to consider stakeholder context and to identify vulnerable sub-populations within the impacted community:

- *Stakeholder context* is defined by community demographics, socio-cultural factors (e.g., views on environmental stewardship and cleanup activities), psycho-social factors (e.g., diversity in individuals' beliefs, attitudes, values, and inhibitions, including trust of authorities), knowledge base (e.g., understanding of PFAS exposure and "safe levels"), and the presence of limitations on mobility that may hinder adequate involvement in community outreach events (e.g., public meetings).
- *Vulnerable sub-populations* may include non-native speakers, low income groups, and sensitive populations, such as children and the elderly (Government of Canada 2005; USEPA 2007). For example, Emmett and Desai (2010) observed the distribution of blood serum PFOA was age-dependent, with significantly higher values in children aged 5 or under, and in those over 60.

Consideration of stakeholder context can assist remedial professionals to identify factors contributing to community skepticism with respect to actual risk levels. Heightened community concern and skepticism at the PFOA site in Little Hocking, Washington County, Ohio (herein referred to as the "Little Hocking Site") was likely caused in part from distrust due to the initial lack of communication of PFOA detections in tap water and differences among recommended "safe level" concentrations (Emmett et al. 2009). Emmett et al. (2009) state that, "Collectively these developments eroded the credibility of both government and the fluoropolymer facility in the affected community." While engaging all stakeholders meaningfully can be a complex process, when undertaken successfully, effective risk communication can streamline projects, enhance transparency, and alleviate stakeholder concerns (Government of Canada 2005; Harclerode et al. 2015; USEPA 2007).

Disclaimer: This publication is a collaborative effort to try to set forth best suggested practices on this topic but science is always evolving, and individual situations and local conditions may vary, so members and others utilizing this publication are free to adopt differing standards and approaches as they see fit based on an independent analysis of such factors. This publication is provided for informational purposes only, so members and others utilizing this publication are encouraged, as appropriate, to conduct an independent analysis of these issues. The NGWA does not purport to have conducted a definitive analysis on the topic described in this publication, and it assumes no duty, liability or responsibility for the contents or use of the publication.

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RESPONDING TO STAKEHOLDER QUESTIONS AND CONCERNS

Environmental and public health regulatory agencies have prepared information documents to assist professionals in performing effective risk communication for PFAS sites. Table 1 provides a summary of available supporting materials published to date. Based on a review of supporting materials and experience of NGWA's technical professionals, additional frequently asked questions were identified. These questions and recommended responses are presented below:

1. *Question:* Why are laboratory methods not available to determine whether PFAS are not present (i.e., the detection limit is zero)?

   Answer: There is no technology that is sensitive enough to analyze down to a "zero" concentration (i.e., not a single molecule is present) for any chemical. However, there are US EPA-approved methods that are sensitive enough to detect PFOS and PFOA at levels lower than the current drinking water health advisory of 70 parts per trillion (ppt). Therefore, public health can be protected.

2. *Question:* Does the presence of other pollutants and/or byproducts exacerbate the effects of exposure to PFAS on human and environmental health?

   Answer: The US EPA has developed an approach to evaluate the potential effects of exposure to multiple chemicals. However, each situation is different, and depends on the amount and type(s) of chemicals that may be present as well as whether the chemicals contact humans or the environment. In addition, there are no known combinations of PFAS with other chemicals that exacerbates the risks associated with exposure.

3. *Question:* How do my blood level results compare to others?

   Answer: Certain state public health agencies, including the Minnesota Department of Health, have published results of biomonitoring performed in their state as well as information from the entire U.S. population (https://apps.health.state.mn.us/mndata/biomonitoring_pfc#longterm). An internet search using "biomonitoring", "PFCs", "public health" and your state agency as keywords can assist with finding informative material. In addition, you can contact your county or state health department for information.

In addition to fact sheets, a communication plan can be developed to assist with engaging and disseminating information to stakeholders. As showcased by the Little Hocking Site, development of a comprehensive stakeholder outreach strategy can address and potentially overcome distrust present between community members and decision-makers (such as regulatory authorities and responsible parties). The communication plan developed for the Little Hocking Site was comprised of the following, presented in chronological order (Emmett et al. 2009):

1. *Notifications to Participants and Authorities* – Next-day-delivery mailings of results to individual study participants, with the individual's blood PFOA and biomarker levels. Comparative information on PFOA levels was included and a toll-free telephone number to contact a study physician with any questions. Letters were sent simultaneously to identified authorities and CAC members, to ensure that recipients would be able to respond appropriately to inquiries from the public.
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 mailing 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.
3. *Closed Rehearsal of Community Presentation* – A strictly closed to the public, full rehearsal presentation was made to the Community Advisory Committee (CAC) on the night preceding the community meeting. CAC members provided feedback on the order of the agenda, comprehensibility of slides, choice of wordings, structure of the presentation, and dealing with likely ques-

Table 1 (See Appendix) provides a summary of available supporting materials published to date.

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tions. In addition, the closed rehearsal ensured the community meeting presentation was as inclusive and useful as possible.

4. *Community Meeting* – Detailed study results were presented at the community meeting, approximately three weeks after the initial participant letter. 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. The presentation made it clear that this was not the be-all and end-all of studies, but part of a continuum of information.
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 frequently asked questions was also developed.

The performance of meaningful stakeholder engagement at the Little Hocking Site was underlain by two important risk communication process factors. The first is that the investigators worked with the community through the CAC before any results were available to establish the community's preferences with regards to communication. These were explicitly developed as a set of principles for the risk communication practitioners and a set of community priorities reflective of stakeholder values. This process was important to enhance trust and eventual community ownership of the investigative results prior to site activities. Secondly, evaluation of the success and effectiveness of the communication process was accomplished by 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 investigative results.

OVERCOMING RISK COMMUNICATION CHALLENGES

Performing effective risk communication is not without its challenges, especially in contentious settings when exposure routes and human health impacts have been identified. These potential challenges include: (1) uncertainty/variability in regulatory cleanup criteria and policies; (2) misperception of proposed risk management strategies; (3) inability to provide effective risk communication to vulnerable sub-populations; and (4) difficulty managing stakeholder expectations. The following subsections present a discussion of these terms and concepts, and provide stakeholder engagement methods that can be utilized to address these challenges and facilitate meaningful risk communication.

Uncertainty/Variability in Regulatory Cleanup Criteria and Policies

One of the purposes of risk communication is to assist stakeholders in understanding the process of risk assessment and risk management. Due to the nature of emerging contaminants such as PFAS and the number and complexity of PFAS compounds, current regulatory cleanup criteria and policies issued by federal and state agencies can be in conflict. Policies and criteria are also subject to change based on developing sampling methodologies, analytical procedures, and risk assessment evaluations. For example, USEPA recommended a PFOS Provisional Health Advisory of 0.2 micrograms per liter (µg/L) in January 2009 which was subsequently replaced in 2016 with a Health Advisory of 70 parts per trillion (ppt).

In the context of risk communication, it is important to communicate these uncertainties and variabilities, while maintaining stakeholder trust and meeting their needs (USEPA 2005, 2007). In addition to relying on cleanup criteria as a primary risk management performance metric, secondary risk management performance metrics can be used to communicate and evaluate success of a proposed PFAS risk management strategy, thus alleviating perceived uncertainty and associated risks (e.g., failure to gain acceptance and delays due to antagonistic relationships among the community and decision makers) (Cundy et al. 2013; Harclerode et al. 2016a; REVIT 2007; RESCUE 2005). Examples of secondary performance metrics may include source/plume containment, establishing that the PFAS is not bioavailable and/or mobile, and that there are no complete exposure pathways associated with the site. Evaluation tools, such as exposure scenario evaluation, Use Attainability Analysis (UAA), and contaminant

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concentration and/or loadings can be used to assess and communicate performance of site-specific secondary risk management objectives (Harclerode et al. 2016a).

Misperception of Proposed Risk Management Strategies

Effective risk communication is dependent upon the decision makers' ability to assist affected stakeholders in forming scientifically valid perceptions of their risk to PFAS. Risk perception[1] refers to the difference between expert and layman perception (see the landmark report by Pidgeon et al. 1992, p. 89). As the public is exposed to hazards, the community and broader society reacts, and in turn directly influences stakeholders' perceived risk of those hazards.

A phenomenon termed "risk attenuation" occurs when experts judge hazards as relatively serious, while impacted parties do not perceive the risk as serious and provide comparatively little attention to that risk. Under this scenario, risk perception creates a challenge in engaging stakeholder participation in prevention and mitigation activities (i.e., installing a residential water treatment system or obtaining an alternate water source).

In contrast, "risk amplification" occurs when experts assess a hazard as carrying some degree of risk (e.g., low or moderate) and the community—and sometimes broader society—perceives it as a major concern. This scenario often results in barriers to stakeholder acceptance of proposed risk management strategies and contention among stakeholder groups (e.g., the regulatory authority and impacted community). The degree of risk attenuation or risk amplification influences how stakeholders view the legitimacy of experts and their compliance with policies and protective measures (Botzen et al. 2009; Lewis and Tyshenko 2009; Kasperson and Kasperson 1996).

Stakeholders' risk perception is shaped by a wide variety of factors including demographics, direct experiences, sense of trustworthiness with authorities, and an individual's ability to bring about change (Bickerstaff 2004; Botzen et al. 2009; Glatron and Beck 2008). These risk perception factors can be identified to assist environmental professionals refine education outreach activities and can also help to identify the mode of delivery that can most effectively communicate actual risk and overcome barriers associated with perceived risk. Risk perception factors can be identified by performing surveys, interviews, and conducting focus groups (Bickerstaff 2004; Botzen et al. 2009; Burger and Gochfeld 1991; Chappells et al. 2014; Gerber and Neeley 2005; Harclerode et al. 2015, 2016b; Palma-Oliveira and Gaspar 2004; Tam and McDaniels 2013; Weber et al. 2001; Vandermoere 2008). In addition, understanding site-specific risk perception factors and barriers to acceptance can assist in identifying applicable secondary risk management performance metrics to be used during risk communication.

Risk perception factors utilized by the Little Hockings Site community outreach team were resident knowledge of PFOA results and associated illnesses, ability to access a physician, presence of vulnerable sub-populations (i.e., higher PFOA levels in children and the elderly), proximity of individual residences to study results (i.e., sense of a safe place), and possible interactions of elevated PFOA levels and particular medical conditions. Various behavioral changes by residents, including perception of risk to consumption of contaminated water, were observed after implementation of the Little Hocking Communication Plan. Approximately 95 percent of the study participants had made a change in their water source, primarily the use of bottled water, which subsequently led to a median reduction of 26 percent in blood serum PFOA levels. Subsequently, trust with authorities was regained due to active, transparent, and continuous community involvement that was scientifically credible and independent of decision-makers. This process, defined as Community-First Communication, resulted in overcoming risk perception barriers, community empowerment, and meeting stakeholder needs (Emmett and Desai 2010).

Inability to Provide Effective Risk Communication to Vulnerable Sub-Populations

One of the primary purposes of risk communication is to engage affected stakeholders in the risk management decision-making process. Communities vulnerable to environmental and health risks

1 Risk perception refers to the difference between expert and layman perception, as defined by the Royalty Society's landmark 1992 report on risk as involving "people's beliefs, attitudes, judgements and feelings, as well as the wider cultural and social dispositions they adopt towards hazards and their benefits" (Pidgeon et al. 1992, p. 89).

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are often concentrated in low-income, underserved, disenfranchised, ethnically diverse, and marginalized communities (Bickerstaff 2004; Bullard 1990; Coughlin1996; Slovic1987, 2003). Understanding the perspective of these vulnerable sub-populations is essential in performing effective risk communication. Therefore, decision-makers should consider the following: (Covello and Allen 1998; Government of Canada 2005; Pope et al. 2004; USEPA 2007):

- Accept and involve the public as a partner.
- Plan carefully and evaluate the outcome of the communication efforts. Different goals, audiences, and media require different actions.
- Listen to the public's concerns. People often care more about trust, credibility, competence, fairness and empathy than about statistics and details.
- Work with other credible sources. Conflicts and disagreements among organizations make communication with the public much more difficult.
- Meet the needs of the media.
- Speak clearly and with compassion.
- Resolve mobility and information access issues to ensure adequate involvement.
- Communicate in nontechnical, appropriate terms.
- Understand demographic and socio-cultural factors.

Several methods from the social sciences are available to help environmental professionals determine if the heterogeneity of the community is represented and vulnerable sub-populations are identified during risk communication activities. The most basic method is to assess demographic data collected during stakeholder engagement events to evaluate if a representative sample of the community's population is participating. If a select sub-population is not participating in risk communication activities, an alternate mode of information transfer may be required to meet the needs of that demographic group (Bickerstaff 2004; Wester-Herber and Warg 2004; USEPA 2005). More complex stakeholder engagement methods, such as actor-linkage mapping and interest-influence matrices, can be performed to understand relationships and trust among stakeholder groups and their relative interest and influence on project outcomes (Alexandrescu et al. 2016; Harclerode et al. 2015; Reed 2009). The more complex engagement methods can be beneficial in scenarios where affected stakeholders are in conflict with decision-makers, as well as to address challenges posed to effective risk communication activities.

Difficulty Managing Community Expectations

It is not uncommon for risk communication activities to involve a diverse group of stakeholders with opposing sets of views, knowledge, or beliefs. Thus, obtaining unbiased, collective agreements that are representative within and between groups is challenging, but can offer significant benefits to the project and community. Therefore, risk management performance metrics should be in alignment with stakeholder needs and should address site-specific concerns. Stakeholder needs can be identified via public meetings, interviews, focus groups, and surveys. Additional stakeholder engagement methods can be conducted to evaluate, prioritize, and communicate multiple conflicting needs, including multi-criteria decision analysis and rating and scoring system evaluations (Harclerode et al. 2015). Retreats and interactive workshops also provide opportunities to facilitate trust building and collectively gain a common understanding of the problem from which to formulate solutions.

At the Little Hocking Site, a list of General Principles and Principal Targets were developed by the CAC to aid the communication process and manage community expectations (Emmett et al. 2009):

General Principles for Communications:

- 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.

Principal Targets:

- The community, i.e., residents of the water district.
- Community Advisory Committee.

- Relevant authorities and representatives (county and state health departments, state department of environment, local water authorities, state and federal elected government representatives for the area, local townships, sheriff's departments, USEPA).
- Local medical providers.
- Local media.
- National media as necessary.

The conceptual site model (CSM) is also a valuable tool for managing community expectations by providing a concise summary communicating site risks and the project team's understanding of data as it pertains to the management of risk in short and long terms. The CSM should communicate the investigative team's understanding of current data, knowledge gaps, and the likely path forward (including a project timeline), as presented in Section 8. By carefully constructing a CSM that addresses contaminant types, human and ecological health impacts/metrics, potential exposure pathways, and the geological uncertainties that can impact fate and transport, the investigative team gains a valuable tool for management and communication of risk. The CSM should regularly be presented at public outreach meetings, as well as updated by incoming data, new developments, and other pertinent information. The repetitive presentation of the updated CSM creates a sense of transparency that is important to the public, shows stakeholders the value for the effort being put forward, and builds trust among all parties involved.

SUMMARY

Effective risk communication engages stakeholders in the process of risk assessment and management, communicates actual risk, and facilitates participation during the risk management decision making process. Supporting materials to facilitate risk communication are publicly available from a wide range of public health and environmental agencies to assist professionals in communicating potential risks of PFAS exposures to affected parties. In addition, stakeholder engagement techniques and expertise are available from consulting companies, regulatory agencies, private organizations, and academia. As shown in the Little Hocking Site, these resources can be used to overcome challenges associated with questions concerning the legitimacy of risk management guidelines, unacceptance of the proposed risk management strategy, and effective risk communication for vulnerable sub-populations. Performance of successful risk communication throughout a project's life cycle raises the community's awareness of environmental hazards, leads to community empowerment through participation in risk reduction measures, and helps increase the quality of life for the community impacted by contamination and related risk management activities (Harclerode et al., 2016b; USEPA, 2007).

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APPENDIX 1

Summary of Available Supporting Materials

Agency	Document Type	Topics/Questions	Source (Weblink)	Reference
Agency for Toxic Substances and Disease Registry	FAQs	• What are PFASs? • How can I be exposed to PFASs? • How can I reduce my exposure to PFASs? • How can PFASs affect people's health?	https://www.atsdr.cdc.gov/pfc/docs/pfas_fact_sheet.pdf	PFAS Frequently Asked Questions (CS2625744)

Vermont Agency of Natural Resources Department of Health	Fact Sheet	• What is PFOA?
		• Why is PFOA contamination a heath concern?
		• Where can I learn more?
		• Impacted well water:
		  ○ Should I drink the water?
		  ○ Is it OK to shower?
		  ○ What about brushing teeth?
		  ○ Can I do laundry and wash my dishes?
		  ○ Can I use a humidifier?
		  ○ What about water in my swimming pool?
		• Is it okay to eat produce from my garden? Eggs from my chickens? Fish from the river?
		• Should I be concerned about fishing?
		• Is PFOA found in humans?
		• What are the health effects of the levels that have been measured in drinking water?
		• What are the effects on animals?
		• Has EPA developed exposure limits for PFOA?
		• Is there a medical test that can tell me if I've been exposed to PFOA?
		• When should I see a health care provider?
		• Should we wait for the water tests before seeing our doctor?
		• What can be done to take PFOA out of the body?
			http://healthvermont.gov/enviro/pfoa/PFOA_health_facts.pdf	Facts about PFOA for Concerned Residents (April 11, 2016)

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Agency	Document Type	Topics/Questions	Source (Weblink)	Reference
Vermont Agency of Agriculture, Food, & Markets	FAQs	• Is it okay to plant and eat vegetables from my garden this year? • Does it make a difference what vegetable or fruit I am growing in my garden? • I watered my garden from my well last year. My well was found to be contaminated. What should I do this season? • I am a commercial grower; can I have my agricultural soil and products tested? • What about maple syrup? • What about livestock?	http://healthvermont.gov/enviro/pfoa/PFOA_AgProductsFAQ.pdf	Frequently Asked Questions about Gardening, Commercial Produce and PFOA (April 22, 2016)
Vermont Department of Health	Exposure and Health Study	• PFOA contamination background • "Probable "and "No Probable" links between PFOA exposure and health symptoms • Additional studies • Consistent findings	http://healthvermont.gov/enviro/pfoa/PFOA_c8_health_project_summary.pdf	PFOA Exposure & Health Studies (March 16, 2016)
New Hampshire Department of Health and Human Services	Fact Sheet	• Sources of PFCs • Interpreting PFC blood tests • Blood testing options	http://www.dhhs.nh.gov/dphs/pfcs/documents/pfc-fact-sheet.pdf	Perfluororchemical (PFC) Fact Sheet (July 19, 2016)
Biomonitoring California	Presentation	• PFAS definition • Exposure or potential exposure • Known or suspected health effects • Past biomonitoring studies • Bioaccumulation • Persistence	http://biomonitoring.ca.gov/sites/default/files/downloads/PFASs_031315.pdf	Potential Designated Chemicals PFASs Perfluoroalkyl and polyfuoroalkyl substances (Presentation to the Scientific Guidance Panel) (March 13, 2015)
Minnesota Department of Health	Facts & Figures	PFC Blood Levels: • In US Population • In MN community exposed through water • In MN community not exposed through water	https://apps.health.state.mn.us/mndata/biomonitoring_pfc#longterm	Chemicals in People: Biomonitoring PFCs Facts & Figures

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Agency	Document Type	Topics/Questions	Source (Weblink)	Reference
Michigan Department of Health & Human Services	Fact Sheet	• What are PFCs? • What is the drinking water standard for PFCs? • Will I get sick if I have been drinking PFC-contaminated water from my well? • Why issue advice when PFC levels are not an immediate health concern? • Are there PFCs in municipal water? • What is being done about this issue?	http://www.michigan.gov/documents/mdhhs/PFCs_in_Drinking_Water_Wells_532618_7.pdf	Perfluorinated Chemicals (PFCs) in Drinking Water Wells Near the Former Wurtsmith Air Force Base (August 19, 2016)
Agency for Toxic Substances and Disease Registry	ToxFAQs	• What are perfluoroalkyls? • What happens to perfluoroalkyls when they enter the environment? • How might I be exposed to perfluoroalkyls? • How can perfluoroalkyls affect my health? • How likely are perfluoroalkyls to cause cancer? • How can perfluoroalkyls affect children? • How can families reduce the risk of exposure to perfluoroalkyls? • Is there a medical test to show whether I've been exposed to perfluoroalkyls? • Has the federal government made recommendations to protect human health?	https://www.atsdr.cdc.gov/tfacts200.pdf	Perfluoroalkyls – ToxFAQs (CS265956-A, August 2015)
U.S. Environmental Protection Agency	Fact Sheet	• Background on PFOA and PFOS • EPA's 2016 Lifetime Health Advisories • Recommended Actions for Drinking Water Systems • Other Actions Relating to PFOA and PFOS • Non-Drinking Water Exposure to PFOA and PFOS • Where to learn more	https://www.epa.gov/sites/production/files/2016-06/documents/drinkingwater-healthadvisories_pfoa_pfos_updated_5.31.16.pdf	EPA Fact Sheet PFOA & PFOS Drinking Water Health Advisories (EPA 800-F-16-003, November 2016)
Massachusetts Department of Public Health	Community Fact Sheet	• Should I be concerned about PFOA and PFOS that have been detected in recreational water bodies?	http://www.mass.gov/eohhs/docs/dph/environmental/investigations/cape/jbcc-rec-wtr-fact-sheet.pdf	Recreational Use of Waterbodies On or Near Joint Base Cape Cod (JBCC) Community Fact Sheet (Summer 2016)

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Agency	Document Type	Topics/Questions	Source (Weblink)	Reference
Agency for Toxic Substances and Disease Registry	Health Information Summary	• What are PFCs? • Why was blood testing done for PFCs? • Who was eligible for testing? • Why was the PFC blood testing not offered to children under age 12? • How many PFCs were tested in the blood of participants? • What do these results mean for your health? • Animal, Human, Worker, and General Population studies • Do PFCs cause cancer? • Should members of my family get tested for PFCs? • What can people do to avoid PFC exposure?	https://www.atsdr.cdc.gov/HAC/pha/decatur/Blood%20PFC%20Testing%20and%20Health%20Information.pdf	Blood PFC Testing and Health Information Summary, Morgan, Lawrence, and Limestone Counties, Alabama
Naval Facilities Engineering Command	FAQs	• PFC/PFAS general information • Uses with Department of Navy/Military • Releases and Behavior of PFC/PFAS in the environment • Dpt. of Navy policies and Approach on PFC/PFAS • Regulatory Frameworks • Health Effects • Exposure and Biomonitoring • What Federal action is being taken?	http://www.navfac.navy.mil/content/dam/navfac/Specialty%20Centers/Engineering%20and%20Expeditionary%20Warfare%20Center/Environmental/Restoration/er_pdfs/p/DASN-PFAS-PFC-FAQ-20160615.pdf	Frequently Asked Questions: Perfluorinated Compounds (PFC)/Perfluoroalkyl Substances (PFAS) (June 15, 2016)
Agency for Toxic Substances and Disease Registry	Public Health Statement	• What are Perfluoroalkyls? • Where are perfluoroalkyls found? • How might I be exposed? • How can perfluoroalkyls enter and leave my body? • How perfluoroalkyls can affect your health? • How can perfluoroalkyls affect children? • How can families reduce the risk of exposure to perfluoroalkyls? • Are there medical tests to determine whether I have been exposed to perfluoroalkyls?	https://www.atsdr.cdc.gov/toxprofiles/tp200-c1-b.pdf	Public Health Statement Perfluoroalkyls, Division of Toxicology and Human Health Sciences (August 2015)
Agency for Toxic Substances and Disease Registry	Guidance for Clinicians	• PFAS background • Routes of Exposure and Health Effects • Health Studies • Patient Questions and Key Message Answers • Resources	https://www.atsdr.cdc.gov/pfc/docs/pfas_clinician_fact_sheet_508.pdf	An Overview of Perfluoroalkyl and Polyfluoroalkyl Substances and Interim Guidance for Clinicians Responding to Patient Exposure Concerns (9/20/2016)

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Agency	Document Type	Topics/Questions	Source (Weblink)	Reference
Agency for Toxic Substances and Disease Registry	ToxGuide	• Sources of Exposure • Toxicokinetics and Normal Human Levels • Biomarkers/Environmental Levels • Chemical and Physical Information • Routes of Exposure • Relevance to Public Health (Health Effects)	https://www.atsdr.cdc.gov/toxguides/toxguide-200.pdf	ToxGuide for Perfluoroalkyls (August 2015)
New Jersey Department of Health	Fact Sheet	• What levels of PFCs found in drinking water are safe to drink? • What should I do if I am concerned about PFCs in my drinking water? • What can I learn from getting my blood tested for PFCs?	http://www.state.nj.us/health/ceohs/documents/eohap/generic_pfc_fact-sheet.pdf	Drinking Water Facts: Perfluorinated Chemicals (PFCs) in Drinking Water (May 2016)

National Collaborating Centre for Environmental Health (Canada)	Fact Sheet	• Overview of PFCs
		• Animal Studies
		• Human Studies
		  ○ Birth outcomes, pregnancy outcomes and developmental effects
		  ○ Fertility
		  ○ Effects on thyroid hormones
		  ○ Increased cholesterol
		  ○ Immune system effects
		  ○ Uric acid
		  ○ Cancer
			http://www.ncceh.ca/sites/default/files/Health_effects_PFCs_Oct_2010.pdf	Potential human health effects of perfluorinated chemicals (PFCs) (October 2010)

New York State Department of Environmental Conservation	FAQs	• What is PFOA? • Can PFOA be present in soils? • How can I find out if PFOA is in my water or soil? • What do I do if a test shows PFOA in my water? • Can I garden or engage in other activities that involve contact with soil on my property? • I have a backyard garden. Can I eat what I've grown on my property? • Is it safe to consume dairy products from cows that may have been exposed to PFOA? • I raise livestock or meat. What do I need to know? • I raise chickens for eggs and meat. What do I need to know? • Should I be concerned about local maple syrup?	http://www.health.ny.gov/environmental/investigations/drinkingwaterresponse/docs/pfoa_agriculture.pdf	Frequently Asked Questions: PFOA in soils, water, and impact on agriculture (August 2016)

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Agency	Document Type	Topics/Questions	Source (Weblink)	Reference
New York State Department of Health	FAQs	• Should people expect to find PFOA in their blood? • How high will PFOA levels be in blood? • Will PFOA blood levels ever go down? • Can PFOA blood levels predict the likelihood of having health problems? • What do the studies show about health effects, cancer, and PFOA exposure? • Do some people tend to have more PFOA in their blood than others? • How will people be able to compare their levels to others? • Were there other biomonitoring studies of PFOA exposure? • What do we know about levels of PFOA in blood in the U.S. population? • How are people exposed to PFOA? • How does PFOA leave the body? • Should mothers exposed to PFOA breastfeed their children?	https://www.health.ny.gov/environmental/investigations/hoosick/docs/pfoa_blood_sampling_q_and_a_9_2_16.pdf	PFOA Biomonitoring (Blood Sampling) Program (September 2016)
California State Water Resources Control Board	Fact Sheet	• PFOA general information • Regulatory and water quality levels • Summary of detections in public drinking water wells • Analytical information • Occurrence: Anthropogenic sources, natural sources, history of occurrence, contaminant transport characteristics • Remediation and treatment technologies • Health effect information	http://www.swrcb.ca.gov/gama/docs/pfoa.pdf	Groundwater Information Sheet Perfluorooctanoic Acid (PFOA) & related Compounds, State Water Resources Control Board, Division of Water Quality, GAMA Program (May 2016)

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Groundwater and PFAS: State of Knowledge and Practice

Remediation and Treatment
Section 8

One of eight sections prepared by National Ground Water Association volunteers. Each section was prepared to stand independently, or to be integrated with the other seven sections.

NGWA Press
The Groundwater Association

Remediation and Treatment

INTRODUCTION

This guidance has been prepared to provide groundwater professionals with sufficient background and technical information to make informed decisions about treating groundwater impacted with per- and polyfluoroalkyl substances (PFAS). As described below, PFAS in groundwater present unique challenges with respect to treatment. Specifically, some PFAS are very stable chemicals that do not readily degrade in the environment and/or are not effectively treated by conventional remedial technologies or wastewater treatment plants. In situ remediation of some PFAS may result in by-product PFAS that are more mobile and/or exhibit properties that make them less amenable to remediation.

This guidance identifies potential treatment technologies that can be considered for remediating groundwater containing PFAS. This guidance focuses on the six PFAS currently listed in USEPA's Third Unregulated Contaminant Monitoring Rule (UCMR 3) ["the UCMR3 Six"], which was published on May 2, 2012:

- Perfluorooctane Sulfonate (PFOS)
- Perfluorooctanoic Acid (PFOA)
- Perfluorononanoic Acid (PFNA)
- Perfluorohexanesulfonic Acid (PFHxS)
- Perfluoroheptanoic Acid (PFHpA)
- Perfluorobutanesulfonic Acid (PFBS)

From the perspective of establishing remedial objectives, USEPA and many states have provided guideline concentrations for PFOA and PFOS, the two PFAS most commonly detected in source or drinking water. USEPA recommends that drinking water containing PFOA or PFOS individually or in combination at concentrations greater than 0.070 µg/L (70 ng/L) should undergo further testing and efforts to limit exposure. In addition, some states, like Minnesota and New Jersey, have guidelines for a number of other PFAS and indications suggest that USEPA and many states will establish new criteria for yet to be regulated PFAS and existing regulatory criteria may become more conservative.

To responsibly manage sites with PFAS groundwater contamination, it is important to be aware of the reaction pathways for these chemicals and monitor for the relevant compounds. PFOS is produced by electrochemical fluorination, while PFOA can be produced through both electrochemical fluorination and by a telomerization process that adds two carbon units to a polymer in a linear fashion. The processes generate different residual and associated chemicals, some of which are PFAS themselves and some of which degrade into other PFAS contaminants encountered in the environment.

The remedial options available to address PFAS contamination are limited by the unique physicochemical properties of these compounds. Technologies currently used for the remediation of PFAS-contaminated sites include soil incineration or excavation to landfill (where authorized) and groundwater extraction with PFAS adsorption onto granular activated carbon (GAC) or ion-exchange resins (IX). Other remedial techniques that may decrease PFAS groundwater concentrations include soil washing, soil solidification and the use of in situ permeable reactive barriers or funnel and gate systems.

Many remediation methods used to effectively treat other contaminants are not effective on PFAS.

Disclaimer: This publication is a collaborative effort to try to set forth best suggested practices on this topic but science is always evolving, and individual situations and local conditions may vary, so members and others utilizing this publication are free to adopt differing standards and approaches as they see fit based on an independent analysis of such factors. This publication is provided for informational purposes only, so members and others utilizing this publication are encouraged, as appropriate, to conduct an independent analysis of these issues. The NGWA does not purport to have conducted a definitive analysis on the topic described in this publication, and it assumes no duty, liability or responsibility for the contents or use of the publication.

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For example, technologies used to address hydrocarbon contamination, such as air stripping, sparging, soil vapor extraction, and bioremediation, are ineffective due to the low volatility of these compounds and their resistance to microbial degradation. Landfilling does not inherently include a destruction of the PFAS molecules and may lead to leachate issues in the future. Additionally, emerging water treatment technologies for PFAS, such as photolysis/photocatalysis, reductive decomposition, advanced oxidation, and sonolysis, may require high energy input per unit water volume and long residence times. Consequently, these technologies are unlikely to be feasible for high flow rate, low concentration applications. Careful monitoring of treatment performance is also required to ensure complete breakdown of the various PFAS substances that may be present.

Groundwater extraction volumes may be high if remediation is required to reach very low environmental quality standards (e.g., for PFOS). Although the degree of sorption of PFAS to sediment is generally low, it can be significant if organic material is present. PFAS sorption to sediment, leading to retardation of transport in groundwater, increases with perfluorocarbon chain length and may extend beyond the duration of groundwater extraction.

Current best practice disposal routes for spent PFAS adsorption media are high temperature incineration at > 1,000°C, high temperature reactivation (for GAC) or chemical regeneration (for IX) at a specialized facility.

The background section in this chapter provides information on the unique PFAS properties that may affect remediation. The subsequent section provides an overview of water/groundwater treatment approaches, identifying the relative effectiveness of each approach. Subsequently, a more detailed discussion on individual treatment technologies is provided, identifying advantages and disadvantages of each approach, and potential by-products that could be formed. The remediation approach will need to be tailored to site-specific conditions. Given the complexity of PFAS, and their multiple potential interactions, due diligence is required by a groundwater professional in developing the conceptual site model for PFAS. This chapter identifies key information that groundwater professionals need to know in order to properly select, design, construct, implement, and maintain a remedial approach; and how to vet potential treatment technologies from concept to full-scale field application.

BACKGROUND

Per- and polyfluorinated alkyl substances (PFAS) are a large group of manufactured chemicals used in industrial applications and consumer products. For further detail on PFAS terminology and classification, the reader is referred to Buck et al. (2011). Manufactured to be chemically and thermally resistant, many PFAS maintain these characteristics when released into the environment and do not readily degrade in the environment. Moreover, PFAS have unique properties that cause some PFAS to be very stable, slow to degrade in the environment, and very difficult to remediate.

Specifically, as described below, PFAS contain fluorine atoms bonded to a chain of carbon atoms; and they tend to be dual-natured, as the per- or polyfluorinated carbon chain "tail" and the functional group "head" prefer different interactions. PFAS can be cationic, zwitterionic, and anionic, resulting in very different fate and transport behaviors in the environment.

Additionally, and importantly, PFAS are a large group of substances that have unique properties unto themselves. As described below, chain length and functional group "head" can greatly influence PFAS behavior in the environment and how they could be effectively remediated. PFAS precursors (i.e., those compounds that will degrade or transform into more stable and harder to remediate compounds) add another level of complexity to remediation, as remediation may transform precursors into these more recalcitrant compounds.

Finally, as is the case with the historical use of aqueous film forming foam (AFFF) containing PFAS, PFAS impacts are often found co-mingled with other contaminants (e.g., petroleum hydrocarbons) and remediation must consider how these other contaminants may affect the efficacy of any proposed remedial approach. How each of these factors affects fate and transport has been discussed previously in this document. Their impacts on remedial efficacy are summarized in Table 8.1.

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Table 8.1. PFAS Factors That Affect Remedial Efficacy

Affect Remedia	Summary of Impacts
Carbon-Fluorine Bond	The dense packing of fluorine electrons can act as a "shield," protecting PFAS from external attacks, resulting in increased thermal, chemical, photolytic (UV-radiation), and biological stability of these materials. This results in a backbone of the compound that is non-reactive, stable, and persistent.
Dual Nature	Many PFAS were broadly used for their surfactant-like properties. These surfactant properties include hydrophobic, lipophobic, hydrophilic, and zwitterionic interactions between the PFAS molecules and their surrounding environment. In contrast to traditional surfactants, the C-F chain can also be lipophobic, which renders many PFAS coatings resistant not only to water, but also to oil, grease, and other non-polar compounds and particles. Not all PFAS exhibit surface properties, e.g., the hydroxyl group found on telomeric alcohols is too small to act as a surfactant. These properties not only affect where they end up in the environment (e.g., interfaces, ability to form micelles), but can also influence the efficacy of different remediation approaches.
Chain Length	The toxicity and degradability of PFAS is mostly influenced by the chain length and the functional group (Ahrens et al. 2011). The chain length also affects their water solubility (i.e., longer C-F chain, less soluble PFAS compound). The physicochemical properties within a homologous PFAS series (e.g., the same terminal functional group, with different CF2 chain length) can change non-linearly. This has been attributed to the increasing chain length. With increasing chain length, the geometry of the molecule changes (Wang et al. 2011). Many types of remediation technologies are dependent upon both charge and chain length.
Mobility	Low sorption to soil and high solubility can create large diffuse plumes and challenges to many sorption based remediation techniques
Characterization	A wide range of compounds can be present from sustained use of multiple PFAS containing products. A mixture of compounds could require several separate analyses for quantification and identification of all source areas, and costs can be substantial.
Low Vapor Pressure and Henry's Law Constant	Characteristically, PFAS have low vapour pressure, and have a wide range of Henry's Law coefficients (range over nine orders of magnitude). The low vapor pressure affects decision-making processes as to which remediation approaches are no longer viable. Since PFAS do not volatilize readily, methods such as air stripping are not practical remedial solutions.
Precursors	Formulations that contain regulated PFAS like PFOS and PFOA can also contain precursor compounds, compounds that can degrade to more PFAS such as PFOS and PFOA.
Commingling	PFAS in the environment are often attributed to the use of AFFFs which contain a mixture of different compounds. Each compound has unique physicochemical characteristics, be it chain-length, functional group, vapor pressure, etc., that can affect its individual environmental fate and transport, and amenability to various remediation approaches. Other co-contaminants can include: petroleum hydrocarbon fuels, metals, polycyclic aromatic hydrocarbons.

TREATMENT APPROACHES

Overview

Given the challenges identified above, development of proven remedial technologies for PFAS has been elusive. Recent publications have discussed some bench scale success with degradation or destruction using advanced oxidation (Liu et al. 2011/2012), enhanced photochemical approaches (Hori et al. 2004, 2007a, 2007b), and irradiation methods (Zhang et al. 2014); however, these technologies are often not practical for field-scale implementation (Vecitis et al. 2009). Traditional methods, such as "excavation and disposal" and "pump and treat" have been successfully applied in the field, but maintain the limitations that are typically associated with these methods (and would likely be exacerbated by the nature of some PFAS). With excavation and disposal, contamination is just being transferred to another site; with groundwater treatment via "pump and treat," high costs of operation and maintenance are ongoing for long periods of time.

Due to the unique properties illustrated in Figure 8.1, remediation of PFAS in groundwater is a challenge. While there are a large number of studies on treatment technologies for PFAS in waste and drinking water, there has been (until recently) limited demonstrable success with remediating groundwater

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impacted by PFAS. Many conventional groundwater treatment technologies are ineffective in addressing PFOS and PFOA and many technologies that seem to be effective for PFOS or PFOA appear to be less efficient with shorter-chain PFAS compounds.

Figure 8.1. Remedial approaches inhibited by PFAS physicochemical properties.
(O'Hagan 2008).

Properties	Remedial Approaches
Strong C-F bond No aromatic features No double bonds Electron withdrawing functional groups	Hydrolysis Photolysis Oxidation Microbial degradation
No H atoms to withdraw Low vapor pressure	Air Stripping

Different remedial approaches will be successful at varying degrees with each compound and, like environmental remediation in general, the multitude of site-specific factors will greatly affect the effectiveness of any given remedial approach. For example, the strong fluorine-carbon bond and low vapor pressure means that some PFAS (e.g., PFOA and PFOS) are resistant to a number of conventional water treatment technologies, including direct oxidation, biodegradation, air stripping and vapor extraction, and direct photolysis (UV). Moreover, with PFAS, degradation of select precursors if present (or had been historically present) within AFFF can compound the issue by generating additional persistent PFAS (Thalheimer et al. 2017). Similarly, efforts to remediate the recalcitrant PFOA and PFOS have reportedly resulted in mobilization of shorter-chain PFAS.

The following sections identify and discuss those remedial technologies that may be effective in treating the UMCR3 Six in groundwater, in part and/or in conjunction with other remedial technologies. As with other environmental remediation of groundwater, remedial approaches can be either ex situ or in situ. Based on available evidence, groundwater professionals should anticipate that more than one technology may be required in the treatment train to address the potentially numerous PFAS that one may encounter in groundwater.

Drinking Water Treatment Technologies

The physicochemical properties that challenge groundwater remediation affect drinking water technologies in the same way. Many of the current guidelines and regulations surrounding PFAS in water are derived for the protection of human health (i.e., drinking water). As a result, drinking water and wastewater treatment plants were forced to comply and develop treatment trains that would effectively remove the regulated substances from the water matrix.

Dickenson and Higgins (2013) and Rahman et al. (2014) have evaluated a variety of full-scale treatment approaches in their ability to remove PFAS from raw water, or potable water reuse plants. Treatment trains (combinations of techniques in sequence) varied, but generally consisted of coagulation, followed by a physical separation, aeration, chemical oxidation, UV irradiation, and disinfection. Full-scale drinking water treatment plant occurrence data indicate that PFAS, if present in raw water, are not substantially removed by most drinking water treatment processes (i.e., coagulation, flocculation, sedimentation, filtration, biofiltration, oxidation (chlorination, ozonation, advanced oxidation processes [AOPs]), UV irradiation, and low pressure membranes). Preliminary observations have suggested that activated carbon adsorption, ion exchange, and high pressure membrane filtration may be effective in attenuating these compounds. As indicated in Table 8.2, conventional technologies of aeration, coagulation dissolved air floatation, coagulation, flocculation, sedimentation, filtration, and conventional oxidation are not effective on the UCMR3 Six. Consequently, this section discusses those commercially available and emerging technologies that have demonstrated success in field-scale remediation of PFAS in groundwater (see Table 8.3).

Much of the current literature on the successful application of treatment technologies has been shown for water treatment plants (Table 8.2, Table 8.3). While the principles remain the same (e.g., inlet flow of PFAS in water, PFAS sorb to granular activated carbon [GAC]/removed by membrane, "treated" effluent), the inlet concentrations, quantity of reactive media required, and timeframe to treat PFAS-impacted groundwater may be very different. Unfortunately, these technologies (i.e., those that are effective on potable water) are not always directly applicable (nor equally effective) to the in situ treatment of contaminated groundwater.

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Table 8.2. Efficacy of Different Remedial Treatments on PFAS (adapted from E. Dickenson et al. 2016)

Compound	Acronym	Molecular Weight (g/mole)	Aeration	Coagulation Dissolved Air Floatation	Coagulation Flocculation Sedimentation Filtration	Conventional Oxidation (MnO_4, O_3, ClO_2, CLM, UV-AOP)	Anion Exchange (Select Resins Tested)	Granular Activated Carbon	Nano Filtration	Reverse Osmosis
Perfluorobutanesulfonic Acid	PFBS	300								
Perfluoroheptanoic Acid	PFHpA	364								
Perfluorohexanesulfonic Acid	PFHxS	400								
Perfluorooctanoic Acid	PFOA	414								
Perfluorononanoic Acid	PFNA	464		unknown			assumed	assumed		
Perfluorooctane Sulfonate	PFOS	500								

Table modified from E. Dickenson and C. Higgins 2016

> 90% removal | >10%, < 90% removal | < 10% removal

Notes:
"assumed": treatment performance is assumed based on the PFAA size/charge and/or known removal data of shorter or longer chain homologues
CLM: Chloramination, Cl2: Hypocholorous/Hypocholorite, ClO2: Chlorine Dioxide, O3: Ozone, MnO4: Permanganate, RO: Reverse Osmosis, SED: UV: UV Photolysis, UV-AOP: UV Photolysis with Advanced Oxidation (Hydrogen Peroxide)

Groundwater Remediation Technologies

Pump and Treat

Pumping and ex situ treatment of groundwater (usually with activated carbon filters on site) to stop off-site transport, and/or to promote mass removal, is a viable and appropriate method, although experience from a number of sites worldwide has shown that the efficiency of activated carbon filters is variable. There is ongoing research to identify more optimized filter materials. Efficiency will also be very dependent upon the treatment target. If very low concentrations are required, the groundwater pumping may have to be in place for a very long time (in some cases > 100 years), which can be a disadvantage with this technology.

Extracted groundwater volumes may be high if remediation is required to meet low concentrations. The presence of mineral sorptive surfaces and organic carbon content in sediments with PFAS mass storage capacity can reduce the plume's treatability. Although the degree of sorption of PFAS to sediment is generally low, it can be significant if organic material is present. Sorption of PFAS to sediment, leading to retardation of transport in groundwater, increases with perfluorocarbon chain length and may extend the duration of groundwater extraction.

Granular activated carbon (GAC)

The application of GAC as a total treatment solution for PFAS removal in both drinking water and remediation applications has been practiced for over 15 years at over 40 installations, at the time of publication. GAC can remove typical levels of PFOA and PFOS to non-detect levels (Ochoa-Herrera et al. 2008). Thus, even if state regulations require lower PFAS concentrations than the USEPA health advisory, GAC may be an effective solution for PFOS and PFOA. Temporary and permanent GAC systems can be rapidly deployed and require little operator involvement. The application of GAC also imparts the added benefits of the reduction of disinfection by-product formation, the removal of taste and odor, and a wide variety of other emerging contaminants.

The effectiveness of GAC for PFAS removal does decrease with decreasing chain length of the PFAS (Xiao et al. 2017). However, recent accelerated column tests have shown the successful removal of a variety of shorter PFAS including the butyl, pentyl, and hexyl compounds (Appleman et al. 2013; Dickenson and Higgins 2016). To determine whether or not GAC will be an economically viable solution for a given application, testing is critical to determine system design and cost performance. Since each water source contains different combinations and levels of PFAS, pH, and ionic strength, as well as different levels of total or dissolved organic carbon (TOC, DOC) that can compete for adsorption sites and decrease GAC efficiency, it is strongly advised that a lab or pilot test (e.g., Rapid Small Scale Column Testing (RSSCT), Accelerated Column Test or ACT) be performed on a representative water sample to determine the

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Table 8.3. Summary of Treatment Options for Removal of PFNA, PFOA, and PFOS for Drinking Water (Cheremisinoff 2016)

Treatment Option	Notes	Application	Removal Rates		
			PFNA	PFOA	PFOS
Granular Activated Carbon (GAC)	GAC is the most common treatment method for long-chain PFAS removal. Competition for adsorption with other contaminants can reduce effectiveness. Thermal reactivation of GAC is effective.	Surface Water, Groundwater, PWSs, Households	>90%	>90%	>90%
Powdered Activated Carbon (PAC)	High concentrations of PAC are necessary. PAC may be useful in responding to spills but the required high concentrations may make this an infeasible option for water treatment. PAC combined with waste residuals may create a challenge for disposal of waste products.	Surface Water, Groundwater, PWSs, Households	>90%	>90%	>90%
Membrane Filtration (Reverse Osmosis and Nanofiltration)	Multi-contaminant removal. Rejection rate can be high. Waste/by-products must be managed. Mineral addition may be necessary.	Surface Water, Groundwater, PWSs, Households (RO)	>90%	>90%	>90%
Anion Exchange (Special ion exchange material shaped as beads exchange anions and replace hydroxyl groups)	Single-use systems do not produce contaminant-containing brine but require replacement and proper disposal. High capacities may lead to less frequent changeouts compared to GAC. Regenerable systems produce brine that must be disposed of responsibly; such systems are automated, have small footprints and high regeneration efficiencies. Competition with common ions for binding sites on resins can impact effectiveness. Organics, total dissolved solids, minerals can clog resins and reduce efficiency.	Surface Water, Groundwater	>67%	10-90%	>90%
Advanced Oxidation (UV/H2O2; UV/S2O8)	Low removal rate. Can destroy pollutants to produce less complex compounds. Other organic contaminants will compete for hydroxyl radicals and reduce efficiency.	Surface Water, Groundwater	<10%	<10%	<10 - 50%

adsorption zone needed, as well as the estimated carbon exhaustion rate to properly design an activated carbon adsorption system to meet a given target.

There are different types of GAC available on the market with varying PFAS removal performance. For example, GAC with a pore size distribution that is largely microporous tends to suffer from competitive adsorption of the ppm levels of TOC that are typically present in groundwater and to exhibit much quicker breakthrough of PFAS compared to other types of GAC. GACs with a broader distribution of pore sizes are recommended.

One of the most important advantages to GAC is that it removes PFAS without generating a concentrated waste stream that becomes a disposal concern. Spent activated carbon that contains PFAS can be thermally reactivated, thereby destroying the compounds and eliminating the potential future liability of disposed PFAS wastes streams, and then reused.

Coagulation and Activated Carbon

Coagulation-flocculation is a chemical water treatment technique typically applied prior to sedimentation and filtration (e.g., rapid sand filtration) to enhance the ability of a treatment process to remove particles prior to subsequent polishing treatments, such as PAC (powdered activated carbon) or GAC. If the coagulation techniques provide initial PFAS mass removal, they can also significantly increase the life span of downstream sorbent media. The coagulation process works with chemicals that exhibit a charge (zwitterionic, cationic and/or anionic), such as PFAS. It should also be noted that coagulation/flocculation used for PFAS removal may result in the generation of a PFAS-impacted solid waste stream that would need to be managed.

A recent study found that a combination of coagulation and adsorption by PAC was effective (>90 percent removal) at removing both PFOS and

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PFOA from water (Bao et al. 2014). Coagulation alone is not an effective means of removal for long-chain PFAS like PFNA, PFOS, and PFOA (Rahman et al. 2014; Appleman et al. 2014). Removal of PFOS and PFOA by coagulation works by adsorption of the contaminants onto the surface of the coagulants; anions adsorb onto the positive surface of coagulants and flocs and are then removed with sedimentation and filtration. Subsequent to coagulation-flocculation treatments, PAC was shown to have a significantly higher absorption rate and capacity than GAC, and higher absorption efficiency for PFOA than PFOS (Bao et al. 2014). The removal ratios for PAC increase with decreasing pH and with increasing coagulant dose, which was consistent with other research results evaluating pH on PAC efficacy for PFAS removal (Dudley et al. 2015).

Ion Exchange Resins

Ion exchange (IX) involves the use of resins, very small plastic porous beads with a fixed charge, that are used to exchange contaminant ions with hydrogen or hydroxyl ions. The removal rate is dependent upon many factors including:

- Initial contaminant concentration
- Competing ion concentration
- Treatment design (e.g., flow rate, resin bead size)
- Resin ion properties.

IX resins, specifically anion exchange treatments, have been investigated in pilot studies for application in pump-and-treat systems for removing PFAS (Woodward et al. 2017). The removal of PFOA and PFOS has been reported at a New Jersey drinking water treatment plant using porous anion exchange resin impregnated with iron oxide (Rahman et al. 2014). Researchers have noted that the shorter-chain PFAS were not removed through the documented IX treatment processes (Appleman et al. 2014). A possible alternative for PFAS removal could be a hybrid adsorption/anion exchange treatment approach, in which more strongly adsorbing PFAS are initially removed by activated carbon and the more weakly adsorbing PFAS subsequently by anion exchange. The hybrid approach may facilitate resin regeneration, which is more readily accomplished if only PFAS that interact more weakly with the resin need to be removed.

The management of the spent resin (e.g., incineration, landfill, regeneration) and of the PFAS-laden brine resulting from resin regeneration (e.g., chemical processes or disposal) must be considered with this technology.

For PFOS, different ion exchange resins can be suitable. Sorption using ion-exchange polymers is based on the attraction of the negatively charged functional group of PFOS, and also on the relatively negatively charged tail (due to electronegativity of the fluorine atoms). Hydrophobic interactions with the resin may also play a role. Non-ion exchange polymers usually show weaker bonding between the adsorbent and adsorbate, which makes regeneration easier and regeneration can occur, for example by solvent washing (Senevirathna et al. 2010). Anion-exchange resins exhibit higher adsorption capacity (Du et al. 2014). In general, sorption capacities decrease in the following order:

Ion-exchange polymers >
Non-ion-exchange polymers > GAC

However, at lower concentrations (100 ng/L) non-ion exchange polymers reportedly showed higher adsorption capacity than other adsorbents. Adsorption kinetics highlight that GAC and ion-exchange polymers show fast sorption kinetics, much faster than non-ion exchange polymers (Senevirathna et al. 2010).

Membranes (Nano and RO)

Nanofiltration (NF) polymers vary with the membrane manufacturer and as the removal of contaminants by membranes is a "sieving" process, some of the NF polymer's molecular weight cut-off (MWCO) properties may not be low enough. The MWCO of reverse osmosis (RO) membranes is between 100 and 200 Daltons (Daltons are three-dimensional molecular weight units).

The crossflow, pressure-driven membrane separation technologies of microfiltration, ultrafiltration, nanofiltration, and reverse osmosis are mature, and have been widely applied to water purification and wastewater treatment for over 50 years at water treatment plants and in residential systems

The removal of nonionic PFAS contaminants by these technologies is by sieving, or size selection. Chemicals that are too large to pass through the membrane pores will be held back, or rejected by the membrane. The sieving properties of the membranes are known as molecular weight cut-off (MWCO), and because the molecular weights of the PFAS range from 300 to 500 Daltons, the much higher MWCO

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properties of microfiltration and ultrafiltration membranes make them unusable for this application.

Several different membrane polymers may be used for nanofiltration (NF) membranes, and since their MWCO properties vary from one to the other, NF may or may not be applicable; however, the application will have to be thoroughly tested. To date, there are limited data on the effectiveness of NF for PFAS removal, but positive bench scale results have been reported (Steinle-Darling et al. 2008; Appleman et al. 2013).

Most reverse osmosis (RO) membranes manufactured today are based on thin film composite construction, using a variation of the same polymer. As a result, their MWCO properties are the same (100-200 Daltons); therefore, RO should exhibit greater than 90% removal of PFAS (Flores et al. 2013).

These membrane technologies generate a waste stream containing a high concentration of the rejected contaminants. Depending on the system design, this stream volume may range from 5% to 30% of the total volume treated. In the case of RO, this stream will also contain the salts and most of the other contaminants in the water supply. This waste stream must be considered in the total system design and operation.

Given anticipated low total dissolved solids (TDS) in groundwater, the cost of RO systems may be reasonable for groundwater systems. Low pressure RO could be applied (operating at <250 psi) for treatment. The use of centralized reject (concentrate) processing/management facilities to serve several local satellite water treatment plants could be considered to minimize capital and operating costs. RO and nanofiltration treatment systems have not yet been implemented at the field-scale for PFAS groundwater remediation.

Permeable reactive barrier (PRB)

Permeable reactive barriers (PRBs), which essentially are vertical walls (or trenches) created below ground to clean up contaminated groundwater, have been investigated for use in treating PFAS-impacted groundwater. PRB designs are based on detailed hydrogeological assessments and mass flux estimates, and may include "funnel and gate" systems, designed to direct groundwater flow through the PRB "gate." The wall is permeable, which means that groundwater can flow through it. As groundwater passes through the PRB, it reacts with the material in the wall as it flows through. Media for PRBs are chosen based on ability to retain and/or treat given the known groundwater conditions.

Activated carbon is commonly used to adsorb contaminants found in water. Activated carbon, which is used in a granulated or powdered form, is an effective adsorbent because it is highly porous, and provides a large surface area on which contaminants may adsorb. Several case studies have indicated that granulated activated carbon (GAC) is a common and effective (>90 percent removal) treatment for long-chain PFAS contamination. However, short-chain PFAS have been observed to break through. The efficiency of this method varies based on several factors including:

- Target effluent contaminant concentration
- pH
- Water temperature
- Contact time
- Properties of the selected carbon
- Concentration of inorganic substances in the water
- Ambient natural organic matter
- Chlorine concentrations in the water.

Use of activated carbon has also been shown to be less effective at removing shorter-chain PFAS (Appleman et al. 2013, 2014). There are different types of GAC available on the market with varying PFAS removal performance. Removal effectiveness must be considered given the overall uncertainty associated with PFAS ecotoxicity, synergistic effects, and environmental fate and transport. Modified sorbents other than activated carbon (e.g., amine-treated clays) have also been evaluated at the bench-scale for applications to groundwater. Research into using GAC as a reactive medium to induce ECOHR (enzyme-catalysed oxidative humification reactions) through mediators and laccase has been conducted at the bench-scale, with some success in PFOA reduction (Huang 2013). Concerns with observed breakthrough in column experiments (Gellrich et al. 2015; Chularueangaksorn et al. 2014) have slowed application of PRBs in the field for PFAS-impacted groundwater.

To date, there is no published field experience available with permeable reactive barriers (PRB) or funnel and gate systems and PFAS, but the remediation approach may be feasible, as the treatments described in the previous paragraph (GAC, Ion

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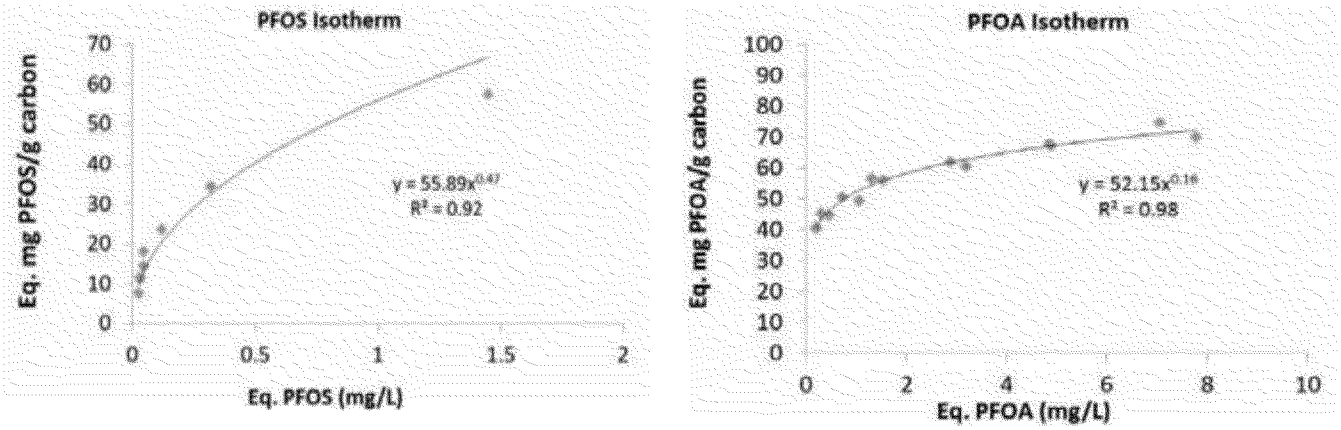
Figure 8.2. Experimentally derived Freundlich sorption isotherms for PFOS and PFOA on colloidal activated carbon (Regenesis 2016).



Exchange Resins) are theoretically compatible with a GAC-sand PRB or a funnel and gate with exchangeable cassettes. Current research is being conducted regarding the applicability of several PRB technologies (e.g., SERDP/ESTCP projects ER-2423 and ER-2425).

Dispersive Colloidal Activated Carbon

An alternative to ex situ GAC, PRBs, and pump and treat is the use of diffuse colloidal activated carbon emplacement in the subsurface (Birnstingl et al. 2014). This provides a means of retarding plume migration without the need for ongoing active intervention. The relatively high sorption of PFAS compounds to activated carbon (Hansen et al. 2010) coupled with the ability to emplace a thin activated carbon coating to the soil particles within the subsurface flux channels, after the polymeric colloidal coating degrades, provides a means of significantly increasing the retardation factors of PFAS species without impact to groundwater flow. This results in passive plume control, eliminating the requirement for pumping equipment and infrastructure installation, operation, maintenance, and energy costs.

Experimentally-derived sorption isotherms for PFOS and PFOA on flow-emplaceable colloidal activated carbon (Regenesis 2016) are presented in Figure 8.2 (Freundlich fit). The capture efficiency compares favorably to common contaminants such as PCE/TCE or BTEX. The convex isotherms result in increased capture efficiency at lower concentrations. This is advantageous given the low treatment targets of PFAS; however, like GAC, some PFAS compounds will be more readily adsorbed than others by the emplaced activated carbon; e.g., longer-chain species and sulfonates will be more readily adsorbed than shorter chain species and carboxylates, respectively.

Example retardation factors (Zheng et al. 1999) for PFOS and PFOA (as single species) based on these isotherms are presented in Table 8.4. Corresponding transit times relative to groundwater across a theoretical emplaced colloidal carbon barrier are also given. These would be in addition to any retardation by natural organic matter. The emplaced colloidal carbon mass relative to soil mass in these examples is 0.0015 (i.e., fraction of colloidal carbon, fcc is 0.0015, which is analogous to foc, fraction of organic carbon). This would have a negligible influence on groundwater flow.

The contaminant transit times through the barrier in Table 8.4 indicate capture for years or decades. The actual duration will depend on the specific concentrations and sorption parameters of the PFAS species, competitive sorption interactions of target and non-target compounds, the mass of carbon emplaced, barrier dimensions, and the groundwater velocity. Given the headroom evident in the examples given, the resultant capture duration may still be considerable.

Since most PFAS species are not amenable to complete biodegradation, the plume-retardation approach remains one of containment rather than extraction or destruction. Contaminant breakthrough will eventually occur. A variety of alternatives exist at this stage. The captured PFAS may be bulk-desorbed and extracted in a focused program, the material may be excavated, or a supplementary colloidal carbon addition may be made—analogous

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Table 8.4. Example PFOS and PFOA Retardation Factors (as single species)

PFOS			
Concentration	Retardation Factor	Transit Time (days)	Transit Time (years)
1,000 µg/L	260	9,490	26
100 µg/L	880	32,100	88
10 µg/L	3,000	110,000	300
Groundwater	1	36.5	0.1
PFOA			
Concentration	Retardation Factor	Transit Time (days)	Transit Time (years)
1,000 µg/L	80	2,920	8
100 µg/L	570	20,800	57
10 µg/L	4,000	146,000	400
Groundwater	1	36.5	0.1

Transit time is relative to groundwater based on a 16-foot barrier width (parallel to flow) and 160 feet per year seepage velocity. Emplaced colloidal carbon fraction (fcc) is 0.0015.

to repainting a fence after some years. The supplementary addition may be overlying or downgradient from the initial carbon placement. It is also possible that new treatment approaches may then be applied that have been developed in the interim. Either way, the plume has been contained and is not significantly larger.

It is also possible that the PFAS source may meanwhile have been addressed, eliminating further ingress of PFAS. This raises the question as to whether the sorbed PFAS would then slowly release as a secondary source. Given that the capture is an equilibration phenomenon, a reduction of influent concentration would shift the equilibrium in the upgradient reaches of the barrier, and mass would desorb. However, as the sorption isotherms are convex (Figure 8.2), the lower concentrations are sorbed (and retarded) more strongly than the higher concentrations. Equilibrating mass desorbing from the upper reaches of the barrier is therefore captured and retained by the downgradient reaches of the barrier and the equilibrium solution concentration once more becomes negligible. The process is analogous to the more familiar ex situ carbon filters —these do not typically bulk-release their captured mass as soon as the influent water becomes clean.

PFAS Degradation Remediation Technologies

Bioremediation

There is evidence of incomplete biodegradation of some poly- and perfluorinated compounds, leading to the formation of other PFAS. For example, recent publications have demonstrated that 8:2 fluorotelomer alcohol can be transformed by bacteria and fungi from soil and wastewater treatment plants to PFOA (Dinglasan et al. 2004; Wang et al. 2005; Tseng 2012). Similarly, 2-N-ethyl (perfluorooctane sulfonamido) ethanol can be transformed by wastewater treatment sludge to PFOS (Meesters and Schröder 2004). No evidence was found that these two products (PFOA and PFOS) are biodegraded any further. Therefore, the question remains as to whether there is any potential for defluorination and biodegradation of PFAS that contributes significantly to their environmental fate.

The lack of mineralization observed is likely due to the stability of the C–F bond, although there are examples of microbially catalyzed defluorination reactions. As is the case with reductive dechlorination or debromination, reductive defluorination is energetically favorable under anaerobic conditions and releases more energy than that available from sulfate reduction or methanogenesis. Consequently, we should consider the possibility that bacteria will adapt to utilize this source of energy, although evolving mechanisms to overcome the kinetic barriers to degradation of these compounds may take some time. The fact that such reactions are absent for some PFAS to date, it may be because too little time has passed for microorganisms to adapt to these

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Table 8.5: Examples of Oxidation Approaches

Technique	Effectiveness as per literature reviewed
Persulfate photolysis using liquid CO2	Viable method for photolysis of PFOS and PFOA.
Activated persulfate	Proprietary persulfate based formula. Destructive technology, in situ. Lab scale demonstrated on destruction of PFOS and PFOA. Field demos were slated for 2016. (Pancras et al. 2013)
Heteropolyacetic acid such as phosphotungstic	Viable method for PFOA, but at a much slower rate than the liquid CO_2 technique.
Heat activated persulfate oxidation	PFOA transformation to complete mineralization (72 hours at 50°C). PFOS is not transformed. (Park et al. 2016)
Titanium oxide	Not effective on sulfonates.
Photo-Fenton reaction/ ferrioxalate photolysis	Moderately effective on PFAS.
UV-potassium iodide photolysis	Effective for the treatment of water contaminated with PFAS, resulting in defluorination and the generation of some volatile fluoro-organics, which would require subsequent treatment.

potential substrates. Hence, the situation may be comparable to that of chlorinated organic compounds several decades ago. For many years, organochlorine compounds were considered to be catabolically recalcitrant; today, reductive chlorination reactions of many organochlorines, including PCBs and dioxins, are regularly observed in anaerobic environments. Hence, it is important to continue studying the potential degradation of perfluorinated compounds in carefully designed experiments with either microbial populations from contaminated sites or cultures of bacteria known to dehalogenate chlorinated compounds.

An extensive analytical study of the biodegradation of PFAS was reported by Schröder (2003). Wastewater samples were spiked with a number of perfluorinated surfactants (PFOS, PFOA, and nonionic surfactants including partially fluorinated alkyl ethoxylates, perfluorooctanesulfonyl-amidopolyethoxylate, and perfluorooctanesulfonyl- amido-polyethoxylate methyl ether) and incubated under aerobic and anaerobic conditions. Rapid biodegradation was observed in aerobic wastewater of the partly fluorinated compounds to form carboxylic acids (identified by LC-MS/MS). For the perfluorinated compounds, in contrast, there was a rapid removal of PFOS (within two days) under anaerobic conditions followed by a slower removal of PFOA. Of the nonionics, only the sulfonyl compounds were removed. Metabolites were neither detected in the anaerobic incubations nor was there any increase in fluoride concentration observed. A further study of the biodegradation of PFOS and PFOA was performed in aerobic and anaerobic reactors containing sludge from German wastewater treatment plants (WWTPs) (Meesters and Schröder 2004). No primary biodegradation was observed under aerobic conditions, but removal, first of PFOS and subsequently of PFOA, was observed under anaerobic conditions. Neither compound could be detected after 26 days; however, no metabolites or increases in fluoride ion concentration were detected that could corroborate any real biodegradation having occurred.

A detailed report by Dinglasan et al. (2004) that provided evidence for environmental biotransformation of PFAS precursors was a study of the biotransformation of 8:2 fluorotelomer alcohol (FTOH) by a mixed microbial consortium enriched from sediment and soil, using 1,2-dichloroethane and ethanol as carbon sources. Analysis of the aqueous phase by LC-MS/MS revealed formation of acid metabolites: 8:2 fluorotelomer carboxylic acid (FTCA), 8:2 fluorotelomer unsaturated carboxylic acid (FTUCA), and PFOA as major products. The proposed pathway consisted of the oxidation of FTOH to FTCA and the formation of FTUCA from FTCA, presumably by loss of HF and subsequent conversion of FTUCA to PFOA.

Wang et al. (2005a, 2005b) and Tseng (2012) also performed extensive studies with 8:2 FTOH and 6:2 FTOH. Wang et al. showed that microbes in a diluted sewage sludge from a domestic WWTP degraded FTOH to the 8:2 FTCA, the 8:2 FTUCA, and PFOA, consistent with the data reported by Dinglasan et al. (2004). The authors also identified a new transformation product, 2H,2H,3H,3H-perfluoroundecanoic acid, also referred to as 7-3 acid, which is a potential

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substrate for beta oxidation in the degradation pathway. It was proposed that this compound was formed from the saturated acid by reductive defluorination. Several minor products were identified: 7:2 FTOH, 7:3 FTUCA, and 7:3 fluorotelomer unsaturated amide, as well as PFNA. The release of fluoride to the medium was also significant (about 12% of that present in the telomer alcohol). Tseng (2012) indicated that P. chrysosporium (fungi culture) was able to transform about 50% 6:2 FTOH and 70% 8:2 FTOH in 28 days. Major metabolites of 6:2 FTOH included 5:3 polyfluorinated acid (40%), 5:2 sFTOH (10%), PFHxA (4%), and others (about 1% each). Fewer metabolites were produced after 8:2 FTOH degradation, such as 7:2 sFTOH (6%), PFOA (5%), 7:2 Ft ketone (3%), and others (< 1% each). These results demonstrate that several metabolites, including PFOA and PFOS, are produced but there is no evidence presented that shows these metabolites are biodegraded any further.

Chemical Oxidation

Chemical oxidation is a form of redox manipulation that can convert hazardous contaminants to nonhazardous or less toxic compounds that are more stable, less mobile, and/or inert. Some examples of PFAS oxidation are shown in Table 8.5. PFOS and PFOA oxidation has been observed to be slow due to the high electronegativity of the fluorine atoms surrounding the carbon chain (Vecitis et al. 2009). Both compounds are recalcitrant towards oxidation due to the complete substitution of fluorine (C-F bond) for hydrogen (C-H bond). The perfluorinated backbone of PFOS and PFOA will also reduce the oxidizability of the ionic functional group (-SO3- for PFOS and –CO2- for PFOA), since it inductively reduces functional group electron density. Thus, the perfluorination of PFOS and PFOA renders these compounds very difficult to degrade by oxidation techniques. The presence of other dissolved organic compounds in addition to PFOS and PFOA will competitively inhibit degradation by oxidation, due to the lower reaction rate of these PFAS (Buxton et al. 1988). Several laboratory studies attest to the feasibility and varying degrees of effectiveness of chemical oxidation for PFOA destruction (Hori et al. 2005, 2008; Ahmad 2012; Hao et al. 2014; Yin et al. 2016). Several variations of oxidation processes using persulfate show promising results for degrading PFOA (Hori et al., 2005, 2008). PFOA was also effectively destroyed by ultraviolet-activated Fenton oxidation (Tang et al. 2012). Although some studies question the ability of the hydroxyl radical to degrade PFOA, chemical oxidation systems can be effective in treating PFOA via alternative radical species (Ahmad 2012). However, these studies focus mainly at treatment of PFOA and have not been validated for treatment of other PFAS. PFSAs (e.g., PFOS) are more difficult to oxidize.

A challenge may be the complex composition of contaminated media and the presence of precursors which have large organic functional groups that can be oxidized via conventional oxidative processes (e.g., hydroxyl radical-mediated) leaving PFCAs or PFSAs.

Some studies have found that conventional chemical oxidation is not an effective treatment for PFAS due to the resistance of the fluorine bond to oxidation (Appleman et al. 2014); however, advanced oxidation processes (AOPs) that generate additional free radicals may be more effective. The radicals are usually formed by some combination of ozone, hydrogen peroxide, and/or UV light or catalysts, but also by electrochemical means or sonolysis. Many of these processes have been shown in the laboratory to degrade PFAS and some have been tested or proposed to be tested with actual contaminated media in the lab and/or field. Whether any particular process is practical for either in situ or ex situ application will be discussed herein. In any case, most processes will need more R&D and field pilot testing before being ready for full-scale field applications. Merino et al. (2016) is an extensive compilation of AOP and other processes for the treatment of PFAS.

AOPs: Activated Persulfate ($S_2O_8^{2-}$) Oxidation

Persulfate is a strong oxidant (E° = 2.9, 2.1 V, various references) that is highly soluble and commonly applied for in situ remediation of many common organic contaminants. Persulfate can generate hydroxyl (OH•–, E° = 2.7 V) and free sulfate radicals (SO4•–, E° = 2.6 to 3.1 V) when activated by UV light, acid, base, transition metals, tungsten trioxide (WO3), ozone, hydrogen peroxide, heat, etc. (Tsitonaki et al. 2010). Some studies have shown that persulfate as well as sulfate radicals and hydroxyl radicals can successfully decompose PFOA, PFDA, and 4:2 FTUCA by stepwise decomposition to shorter-chain PFCAs and elemental components (e.g., fluoride) (Hori et al. 2005; Chen and Zhang 2006; Lee et al. 2009; Wang et al. 2010; Hori et al. 2007a; Hori et al., 2013). Work at

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Purdue Univ. funded by the US Army ERDC found that UV or heat activated persulfate could destroy PFOA (including in the presence of other organic contaminants) but not PFOS (Medina and Lee 2014). Lee at al. (2012) studied UV and heat activated persulfate and reported significant persulfate oxidation of PFOA at 20-40°C (more rapid at higher temperature as well as lower pH but still taking tens to hundreds of hours for complete degradation and high % of fluoriderelease). Yang et al. (2013) presented the results on PFOS degradation by activating persulfate with heat, UV, iron catalyst (i.e., Fenton) and ultrasound. They measured intermediate degradation compounds and fluoride and concluded that sulfate radicals and hydrolysis were the main defluorination mechanisms. The rates were higher at lower pH, higher temperature and UV radiation. Lee et al. (2013) studied the activation of persulfate by activated carbon on the degradation of PFOA and found that much higher rates of degradation at lower temperatures were possible than without activated carbon. Lower pH produced higher rates than higher pH and while intermediates were formed, much of them were eventually converted to fluoride. More recently, Yin et al. (2016) measured 89% PFOA destruction and 24% fluoride release in 100 hours at pH 2 and 50°C.

EnChem Engineering, Inc. has presented data from a field demonstration test (funded by the US Air Force) showing statistically significant reduction in PFAS concentrations in groundwater after injecting a peroxone activated persulfate solution (Ball et al. 2016a) as well as bench scale testing showing up to 99.9% reduction in individual PFAS and up to 86% defluorination based on fluoride release (Eberle et al. 2017; Ball et al. 2016b).

Arcadis has a process that uses permanganate and persulfate to create oxidants and/or reductants that reportedly mineralize PFAS compounds and which will be tested in a field demonstration (Ross et al. 2016; Pancras et al. 2013).

Additional field demonstrations are necessary to determine how these processes can be applied to different environmental matrices, especially for in situ treatment. Processes that rely on UV or heat or extreme pH are probably not practical for in situ applications but may be cost-effective for extracted groundwater treatment in above-ground reactors as an alternative to GAC.

AOPs: Ozone

The use of ozone ($E° = 2.1$ V) for chemical oxidation of PFAS has also been investigated. Lin et al. (2012) reported degrading ~50% of both PFOS and PFOA with alkaline ozonation after ozone pre-treatment. Kerfoot Technologies (2014) reports treating PFOS and PFOA (and other PFAS) with ozone nano bubbles "coated" with hydrogen peroxide to ~98% removal rates in one hour in an aqueous bench scale test, with lower rates in soil slurries and in a soil box simulating saturated soil conditions.

AOPs: Permanganate

Permanganate ($E° = 1.7$ V) has been used for chemical oxidation remediation of many types of organic contaminants, especially in situ. While Carus Corp., the main supplier of permanganate, does not list PFAS in their list of organic contaminants treated, researchers have shown oxidative decomposition of PFOS with permanganate, but only at high temperature (≥ 65 °C), low pH, and over many days (Liu et al. 2011/2012). Similarly, Fanga et al. (2016) measured significant degradation of PFOA, PFOS, and 6:2 FTS, including fluoride release, but over many months while at acidic pH and at room temperature (24°C).

AOPs: Direct Photolysis

Photolysis of PFAS, mainly PFOA, has been studied over a wide range of UV wavelengths and initial PFAS concentrations, but mostly under acidic conditions. Remediation utilizing direct photolysis may need to consider additional treatment methods, since direct photolysis tends to have low removal efficiencies and fluoride yields compared with other processes (Chen and Zhang 2006; Giri et al. 2011; Phan Thi et al. 2013; Cheng et al. 2014).

Dissolved oxygen may also play an important role in the direct photolysis of PFOA (Giri et al. 2012; Jin et al. 2014). Giri et al. (2012) and Jin et al. (2014) also indicated that other chemical reactions likely coexist with direct photolysis. This could be attributed to the scavenging of hydrated electrons which are formed during VUV water splitting. Direct photolysis of four PFAS (PFOS, PFPeA, PFPrA, PFBA and FTUCA) have been tested, mainly as control groups for experiments evaluating photocatalysis (Hori et al. 2007a, 2007b; Yamamoto et al. 2007).

AOPs: Other Photolysis-Induced Oxidation

Adding other anions like periodate, carbonate, or perchlorate (Panchangam et al. 2009a) to photoca-

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talysis has decomposed PFAS through the creation of radicals such as IO4–, IO3•, •OH, O•–, and others that then react with PFAS to produce shorter-chain PFAS, fluoride ions, carbon dioxide, or sulfate (Cao et al. 2010; Phan Thi et al. 2013). Decomposition of PFOA by periodate needed high temperatures (40°C) but carbonate and hydrogen peroxide (H2O2) were able to treat PFOA to nondetectable levels (82.3% defluorination yield) at ambient temperatures and basic pH (8.3–9) but with longer (12 hour) reaction time (Phan Thi et al. 2013). Other UV photolysis testing has not been as successful, including tungstic heteropolyacid (Hori et al. 2004) and high pH 2-propanol (Yamamoto et al. 2007), which required long reaction times (24 hours and 10 days, respectively).

AOPs: Photocatalysis (UV light plus catalysts like titanium dioxide-TiO2 or gallium or indium oxide)

UV photocatalysis has been shown by many researchers to be a potential treatment method for PFAS (mostly PFOA) contaminated water (Linsebigler et al. 1995; Fujishima et al. 2000; Carp et al. 2004). Even sunlight alone in combination with iron and H2O2 or persulfate has been shown to decompose PFOA (Liu et al. 2013a). Experimental results varying light wavelength and intensity, initial catalyst, and water quality (e.g., the turbidity of water, total organic matter content, dissolved oxygen, and bicarbonate) to treat varying PFAS concentrations have been attempted. Reaction products include shorter-chain PFAS, formic acid, fluoride ions, sulfate ions, and hydrogen. Depending on reaction times, PFAS can be degraded to low or non-detect levels. One of the more successful studies used P25 titanium dioxide (TiO2) nanoparticles to achieve almost complete PFOA degradation within four hours (Ochiai et al. 2011b). Experiments have improved the photocatalytic destruction of PFOA by doping with iron: niobium (Fe:Nb), or copper (Cu2+) or iron (Fe3+) ions (Estrellan et al. 2009, 2010; Panchangam et al. 2009a; Song et al. 2012; Sansotera et al. 2014; Bianchi 2015; Chen et al. 2015; Gatto et al. 2015). Cu+2-TiO2 decomposed 91% of PFOA to shorter-chain PFCAs with 19% defluorination (Chen et al. 2015). The use of gallium oxide (β-Ga2O3) (Zhao et al. 2012; Shao et al. 2013) and indium oxide (In2O3) (Li et al. 2012) have more potential than TiO2 but are more expensive than TiO2. Both semiconductor materials were able to decompose PFOA faster than TiO2. For example, with synthesized gallium oxide nanomaterial, 100% PFOA degradation was observed in 45 minutes with 61% defluorination (Shao et al. 2013). All of these photocatalysis methods are probably limited to ex situ treatment in a reactor.

AOPs: (Modified) Fenton's Reagent and Iron Photocatalysis

Modified Fenton's reaction, also called catalyzed H2O2 propagation, uses H2O2 (E° = 1.8 V) and initiators such as soluble Fe+3 or iron chelates, and has been used to remediate different organic contaminants for many years as an ISCO (in situ chemical oxidation) technique. Mitchell et al. (2014) concluded that hydroxyl radical alone from purely H2O2 treatment of PFAS cannot attack PFOA. However, they did report 89% PFOA destruction (in 2.5 hours) and fluoride release with iron catalyzed H2O2 that can produce superoxide and hydroperoxide.

This finding was also seen by researchers in the photocatalysis field where iron photocatalysis was greatly improved with the addition of H2O2, producing a UV-Fenton type reaction and 88% PFOA decomposed in one hour with a 26% defluorination yield (Tang et al. 2012). Iron catalyzed UV photolysis has also been studied for decomposition of PFOA, PFPeA, PFPrA, and PFBA. Oxygen was shown to be important in PFOA decomposition by iron photocatalysis, achieving 79% destruction of PFOA 39% defluorination yield in four hours. Other metal ions were also tested for their ability to decompose PFOA, including Cu2+, Mg2+ (magnesium), Mn2+ (manganese), and Zn2+ (zinc), but could only decompose 4.2 to 7.4% PFOA within four hours (Wang et al. 2008). As an ex situ technique, PFOA treatment with UV-Fenton photocatalysis may be a feasible and applicable AOP.

Electrochemical oxidation

Electrochemical oxidation destroys contaminants either by direct anodic oxidation at the anode or in solution by oxidants created at the cathode. Some electrochemical oxidation devices can have long life spans and be cost-effective (Jüttner et al. 2000). Degradation of PFAS has been most studied with boron-doped diamond (BDD) electrodes, which have shown degradation of PFOA, PFBA, PFHxA, PFDA, PFBS, PFHxS and PFOS under optimized conditions; for example, PFOA degraded by 97% (with 60% fluoride yield) within two hours (Zhuo et al. 2012). The mechanism is believed to be decarboxylation

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Table 8.6. Review of Reductive Approaches

Technique	Effectiveness as per literature reviewed
Vitamin B12 Reduction	This strategy showed the reduction of branched PFOS but not linear chains. Minimal reduction occurred at 30°C with increasing reduction rates at 70°C (Ochoa-Herrera et al. 2008).
UV (254 nm) photolysis	Minimal effectiveness for reduction of PFOS and some PFOA under argon atmosphere conditions. This approach would not be expected to be conducive to in situ conditions (Park et al. 2009).
Boron Doped Diamond Electrode	Some success for PFOS; however, very expensive and not applicable for in situ implementation (Carter and Ferrell 2008).
Zero Valent Iron	Highly effective for the removal of PFOS in near supercritical conditions. The study also reported significant reductions in the presence of zinc (Hori et al. 2006).

pathways that produce shorter-chain PFAS, fluoride ions, and sulfate ions (from PFSAs only). Hydroxyl radicals formed from water on the BDD anode may also degrade PFAS. Other electrode studies have included thin film electrodes made of Ti/SnO2, Ce/PbO2, and Ti/RuO2. For example, 90.3% PFOA degraded (72.9% fluoride yield) to shorter-chain PFCAs and fluoride when using a Ti/SnO2-Sb anode (Lin et al. 2012).

Similar results were observed using groundwater from a former fire training area (Trautmann et al. 2015). Even greater mineralization of PFOA was obtained on ultrananocrystalline BDD electrodes (Urtiaga et al. 2015). Some studies on BDD thin film electrodes were less successful, taking much longer to degrade PFOA (Carter and Farrell 2008; Liao and Farrell 2009; Ochiai et al. 2011a, 2011c).

Electrochemical oxidation has limitations such as toxic by-products if the PFAS-contaminated groundwater contains other contaminants (Trautmann et al. 2015). Only two studies were found that measured PFAS destruction via electrochemical oxidation in the presence of AFFF-impacted or PFAS spiked groundwater (Schaefer et al. 2015; Trautmann et al. 2015). Recent bench scale studies have shown that the presence of chloride electrolyte and a hydroxyl radical scavenger, tert-butyl alcohol, had minimal effects (decreasing rates by <20%) on PFOA/PFOS removal and defluorination for the range of applied current densities (3 to 50 mA/cm^2), at both low (environmentally relevant) and elevated PFOA/PFOS concentrations (Schaefer et al. 2017). The results were comparable with experimental conditions using natural groundwater.

Sonochemistry

In environmental media, in which a far greater number of compounds are present than in demineralized water, lower degradation rates have been observed for sonochemical degradation (Cheng et al. 2008; Panchangam et al. 2009b). Inorganic groundwater constituents can also negatively affect PFAS sonochemical kinetics (Cheng et al. 2010). More recently, Fernandez et al. (2016) have shown that chain length and the types of functional groups present can also impact the degradation rates of individual PFAS compounds and they conclude that the technique shows promise.

Chemical Reduction

Chemical reduction is a form of redox manipulation that can convert hazardous contaminants to nonhazardous or less toxic compounds that are more stable, less mobile, and/or inert. Some examples of PFAS reductive dehalogenation (i.e., defluorination) are shown in Table 8.6; however, reductive defluorination has been shown to reduce primarily PFOS and PFOA, and in very controlled scenarios, limiting the adoption of the approach for in situ applications. Although literature indicates that PFOS degradation, is possible through reductive dehalogenation, additional research needs to be conducted to evaluate implementation as a remedial strategy. The available research either studies PFAS degradation in controlled environments such as oxygen limited and extreme temperature, or is expensive to implement with minimal degradation (Lee et al. 2015). Also, intermediate PFCAs and PFSAs generated during the reductive process have not been substantially studied.

Developing Technologies/Areas of Additional Research

Research is currently being conducted on methods

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Table 8.7. Known Commercialized and Developing Treatment Technologies

Technique	Effectiveness as per literature reviewed
Synthetic media resin by ect	Resin for use in ex situ systems, 4-8x higher capacity for PFOS and PFOA than GAC, improved adsorption of shorter chains, regenerable on site. Lab scale tested and pilot tested at Pease AFB.
PlumeStop® Liquid Activated Carbon by Regenesis	In situ containment strategy for PFAS. Proprietary formulation of colloidal activated carbon that is injectable under low pressures and distributes in subsurface. Lab demonstrated for PFAS, application/distribution has been field demonstrated with other contaminants.
RemBind by Ziltek, distributed by Tersus: Soil treatment/immobilization.	Formulation based on activated carbon, aluminum hydroxide, kaolin clay, other proprietary. Typical dose rate: 2-10% w/w. Demonstrated at lab, pilot, and full scale.
PerfluorAd® by Tersus	Precipitation/sedimentation agent for PFAS in ex situ stirred reactors. Lab demonstrated, potential field demonstrations in Europe.
Nanozox™ by Kerfoot Technologies Inc.	It is consisted of very fine bubbles of ozone/oxygen coated with hydrogen peroxide. Demonstrated at lab and pilot scale. (Kerfoot and Stralin 2014)
OxyZone® by EnChem Engineering Inc.	Peroxone activated persulfate that is injected in the subsurface. Field demonstration test conducted for Air Force at fire training area, Virginia. Results supported with bench scale testing confirmed with PFAS and fluoride analysis. (Eberle et al. 2017)

to achieve degradation of PFAS. A number of the key methods are summarized in this section. However, there are still a number of concerns:

- Contaminated media often contain a complex mix of multiple PFAS. Precursor content is often significant. Incomplete breakdown may result in an increase in PFCAs or PFSAs, an adverse effect.
- Most research is being conducted using demineralized water instead of environmental samples. Matrix effects can play a large role in the efficiency of treatment processes.
- Research is focused mainly on PFCAs (e.g., PFOA) but less on PFSAs (e.g., PFOS), while degradation of PFSAs is more difficult than PFCAs.
- The studies mainly focus on the disappearance of the parent products (e.g., PFOS or PFOA), with less attention given to the reaction products and yield of fluoride.

Treatment Train Potential

Like other recalcitrant and persistent compounds, remediation of PFAS is likely not going to be achieved by a single remedial technology; rather, a successful remedial strategy will likely consist of a combination of remedial approaches applied appropriately (as seen in the data for water treatment plants). For example, treatment can "soften" a compound to be amenable to natural anaerobic or aerobic degradation and/or to a subsequent chemical treatment.

The order and placement of a treatment train for PFAS depends on the proximity to source and types of contaminants present. Any treatment technology that uses oxidants may release more mobile PFAS forms that are subsequently more difficult to remove. Further, given that remediation technologies for PFAS are still under development, a remediation strategy may involve short-term solutions (e.g., pump and treat or administrative measures) to address known unacceptable risks until appropriate remedial approaches have been developed.

Examples of combinations that have been used in field applications for contaminants other than PFAS include:

- ZVI-type treatment zone coupled to natural or enhanced anaerobic treatment zone
- ISCO treatment zone coupled to enhanced or natural aerobic degradation
- Aerobic degradation treatment zone coupled to an anaerobic abiotic (ZVI) or bioremediation (biowall) treatment zone.

Some developing and commercialized remedial approaches specific to PFAS are listed in Table 8.7.

TREATMENT BYPRODUCT DISPOSITION

Incineration

High-temperature incineration (>1,100°C) has proven to be a viable method for PFAS destruction to dispose of treatment by-product (Tsang et al. 1998; Schultz 2003; Yamada et al. 2005). Incineration, however, is expensive and incineration facilities must limit the

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volume of PFAS-impacted material being introduced into their facility at a given time to avoid operational efficiency issues. Producers of by-product from PFAS treatment should consult with incineration facilities prior to remediation to understand the requirements for incineration.

Reactivation of Spent Activated Carbon Containing PFAS

Reactivation of activated carbon is a well-established, high temperature process for the thermal destruction of adsorbed chemicals and the subsequent reuse of the reactivated carbon. The reactivation of spent carbon containing PFOS, PFOA, and other PFAS has been practiced for over 10 years. As described below, the desorbed chemical constituents are thermally destroyed in the process eliminating future PFAS disposal liabilities.

The spent activated carbon enters a multi-hearth furnace or a rotary kiln where it is exposed to temperatures of at least 800°C. During this process, organic adsorbates (including PFAS) desorb and volatilize into the furnace atmosphere where they begin to char and combust. Note that in studying the desorption of PFAS from GAC, Watanabe et al. (2016) found that no PFAS compounds remained on GAC at above temperatures of 700°C in nitrogen. Reactivation kiln gases exit to an afterburner where any volatile organics that survive the furnace are incinerated in air at temperatures in excess of 850°C to meet stringent VOC emission limits. Subsequently, the gas stream is treated by a dry scrubber/spray dryer unit (which removes acid gases such as HF), and a baghouse to collect particulate matter.

Off-Site Disposal Methods

While contaminated soil excavation and disposal to landfill is a remediation option, there may be challenges for the receiving landfill, because PFAS subsequently will become constituents of leachate, and conventional leachate treatment plants may not be able to effectively treat these substances. This is because they do not readily biodegrade (Oliaei et al. 2013). Landfills are already a source for release of PFAS to the environment since many consumer products are being placed into landfills at the end of their product life (e.g., impregnated carpets, textiles). Therefore, before sending soil contaminated with PFAS to landfills, checks should be undertaken to confirm that they are appropriately designed and managed so as to prevent further release into the environment. Transferring PFAS-impacted soils (and leachate) from one site to another facility that is not designed to contain PFAS (or manage the leachate) could be considered as simply relocating the problem, and therefore the best practice is to ensure the receiving facility is appropriately designed to treat and handle PFAS-impacted soils. It should also be kept in mind that some states are considering implementing bans on the placement of PFAS related wastes in landfills.

REMEDIAL TECHNOLOGY IDENTIFICATION AND APPLICATION

Due Diligence

In order for groundwater professionals to develop successful remediation approaches, appropriate due diligence is required. Inadequate understanding of the nature and extent of contamination, lack of proper planning, and taking shortcuts to and through remediation often lead to ineffective and unsuccessful remedial approaches, the need to revisit or change the remedial approach, increased environmental liabilities (e.g., mobilization of the plume, contaminant transfer to different (disposal) site), schedule delays, and significant cost implications. Additionally, failure to deliver an effective remedial approach also potentially leads to public and third-party stakeholder relations problems, additional regulatory scrutiny, and client dissatisfaction. Given the inherent nature of PFAS, proven remediation technologies for the full suite of PFAS remain elusive. Consequently, groundwater professionals should:

- Develop a conceptual site model that effectively communicates the nature and extent of the contamination and associated fate and transport mechanisms, exposure pathways, and receptors.
- Collect appropriate data with respect to the potential effectiveness of the proposed treatment technologies, including potential co-contaminants that may affect the remedial approach with respect to PFAS.
- Conduct the necessary bench-scale and field pilot scale tests.
- Understand site-specific chemistry of PFAS impacted water that affects treatment (precursors, short/long/branched chain composition, calcium concentration, pH, etc.).

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Conceptual Site Model

The conceptual site model (CSM) is a critical component of any site investigation and remedial design project. The CSM should provide a complete and simple presentation of the data, site conditions, and potential exposure pathways that can be understood not only by the technical team members but also by stakeholders, who may not be as familiar with site characteristics that influence contaminant distribution. To support this objective, the CSM should include site figures, maps, and/or visual presentations to provide site-specific details for potential contaminant pathways and potential environmental and human receptors for impacted media. The use of visual aids can be very beneficial to help the non-technical stakeholders understand and use the CSM to support decisions required during the investigation, remediation design, and implementation processes.

Proceeding to remedial design without an adequate CSM may be the most common source of project failure (Payne et al. 2008); therefore, developing and rigorously verifying the CSM is a prerequisite for remedial system design and implementation. The CSM should evolve as site-specific data becomes available and incorporated into the CSM.

A CSM should include the following activities: (1) identification of potential contaminants; (2) identification and characterization of the source(s) of contaminants; (3) delineation of potential migration pathways through environmental media, such as groundwater, surface water, soils, sediments, biota, and air; (4) establishment of background areas of contaminants for each contaminated media; (5) identification and characterization of potential environmental receptors (human and ecological); and (6) determination of the limits of the study area or system boundaries (ASTM 2014).

The initial CSM can be developed by the evaluation of previous investigations at the site including, but not limited to, environmental reports and design reports for the construction of the facility, if available. A general, preliminary understanding of the geologic and hydrogeologic setting of the site can be obtained through a review of published reports from universities and the United States Geological Survey. These and other available reports can provide a good starting point for the development of a CSM. A detailed history of the site which includes the type, quantity, and location of contaminant releases and where potential contaminants were used or stored is also valuable information to support the development of the CSM.

After the development of the initial CSM, the CSM should evolve as new site data is gathered. USEPA's conceptual site model fact sheet (USEPA July 2011) states that development of the CSM occurs in two stages. The initial development stage includes a preliminary CSM to support the investigation planning and a baseline CSM to identify stakeholder consensus/divergence and identify data gaps. The second stage is the evolution and refinement of the CSM and includes: characterization, design remediation/mitigation, and post-remedy evaluation. These tasks represent an iterative approach for the use and refinement of the CSM as new data is gathered and remedial options are evaluated along with the final use of the remediated property. Although it can be difficult to amend the CSM as new data are collected, especially if those data contradict the current CSM. The CSM should be an evolving concept, with changes anticipated as new data become available.

Evaluation of Technologies

PFAS contamination can often involve a mixture of compounds, each with variable properties. Different remedial approaches will be successful at varying degrees with each compound and, like environmental remediation in general, the multitude of site-specific factors will greatly affect the efficacy of any given remedial approach. For instance, at many of the sites where PFAS exist, groundwater conditions may already be depleted in oxygen due to degradation of fuel and other easily biodegradable contaminants.

Due to the numerous design considerations described in Table 8.8, appropriate remedial solutions include precursor studies such as bench scale and field validation testing. Optimally, remedial planning consists of bench-scale testing and pilot-scale testing followed by on-site implementation.

Design Criteria/Considerations

In order to develop appropriate approaches for successful remediation, consideration should be given to developing decision support models to support the choice of short- and long-term remediation strategies for PFAS sites where AFFF had been applied or otherwise released into the environment. The following must be considered:

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- Which PFAS are present, and their physicochemical properties
- Hydrogeological conditions
- Off-site and on-site risks at present and in the future
- Acceptable time frames for remediation
- Technology acceptance and stakeholder involvement
- Costs for remediation
- Acceptable disturbance to day-to-day operations.

Appropriate site-specific and/or application-specific information is necessary to develop and design a remedial approach and/or treatment system.

As discussed above, PFAS have unique properties that complicate remediation and render many conventional approaches ineffective or be prohibitively costly. Moreover, successful remediation of PFAS may require more than one technology in the treatment train. This document is not intended to provide specific design guidance, but is instead intended to identify input parameters that groundwater professionals ought to consider with respect to treating PFAS in groundwater.

Contaminated sites with older formulations of AFFF are more likely to contain precursor compounds with longer chained PFAS (e.g., C8 or greater), that could degrade to PFOA and PFOS. Newer formulations of AFFF contain shorter chained PFAS (e.g., C6 and below), which still have the potential to degrade to persistent daughter products. While many of these precursors are not regulated at this time, groundwater professionals and their clients should be aware of the potential future liability associated with these compounds – i.e., they may become future sources of PFOS or PFOA and/or potentially other currently regulated compounds, or become regulated themselves in the future.

This document and most regulations have focused on the UCMR3 Six PFAS compounds, as they are end products of some PFAS degradation in addition to being parent compounds. Analysis for precursor PFAS is necessary to comprehensively understand PFAS impacts at a given site. If a site has levels of PFOS and PFOA below their regional guidelines, it is possible that remediation efforts could cause precursor compounds to degrade to resilient and regulated PFOS and PFOA.

Table 8.8 identifies key PFAS-related design input parameters and the rationale for their consideration.

In addition to the key input parameters described in the table, groundwater professionals should also be cognizant of potential technology limitations, properties that may affect the efficacy of treatment (e.g., PFAS propensity to stick to materials/filters), and how to dispose of any by-products generated through remediation/treatment.

PFAS remediation is rapidly evolving. Groundwater professionals are advised to review the current research and field trials funded by, for example, the US Environmental Protection Agency (EPA), https://clu-in.org/, and the US Department of Defense (DoD), https://www.serdp-estcp.org/.

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Table 8.8. Design Criteria and Considerations for PFAS Remediation

Input Parameter	Rationale
Remedial Objective	Understanding what the remedial objective is critical to achieving it. Too often, failure to have a clear remedial objective results in the selection of an inappropriate remedial approach or technology.
Effluent guidelines/criteria	Supplemental to the above, understanding the effluent criteria is critical to selecting and designing the remedial system. The remediation criteria are typically based on regulation. With PFAS, the regulatory environment is rapidly evolving, and could change during the lifetime of a PFAS groundwater remediation project. Criteria can be site-specific, risk-based, and/or based on a percent reduction in concentration or mass.
Concentrations of "key" PFAS	Through proper site investigation and analytical procedures, concentrations of key PFAS can be known, establishing the starting point, or baseline concentrations, for remediation. Groundwater professionals should carefully review available data to confirm that the noted concentrations are representative of field conditions (e.g., both branched and linear isomers have been accounted for in the analytical methods).
Type of other PFAS (short chain)	The remediation approach should account for different chain-lengths present with differing physicochemical properties.
Mass of precursors	Consider if there known precursors at the site. Is mobilization of precursors a concern for the selected remediation area?
Presence and nature of co-contaminants	The effect of co-contaminants like petroleum hydrocarbons, chlorinated VOCs, etc. should be considered, as well as any previous remediation that may have altered PFAS distribution
Biological oxygen demand (BOD)	Fluorinated surfactant products (such as firefighting foam containing PFAS) may have increased BOD levels that can cause acute environmental stress through deprivation of the oxygen necessary for water quality and biota survival or well-being.
Total suspended solids (TSS)	Due to their dual nature, PFAS are more prominent at interfaces, and will adhere to suspended particles within a water column (or fines within an aquifer). This presents challenges in groundwater and drinking water treatment (capturing/retaining fines, as well as treating water) and for sampling and analysis that will lead to site characterization.
Flow rate	Groundwater flow rate effects diffusive release (e.g., slow flow rate would likely result in increased aqueous concentrations as PFAS desorbed from available surfaces) and transport times (e.g. advective transport in groundwater).
Capture (focus on PFAS treatment and not on hydraulic capture)	Consider if both the source zone and plume been accounted for.
pH	pH affects sorption and desorption processes between PFAS and surfaces. Under regular conditions in groundwater (pH range 6 - 8.5), PFAS tend to be found in their anionic form.
foc (fraction of organic carbon)	The quantity and quality of organic carbon present in the geological setting may affect PFAS fate and transport behaviors. Elevated foc content may result in sorbed PFAS.
Fluoride	Consider if the treatment technology shows complete mineralization for more than one PFAS. Can any fluoride present at the site be distinguished from background fluoride to indicate that some degradation is occurring?
Are there any naturally occurring issues that would affect treatment?	For example: clay, calcium, high organic carbon content, fast groundwater flows, and other intrinsic site conditions.

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