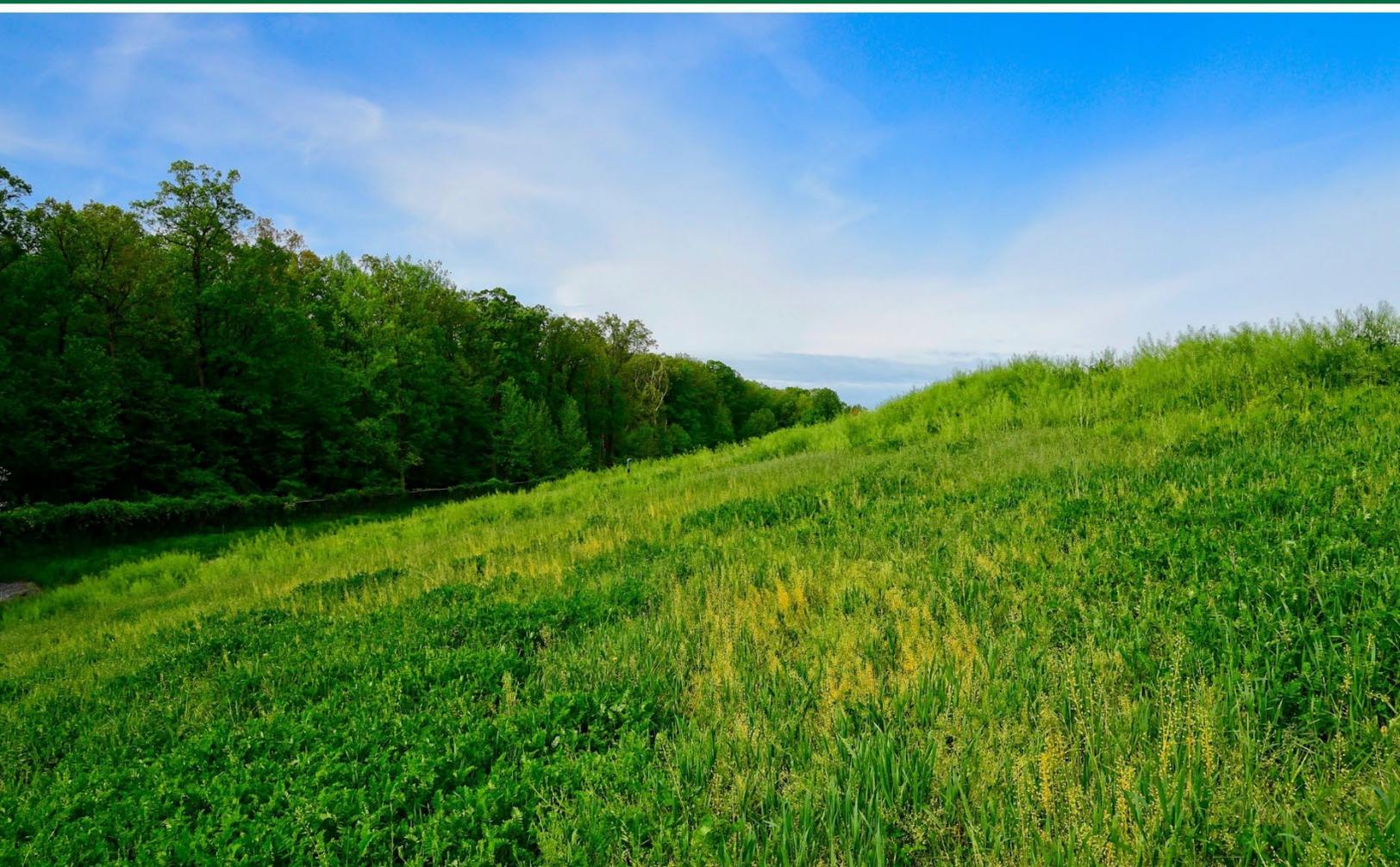


Introduction to PFAS in Groundwater



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by

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LIST OF ACRONYMS

6:2 FTSA – 6:2 Fluorotelomer sulfonic acid
7:3 FTCA – 7:3 Fluorotelomer carboxylic acid
AC – activated carbon
AEC – anion exchange capacity
AFFF – aqueous firefighting foam
Al – aluminum
AOF – adsorbable organic fluorine
AOP – advanced oxidation process
AR-AFFF – alcohol-resistant AR-AFFF
ARP – advanced reduction process
ASTM – American Society for Testing and Materials
BOHP – petitjeanite $\text{Bi}_3\text{O}(\text{OH})(\text{PO}_4)_2$
Br – bromine
BTEX – benzene, toluene, ethylbenzene, and xylenes
Ca – calcium
CAC – colloidal activated carbon
CAS – chemical abstracting service
C-C – carbon-carbon bond
CEC – cation exchange capacity
C-F – carbon-fluorine bond
C-H – carbon-hydrogen bond
CIC – combustion ion chromatography
 Cl^- – chloride ion
Cl – chlorine
CMC – critical micelle concentration
CMT – critical micelle temperature
CNT – carbon nanotubes
C-O – carbon-oxygen bond
CSM – conceptual site model
CVOC – chlorinated volatile organic compound
DO – dissolved oxygen
DOC – demonstration of capability
DoD – Department of Defense
DOM – dissolved organic matter
 eaq^- – aqueous electrons
ECF – electrochemical fluorination
EO – electrochemical oxidation
EOF – extractable organic fluorine
ETFE – ethylene tetrafluoroethylene
 F^- – fluoride anion
F – fluorine
FEP – fluorinated ethylene-propylene
FFFP – foam forming fluoroprotein

foc – fraction organic carbon
FTOH – fluorotelomer alcohols
FTSA – fluorotelomer sulfonates
GAC – granular activated carbon
H• – hydrogen radical
HA – humic acid
HDPE – high-density polyethylene
HF – hydrogen fluoride
HFPO-DA – hexafluoropropylene oxide dimer acid (GenX)
HO• – hydroxide radical
HO₂• – hydroperoxyl radical, also known as the hydrogen superoxide
I⁻ – iodide anion
I – iodine
IUPAC – International Union of Pure and Applied Chemistry
IXR – ion exchange resin
JP 4 – jet fuel 4
K – potassium
K_d – partitioning coefficient between solid phase media and groundwater
KOC – organic carbon partition coefficient
LC – liquid chromatography
LDPE – low-density polyethylene
LLOQ – lower limit of quantitation
LOQ – limit of quantitation
MDEQ – Michigan Department of Environmental Quality
Mg – magnesium
MIP – molecularly imprinted polymer
MNA – monitored natural attenuation
MRM – multiple reaction monitoring
MS – mass spectrometry
MTBE – methyl tert-butyl ether
MWCO – molecular weight cut-off
Na – sodium
Na⁺ – sodium ion
NAPL – non-aqueous phase liquid
NF – nanofiltration
NFDHA – nonafluoro-3,6-dioxaheptanoic acid
N-MeFOSAA – N-methylperfluorooctane sulfonamidoacetic acid
NOM – natural organic matter
NTU – nephelometric turbidity units
nZVI – nano-zerovalent iron
OC – organic carbon
OECD – Organization for Economic Co-operation and Development
OH⁻ – hydroxyl anion
ORP – oxidation-reduction potential
OW – Office of Water (US EPA)
PAC – powdered activated carbon

PBSF – perfluorobutanesulfonyl fluoride
PCE – perchloroethylene (tetrachloroethylene)
PFAA – Perfluorinated alkyl acids
PFAS – per- and polyfluoroalkyl substances
PFBA – perfluorobutyric acid
PFBS – Perfluorobutane sulfonic acid, perfluorobutanesulfonate
PFC – perfluorocarbon
PFCA – perfluorocarboxylic acid
PFDA – perfluorodecanoic acid
PFDS – perfluorodecanesulfonic acid
PFEI – pentafluoroethyl iodide
PFHxS – perfluorohexanesulfonic acid, perfluorohexane sulfonate
PFNA – perfluorononanoic acid
PFOA – perfluorooctanoate
PFOS – perfluorooctane sulfonate
PFPA – perfluorooctane sulfonamide
PFPrA – perfluoropropanoic acid
PFSA – perfluorosulfonic acid
PIGE – particle-induced gamma emission
pKa – acid dissociation constant
PMS – peroxymonosulfate
POSF – perfluorooctanesulfonyl fluoride
PPE – personal protective equipment
PRB – permeable reactive barrier
PTFE – polytetrafluoroethylene
PVC – polyvinyl chloride
PVDF – polyvinylidene fluoride
QA/QC – quality assurance / quality control
RO – reverse osmosis
SAP – sampling and analysis plan
SC – specific conductance
SERDP - Strategic Environmental Research and Development Program
SO₃²⁻ – sulfite anion
SOP – standard operating procedure
SPLP – synthetic precipitation leaching procedure
SSL – site screening level
TCE – trichloroethylene
TFC – thin-film composite
TFE – tetrafluoroethylene
Ti – titanium
TOFA – total organofluorine assay
TOF-CIC (or TOF) – total organofluorine-combustion ion chromatography
TOP – total oxidizable precursors assay
UF – ultrafiltration
UFP-QAPP – Uniform Federal Policy for Quality Assurance Project Plan
US EPA – United States Environmental Protection Agency

UV – ultraviolet

VOC – volatile organic compound

VUV – vacuum ultraviolet

WWTP – wastewater treatment plant

Zn – zinc

ZVI – zerovalent iron

EXECUTIVE SUMMARY

The purpose of this document is to introduce topics relevant to management of groundwater contaminated with per- and poly-fluoroalkyl substances (PFAS). Perfluorinated substances are based on a fully fluorinated carbon chain and polyfluorinated substances are based on a partially fluorinated carbon chain. A modern definition of PFAS is:

PFAS are defined as fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it), i.e., with a few noted exceptions, any chemical with at least a perfluorinated methyl group (–CF₃) or a perfluorinated methylene group (–CF₂–) is a PFAS.

The simplest PFAS to describe are the perfluoroalkyl acids (PFAAs). These prototypical PFAS are comprised of a linear carbon-chain with most or all the bonding sites occupied by a fluorine (F) atom and one of the functional groups from organic chemistry attached to one end. Functional groups can also be attached at any branches in the carbon chain. The fluorinated carbon-chain is referred to as the backbone, the fluorinated end of the backbone is referred to as the tail, and the functional group at the opposite end of the backbone is referred to as the head. The backbone and tail are physically durable, thermally stable, chemically inert, and water- and oil-repellant (hydrophobic/oleophobic). If an attached functional group is hydrophilic then the PFAS is amphiphilic and can function as a surfactant.

PFAS manufacturing methods provide useful information for identifying sources. They are predominantly manufactured using either electrochemical fluorination (ECF) or telomerization. ECF produces many impurities with branched backbones, or even cyclic backbones, and has been the only process used to create the perfluorosulfonic acid (PFSA) subclass of PFAA. Telomerization has been used to produce the perfluorocarboxylic acid (PFCA) subclass of PFAA.

There are several classification systems for PFAS. The most basic division of PFAS is polymer versus non-polymer. PFAS are also classified as short chain versus long chain. PFCA with eight or more carbons (seven or more carbons are perfluorinated) and PFSA with six or more carbons (six or more carbons are perfluorinated) are considered long chain PFAS by US EPA.

There are thousands of PFAS because they have a myriad of applications. Some examples are use in aqueous fire-fighting foams (AFFF), fabric protectants such as Scotchgard™, coatings on nonstick kitchen cookware and food packaging, papermaking, oil production, mining, metal plating, electronics, and additives to cleansers, polishes, waterproofing agents, tanning agents, wax, lubricants, ink, and paint.

The production and widespread use of products containing PFAS have resulted in their introduction to the environment through releases from primary and secondary

manufacturing facilities, releases from industrial and manufacturing facilities, releases of products containing PFAS such as aqueous fire-fighting foams (AFFF) at airports and military bases, escape of landfill leachate, release of wastewater treatment plant (WWTP) effluent to water bodies, irrigation using WWTP effluent, and land application of WWTP biosolids and sludges for soil improvement. PFAS are present in environmental media including air, soil, sediment, surface water, and groundwater, and in locations as remote as the Arctic. PFAS are of concern because they bioaccumulate in plants and animals and they have been linked to conditions such as low birth weight, thyroid hormone disruption, low activity sperm, elevated cholesterol, diabetes, and cancer. Regulatory thresholds are presently in the parts per trillion range but vary between government entities and are still evolving.

Some PFAS are known as “precursors” because they are susceptible to transformation in the environment. Precursors include non-fully fluorinated PFAS species that contain carbon-hydrogen (C-H) or carbon-oxygen (C-O) bonds such as fluorotelomer alcohols (FTOHs) and fluorotelomer sulfonates (FTSAs). Precursors also include side-chain fluorinated polymers with the potential to form PFCAs. Many can degrade either biotically or abiotically in the subsurface to form very environmentally stable endmembers such as the PFAAs, although they may pass through intermediary daughter products. PFAAs include the widely studied PFAS perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS). Precursors tend to be more common in shallow soils and PFAAs tend to be more common in groundwater, but the relative location of PFAS that are intermediate breakdown products of precursors is less predictable.

Subsurface transport of PFAS is not yet fully understood, but it is influenced by the physiochemical characteristics of the environmental media, individual PFAS species, and co-contaminants in both dissolved- and separate-phases. Their subsurface transport is retarded by adsorption of their tails and backbone to other hydrophobic materials such as organic matter (organic carbon). This process is termed hydrophobic interaction. PFAS with one or more polar functional groups are amphiphilic and behave as surfactants. In addition to hydrophobic interactions, subsurface transport of amphiphilic PFAS is retarded by accumulation at media interfaces and electrostatic interactions with charged surfaces such as some clays and minerals. Longer-chain and straight-chain PFAS tend to be more retarded than short-chain and branched isomers, apparently due to the greater hydrophobicity of longer and straight chains and possibly greater hydrophilicity conferred by any additional polar functional groups capping branches. Cationic and zwitterionic PFAS are more retarded than anionic PFAS. The mechanisms by which non-PFAS can interact with PFAS to alter subsurface transformations and transport are not well understood, but adsorption to NAPL appears to be more significant than absorption into NAPL. The complexities of PFAS retardation and the difficulty of quantitating the contributions render the use of the traditional methods for estimating retardation of hydrophobic organic contaminants unsuitable for PFAS.

Developing a site conceptual model (CSM) for a PFAS site can be challenging because their behavior in the environment is not fully understood and available laboratory analyses can only identify a small fraction of the individual compounds. Consequent of

the state of knowledge about the environmental behavior of PFAS, site characterization should include assessment for both total and specific PFAS, all potential co-contaminants in both dissolved and separate-phase form, media characteristics, and groundwater geochemistry. The atypical retardation of PFAS is directly affected by media characteristics such as grain size, organic carbon, clays and minerals, pH, and cation and anion exchange capacity (AEC). Assessing PFAS retardation and the representativeness of water samples also necessitates characterization of parameters such as individual dissolved ions, alkalinity, turbidity, pH, oxidation-reduction potential (ORP), specific conductance (SC), and dissolved oxygen (DO).

Special consideration is needed when planning and performing field activities at PFAS sites because of their broad use in manufactured goods and their widespread occurrence, including the ground surface due to atmospheric deposition. Sampling materials and equipment potentially containing PFAS, or fluorinated materials, should be avoided. Trip blanks and equipment blanks must always be included in the sampling and analysis program.

The US EPA has validated four analytical methods for measuring PFAS in water samples. The US EPA SW-846 Method 8327 quantifies a sampling of 24 PFAS analytes in non-potable water such as wastewater. US EPA Method 537.1 quantifies 18 PFAS in drinking water, and US EPA Method 533 focuses on “short chain” PFAS and quantifies 25 PFAS in drinking water, 11 of which are not included in Method 537.1. US EPA Method 1633 quantifies a larger sampling of 40 PFAS species in wastewater, surface water, groundwater, soil, biosolids, sediment, landfill leachate, and fish tissue. Other analytical methods for individual and total PFAS are available or in development but have not yet been approved by US EPA.

PFAS typically do not respond well to traditional remedial techniques, such as chemical oxidation or bioremediation, due to their unusual properties such as the armoring of the carbon-chain backbone by very strongly bonded fluorine atoms. Currently, ex-situ granular activated carbon (GAC) and ion exchange resins (IXR) are the primary means of removal for PFAS from groundwater. However, these materials have limitations such as interference by co-contaminants, preferential adsorption of some PFAS species or limited adsorption ranges, and issues with management of spent media. Reverse osmosis (RO) and nanofiltration (NF) are also proven technologies for PFAS separation but have shown to be comparatively expensive due to high energy consumption. Innovative methods and adaptations of existing methods are being explored.

INTRODUCTION

The purpose of this document is to provide an overview of topics relevant to management of groundwater contaminated with per- and poly-fluoroalkyl substances (PFAS).

Perfluorinated PFAS are based on a fully fluorinated carbon chain and polyfluorinated PFAS are based on a partially fluorinated carbon chain. Broader overviews for PFAS are provided by [Meegoda et al., \(2020\)](#) and [Evich et al., \(2022\)](#), and a very thorough but lengthy treatment is provided by [ITRC, \(2022\)](#). [Sima and Jaffé, \(2021\)](#) list recent reviews focused on subtopics including occurrence, fate, migration, and remediation.

Description

PFAS are a family of thousands of man-made organic chemicals ([OECD, 2018](#)). The widely used definition of PFAS provided by [Buck et al., \(2011\)](#) has recently been superseded by an update intended to encompass a broader range of structurally related chemicals ([ODEC, 2021](#)):

PFAS are defined as fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it), i.e., with a few noted exceptions, any chemical with at least a perfluorinated methyl group ($-CF_3$) or a perfluorinated methylene group ($-CF_2-$) is a PFAS.

The simplest PFAS to describe are the perfluoroalkyl acids (PFAAs). These prototypical PFAS are comprised of a linear carbon-chain with most or all the bonding sites occupied by a fluorine atom and one of the functional groups from organic chemistry attached to one end. If the carbon chain is branched, functional groups can also be attached there. The fluorinated carbon-chain is referred to as the backbone, the fluorinated end of the backbone is referred to as the tail, and the functional group at the opposite end of the backbone is referred to as the head. Example PFAS are illustrated on [Figure 1](#).

Manufacturing

Knowledge of PFAS synthesis methods and manufacturing history are useful for the developing practice of source identification and separation, known as PFAS forensics. PFAS forensics is a challenging process, and consequently still an active area of research.

Synthesis

PFAS can be synthesized from perfluoroalkyl building blocks via ECF, telomerization (a chain-transfer oligomerization), other methods of oligomerization (e.g., radical oligomerization, oligocondensation, ionic oligomerization and ring-opening reactions), direct fluorination, or photooxidation (Buck et al., 2011; Savu, 2000; Dams and Hintzer, 2016). Only ECF and telomerization are commonly known in the U.S. ECF, also known as the “Simons process” (3M 1999; Kempisty et al., 2018), typically proceeds by electrolysis in liquid anhydrous hydrogen fluoride (HF) of an acyclic, hydrogen-saturated hydrocarbon with a functional group attached to one end. The ECF process replaces the hydrogen atoms bonded to the carbon-chain with fluorine atoms and under suitable reaction conditions all the hydrogen will be replaced by fluorine (3M, 1999). A common example of ECF is treatment of 1-octanesulfonyl fluoride to form perfluorooctanesulfonyl fluoride (POSF), which is used as a feedstock to produce final products such as PFOS. Another example is ECF of octanoyl fluoride to ultimately synthesize PFOA.

Telomerization typically reacts a perfluoroalkyl iodide telomer such as pentafluoroethyl iodide (PFEI) with a taxogen such as tetrafluoroethylene (TFE) to yield longer chain perfluoroalkyl iodides (Buck et al., 2011). The perfluoroalkyl iodides are then reacted with a chemical such as ethylene to form further lengthened fluorotelomer iodides. The fluorotelomer iodides are in turn used as reaction intermediaries to eventually produce final products such as PFOA, fluorotelomer surfactants, and polymer products.

Impurities

PFAS source identification is facilitated by the fact that ECF and telomerization substantially differ by the characteristics of the PFAS building blocks and suites of impurities they produce (Buck et al., 2011). ECF often causes fragmentation and rearrangement of the starting carbon-chain, which results in creation of impurities including homologs of varying chain lengths, up to 20% to 30% branched isomers, some cyclic structures, and perfluorocarbons (PFAS without a functional group, or PFCs) (3M, 1999). Consequently, PFAS mixtures produced from ECF have constituents with both odd and even numbers of carbons in their backbones. In contrast, telomerization does not produce branched isomers of PFAS unless a branched telomer is intentionally used, and only produces a small fraction of odd-numbered carbon-chains, if any. However, like ECF, telomerization can produce PFAS that are not entirely chemical inert in the environment which can be transformed to other PFAS with odd-numbered carbon chains.

Products

PFAS source identification is also facilitated because PFASs such as PFOS were only produced using building blocks generated using ECF. Also, ECF can produce both perfluorinated and polyfluorinated compounds whereas telomerization produces polyfluorinated fluorotelomers, although these can be used as feedstocks to produce perfluorinated products (3M, 1999; ITRC, 2022). The products from both synthesis methods can be used as feedstocks to produce the most studied group of PFAS, the PFAAs. However, as discussed below, only ECF is known to have been used to produce both PFAA subcategories, the PFCAs and the (PFASs). Telomerization is known to have been used to manufacture PFCAs but not PFASs. Thus, presence of PFASs such as PFOS is an indication of source material produced by ECF.

History

PFAS have been in continuous commercial production from nearly the time they were first discovered until the present. The first polymerizations of fluoroethenes, such as polytetrafluoroethylene (PTFE), were studied at IG-Farbenindustrie in Germany during the early 1930's (Wetzel, 2005) and the first patent application for a fluoropolymer was filed in 1934 by Schloffer and Scherer, (1934). PTFE was subsequently synthesized by a DuPont de Nemours (DuPont) chemist investigating fluorinated refrigerants in 1938 (Science History Institute, 2017). Processes to commercially produce PFAS using ECF were developed in the 1940s. DuPont commercialized PTFE in 1946 under the name Teflon™ (Ebnesajjad, 2000). The Minnesota Mining and Manufacturing Company (3M) licensed the Simons ECF process from Dr. Simons of Penn State University in 1945 (3M, 1999) and reportedly began production of PFOA in 1947 (Prevedouros et al., 2006), although they report they built the first manufacturing-scale pilot ECF process in 1949 (3M, 1999). 3M began industrial-scale production via ECF of PFOA, PFOS, and PFAS containing products such as Scotchgard™ in the 1950s (Banks et al., 1994) and it is widely reported that DuPont began purchasing PFOA from 3M circa 1951 to improve their production of Teflon™. Telomerization was later invented by DuPont (Munoz et al., 2019) and its use to produce PFOA began in the 1970s, ameliorating DuPont's need to purchase PFOA from 3M for manufacturing Teflon™.

Environmental concerns brought changes to PFAS manufacturing. During early 2000 3M was the sole producer of perfluorooctane sulfonic acid (PFOS) in the U.S. (US EPA, 2003). However, early in the decade and at the urging of US EPA, 3M began phasing out ECF production of perfluorooctanoic acid (PFOA) and POSF based PFAS, including perfluorohexane sulfonate (PFHxS), PFOS, perfluorodecanesulfonic acid (PFDS), and related compounds (Buck et al., 2011). The phase-out was reportedly completed by 2008, but due to the purported lower toxicity of short-chain PFAS 3M continued to produce the shorter-chain perfluorobutanesulfonyl fluoride (PBSF)-based PFAS such as perfluorobutane sulfonic acid (PFBS) via ECF. PFAS production by ECF also continues in other countries, including China, India, and Russia (ITRC, 2022). PFOA production by telomerization ramped up for a period by other producers in the U.S. after the 3M phaseout, but production of PFOA, some longer chain homologs, and some related

compounds was phased out by most producers by 2015 (US EPA, 2017). Replacements for PFOA include the fluoroalkylether carboxylates GenX and Adona, and a replacement for PFOS is the chlorinated polyfluoroalkyl ether sulfonate F53-B (Munoz et al., 2019). GenX is a trade name for the DuPont spinoff Chemours' process to manufacture fluoropolymers without the use of PFOA, typically hexafluoropropylene oxide dimer acid [HFPO-DA]. Adona is 3M's trade name for dodecafluoro-3H-4,8-dioxanonoate. F53-B has been used in China since the 1970s and has been reported as the trade name for chlorinated polyfluorinated ether sulfonate, 9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid, and 11-chlororeicosfluoro-3-oxaundecane-1-sulfonic acid.

The types of PFAS manufactured expanded over time as new uses were found, eventually including fluoropolymers, fluorotelomer-based substances, perfluoro(poly)ether-based substances, perfluoroalkane sulfonyl-based substances, perfluoroalkane carbonyl-based substances, and polyfluorinated substances (Buck et al., 2011; OECD, 2018; Glüge, 2020). There may be others, as some PFAS mixtures are trade secrets. A list of PFAS that are known to have been manufactured was produced by OECD, (2007) and US EPA maintains a database of PFAS accessible on the web at: [CompTox Chemicals Dashboard \(epa.gov\)](https://www.epa.gov/comp-tox-chemicals-dashboard).

Classification

Several classification systems have been developed for PFAS, including polymer versus non-polymer, partially fluorinated “poly-“ versus fully fluorinated “per-“ backbone, and combinations of these. A combined classification system for “environmentally relevant” PFAS was presented by Buck et al., (2011) in a paper that also attempted to standardize PFAS nomenclature. A recent publication by OECD, (2021) provided recommendations on reconciling terminology for PFAS, and their updated definition of PFAS included forms with side-chain aromatics.

Polymers

Polymer PFAS were divided by Buck et al., (2011) into three primary groups: fluoropolymers, polymeric perfluoropolyethers, and side-chain fluorinated polymers. Fluoropolymers have a carbon-only backbone but perfluoropolyethers have some oxygen atoms included in the carbon backbone. Side-chain fluorinated polymers have non-carbon substitutions included in the backbone and can be further subdivided into fluorinated acrylates and methacrylates, fluorinated urethanes, and fluorinated oxetanes.

Non-polymers

Non-polymer PFAS were divided by Buck et al., (2011) into perfluoroalkyl and polyfluoroalkyl substances. They further classified perfluoroalkyl substances into aliphatic (typically straight-chain) perfluorocarbons, PFAAs, perfluoroalkane sulfonyl sulfides, perfluoroalkane sulfonamides, perfluoroalkane iodides, and perfluoroalkane aldehydes. The polyfluoroalkyl substances were subclassified into perfluoroalkane sulfonamido derivatives, fluorotelomer-based compounds, and semifluorinated *n*-alkanes

and alkenes. The PFAAs have long been the primary focus of environmental research on PFAS. The US EPA defines short- versus long-chain PFCA as having less than eight carbon atoms and short- versus long-chain PFSA as having less than six carbon atoms. Other definitions based on chain length, such as those used in Europe, can vary slightly.

Manufacturing Method

Evich, et al. (2022) provided lists of PFAS groups based on manufacturing method. PFAS groups from direct fluorination included PFCAs, PFSAs, hydrofluorocarbons, hydrofluoroethers, hydrochlorofluoroolefins, hydrofluoroolefins, side-chain fluorinated aromatics, perfluoroalkyl-tert-amines, and perfluoroalkanoyl/perfluoroalkanesulfonyl fluorides. PFAS manufactured using oligomerization (telomerization) included fluoropolymers, perfluoropolyethers, fluorotelomers, perfluoroalkyl (ether) carboxylic and sulfonic acids, and perfluoroalkene derivatives.

Properties

The physiochemical properties of PFAS vary and are difficult to directly measure (Wang et al., 2021; ITRC, 2022). Example PFAS and physiochemical properties are provided in **Table 1**. Most PFAS have low volatility and at room temperature are solid, although shorter-chain PFAS may be liquid.

Backbone and Hydrophobic Interactions

The strong C–F chemical bonds and armoring of the carbon-chain by highly electronegative fluorine atoms render the backbone and tail of PFAS physically durable, thermally stable, chemically inert, nonpolar, and water- and oil/lipid- repellent (hydrophobic/oleophobic) (O’Hagan, 2008; Gagliano et al., 2020)¹. Hydrophobic materials such as PFAS tails and organic matter (“organic carbon”, or OC) appear to be attracted when immersed in a polar solvent such as water. The apparent attraction is the result of the tendency for hydrophobic areas on molecules to avoid contact with the solvent and is termed “hydrophobic interaction”. The hydrophobicity and propensity for hydrophobic interactions of a PFAS backbone increase with increasing carbon-chain length and decrease with increasing carbon-chain branching (Park et al., 2019).

Functional Groups and Electrostatic Interactions

Functional groups such as carboxylates, sulfonates, sulfates, phosphates, betaines, or amines are added to a fluorinated carbon-chain backbone to create a finished PFAS molecule. Functional groups can render PFAS nonionic, anionic, cationic, or zwitterionic (Xiao et al., 2019). Ionic functional groups confer the ability to undergo electrostatic

¹ There are studies that have demonstrated some PFAS can partition to the phospholipid bilayers of bacteria, indicating that they may not exhibit lipophobic (oleophobic) tendencies when dissolved in water (Fitzgerald et al., 2018).

interactions with other charged materials to PFAS. However, electrostatic interactions are significantly more influenced than hydrophilic interactions by the physiochemical properties of the solid matrix materials and the geochemistry of the water solution.

Partitioning to Media Interfaces

The existence of both hydrophobic and hydrophilic regions on a molecule renders it amphiphilic and confers surfactant properties. Surfactants can be divided into nonionic, anionic, cationic, and zwitterionic classes and there are PFAS of each of these types. All types of surfactants reduce surface tension by adsorbing to the interface between two phases such as air and water. The surface tension typically decreases nonlinearly at low surfactant concentrations but otherwise decreases log-linearly until it plateaus near the concentration at which micelles (bubbles) or hemimicelles (bubbles attached to a surface) can form. This concentration is termed the critical micelle concentration (CMC) and is associated with the concentration at which the surfactant has reached saturation at the fluid interface. Additional surfactant merely creates more micelles. The CMC is characteristic of individual surfactants but varies as function of surfactant type, temperature, the alkyl chain length, the ionic head group, and the strength of the binding between the head group and the electrolytes/counterions (complementary ions) available in solution. Surfactants have a minimum temperature termed the critical micelle temperature (CMT) or Krafft temperature, below which micelles will not form. The CMC generally decreases with increasing alkyl chain length but increases with increasing hydrophilicity of the polar head group. Addition of electrolytes such as salt decreases the CMC and addition of alcohol increases the CMC.

Amphiphilic PFAS accumulate at media interfaces, such as between air and water, non-aqueous phase liquids (NAPL) and water, or soil and water. The propensity for accumulation at media interfaces is a concentration-dependent function of the change in surface tension between two fluids, but generally increases with increasing backbone length (Psillakis et al., 2009). Also, the surface tension and affinity for media interfaces decrease with increasing PFOA and PFOS concentrations in a nonlinear way, possibly indicating that factors other than PFAS concentration (e.g., solution pH and ionic strength) affect surface tension (Costanza et al., 2019).

Environmental Transformation of Precursors

PFAS that can undergo transformations in the environment are known as precursors. Precursors are non-fully fluorinated PFAS species that contain C-H and potentially carbon-oxygen (C-O) bonds. Precursor transformations may be natural or influenced by various remedial actions (McGuire et al., 2014). Transformations can occur abiotically or biogenically, aboveground or belowground, and aerobically or anaerobically, but cannot mineralize PFAS because of chemically inert sections within their backbone (ITRC, 2022). Precursors transform either directly or through intermediary daughter products into “terminal” or “endmember” PFAS that are very environmentally stable or fully inert (Suthersan et al., 2016). For example, polymer PFAS such as (FTOH) and (FTSA) can be

transformed into PFAA². Proposed reaction pathways vary but are an area of active research. Biotransformation of PFAS was recently reviewed by [Zhang et al., \(2022\)](#).

Uses

PFAS have a myriad of applications. Over 200 use and sub-use categories were identified by [Glüge et al., \(2020\)](#). Example uses include Class B aqueous fire-fighting foams (AFFF), fabric protectants such as Scotchgard™, coatings on nonstick kitchen cookware and food packaging, papermaking, oil production, mining, metal plating, electronics, and additives to cleansers, polishes, waterproofing agents, tanning agents, wax, lubricants, ink, and paint ([Moody and Field, 2000](#); [Prevedouros et al., 2006](#); [Paul et al., 2009](#); [Wang et al., 2017](#); [Tokranov et al., 2019](#); [OECD, 2020](#)).

Aqueous Fire-Fighting Foam (AFFF)

AFFF use accounts for many of the sites where PFAS have been released to the subsurface environment and migrated to groundwater. AFFF are associated with complex contaminant mixtures in soil and groundwater at facilities such as chemical plants, petroleum refineries, airports, and military installations. Groundwater impacted by PFAS has the greatest concentrations at AFFF sites ([Backe et al., 2013](#)).

Composition

AFFF formulations are mostly proprietary ([Place and Field, 2012](#)) but they are known to contain hydrocarbon surfactants such as sodium alkyl sulfate and PFAS surfactants such as carboxylates, perfluoroalkyl sulfonates, perfluoro betaines, perfluoro sulfonamides, perfluoro sulfonamidoethanol, perfluoro thioamido amino carboxylates, perfluoro sulfonamido amines, and fluorotelomer sulfonates ([Suthersan et al., 2016](#)). They also contain materials such as magnesium sulfate, sodium octyl sulfate, sodium decyl sulfate, ethylene glycol, propylene glycol t-butyl ether, diethylene glycol monobutyl ether, and ethanol. Polyfluorinated precursor compounds are a major fraction of the PFAS detected in vadose soils at AFFF release sites ([Sharifan, 2021](#)).

Legacy AFFF

AFFF manufacturers and formulations have changed over time ([Kempisty et al., 2018](#)). After their development by the U.S. Navy in the 1960s 3M manufactured a “legacy” (manufactured pre-2001) PFOS-based AFFF branded Lightwater™ from the late 1960s through 2002 ([DoD, 2014](#)). Lightwater™ contained PFOS and several precursors that could break down to PFCAs such as PFOA ([Backe et al., 2013](#)). Other brands of fluorotelomer foams were manufactured from the 1970s through 2016 that were comprised mostly of C6-PFAS, some longer-chained PFAS, and polyfluorinated

² Until very recently it was thought that PFAAs were completely recalcitrant in the environment ([Prevedouros et al., 2006](#); [Ferrety et al., 2012](#)), but recent studies raise the possibility that this might not be the case (e.g., [Huang and Jaffé, 2019](#)).

precursors but did not contain PFOA except as a potential impurity (Schultz et al., 2004; Place and Field, 2012; Backe et al., 2013). Not unlike Lightwater™, however, their impurities could break down to PFOA and other PFCAs and as such, are considered precursors (Weiner et al., 2013; Harding-Majanovic et al., 2015). Annunziato et al., (2020) identified more than 100 PFAS in a legacy foam sample dominated by PFOS (31%). Other specific PFAS identified were perfluorohexanesulfonic acid (PFHxS) (5%) and a mixture of other PFAS totaling 3%.

Modern fluorotelomer AFFF

Fluorotelomer foams have been in use since the 1970s and after 2001 became the dominant foam (TRB, 2017; ITRC, 2022) because long-chain foam manufacture (by ECF) was discontinued. These newer AFFF contain shorter chain (predominantly C6) fluorotelomers that are expected to be less bioaccumulative and toxic but may still contain trace amounts of PFOA and PFOA precursors (Scheringer et al., 2014; US EPA, 2018). Nonetheless, a review by Ateia et al., (2019) found that the newer short-chain (four to seven carbon) and ultra-short-chain (two to three carbon) PFAS, like their longer chain homologs, are environmentally persistent and can break down to form stable PFCA and PFSA end products (Hurley et al., 2004; Renner, 2006; Lee et al., 2010a; Liou et al., 2010; Ritter, 2010; Butt et al., 2014). Also, the newer short-chain PFAS are typically used in greater concentrations because they are somewhat less effective for fire-fighting applications than longer chain PFAS (Lindstrom et al., 2011).

Alternative formulations

There are alternatives to traditional PFAS-containing AFFF formulations, so it is possible that some AFFF release sites may not be impacted by PFAS. Fire-fighting foams are grouped into several classes that have distinct characteristics which may be helpful when conducting release forensics (Chemguard, 2005):

- Traditional AFFF – contain synthetic foaming agents (hydrocarbon surfactants), solvents, fluorochemical surfactants (PFAS), stabilizers, and salts.
- Alcohol-resistant AFFF (AR-AFFF) – comprised of a traditional AFFF and a high molecular weight polymer.
- Synthetic detergents – comprised of hydrocarbon surfactants and solvents.
- Wetting agents – similar to Class A foams.
- Protein – based on a hydrolyzed protein mixed with foam stabilizers and preservatives.
- Fluoroproteins – contain protein and fluorocarbon surfactants.

- Foam Forming Fluoroprotein (FFFP) – a derivative of AFFF and fluoroprotein, based on fluoroprotein formulations with increased amounts of fluorocarbon surfactants.

Environmental Occurrence

The production and use of products containing PFAS has resulted in their introduction to the environment through releases from primary and secondary manufacturing facilities, releases from industrial and manufacturing facilities, use of PFAS products such as AFFF at airports and military bases, escape of landfill leachate, release of WWTP effluent to water bodies, irrigation using WWTP effluent, and land application of WWTP biosolids and sludges for soil improvement (Wang et al., 2017; OECD, 2018; Glüge, 2020; Sharifan et al., 2021). PFAS occur in environmental media including air, soil, sediment, surface water, and groundwater, and in locations as remote as the Arctic (Young et al., 2007).

Toxicity and Regulation

Environmental management of PFAS is motivated by their propensity for bioaccumulation and their high toxicity. PFAS bioaccumulate in both plants and animals and are toxic to both animals and humans (OECD, 2002; D'Hollander et al., 2010; US EPA, 2016a and b; OECD, 2018; ATSDR, 2021; ITRC, 2022). Branched PFAS isomers preferentially bioaccumulate in humans and linear isomers preferentially bioaccumulate in most other animal species (Schulz et al., 2020), but both types of isomers preferentially adsorb to albumin in blood as well as other proteins (Forsthuber et al., 2020). PFAS have been linked to low birth weight, thyroid hormone disruption, low activity sperm, elevated cholesterol, diabetes, and cancer (Wang et al., 2013, Domingo and Nadal, 2019).

Permissible exposures to PFAS in the U.S. vary across government entities and are expected to continue evolving as more information accumulates. Although there are many chemical groups of PFAS the most widely studied have been the PFAAs. These include the PFCAs such as PFOA, and PFSAAs such as PFOS. Permissible human exposures to PFAS have been developed based on exposure routes such as air, airborne dust, drinking water, food, food-contact materials (boxes, papers, and wrappers), and breast milk (D'Hollander et al., 2010), and available toxicity evaluations for PFAS are detailed in ASTDR, (2021). Based on the information available at the time, in 2016 the US EPA issued a Lifetime Health Advisory of 70 parts per trillion (ppt) for PFOA and PFOS in drinking water, individually or combined (US EPA, 2016a and b). The US EPA also provides screening levels for its Regions available at: <https://www.epa.gov/risk/regional-screening-levels-rsls-generic-tables>, which include levels for PFBS. The risk-based SSL for PFBS in groundwater is 1,900 ppt and for K+PFBS in groundwater is 3,000 ppt. In 2021 the US EPA issued final Human Health Toxicity Values for PFBS and its potassium salt, potassium perfluorobutane sulfonate (K+PFBS) (US EPA, 2021a). This document indicates that PFBS and K+PFBS are almost an order of magnitude less potentially harmful than PFOA and PFOS.³

³ This may be because PFBS have a shorter retention time in the body than PFOS.

The 2016 advisories were replaced in June 2022 by interim advisories issued by the US EPA Office of Water (OW) ([US EPA, 2022a](#)) for PFOA and its replacement GenX, and PFOS and its replacement PFBS. The new, interim drinking water advisories are 0.004 ppt for PFOA, 10 ppt for GenX, 0.02 ppt for PFOS, and 2,000 ppt for PFBS (<https://www.epa.gov/system/files/documents/2022-06/drinking-water-ha-pfas-factsheet-communities.pdf>).

Environmental Fate and Transport

The fate and transport of PFAS in the subsurface are influenced by the physiochemical characteristics of the individual PFAS species and the site's characteristics. These properties combine to influence PFAS surface chemistry, surfactant properties, solubility, sorption, stability, interactions with solvents, and other properties and behaviors. [ITRC, \(2022\)](#) indicated that relevant PFAS characteristics included chain-length, functional groups and their charge state, and extent of fluorination. They also indicated relevant site characteristics may include atmospheric conditions and precipitation, surface water and groundwater flow rates, soil permeability, surface charge, soil and sediment organic carbon (OC) content, pH, anion exchange capacity (AEC), cation exchange capacity (CEC), mineralogy, water content, depth to groundwater, pH, redox conditions, presence of co-contaminants such as fuel hydrocarbons and halogenated solvents, competitive inhibition amongst PFAS, presence of non-PFAS surfactants and stabilizers typically included in AFFF formulations, and presence of NAPL. However, recent work in the literature indicates that some contributing factors probably need to be subdivided to establish their relationships with PFAS transport, such as measuring individual ion concentrations rather than solution ionic strength ([Pereira et al., 2018](#)).

Subsurface Transformations

Transformations of precursor PFAS have been previously discussed. They can be biotically or abiotically mediated and occur under aerobic and anaerobic conditions, but proposed reaction pathways are still being evaluated.

Vadose Zone

Most PFAS releases are to the ground surface, with the exception of landfill leachate. Substantial concentrations of PFAS often remain beneath the location of the release in the vadose zone and represent a long-term source for groundwater contamination ([Brusseau and Van Glubt, 2019](#); [Barzen-Hanson et al., 2017](#)).

PFAS entering the vadose zone beneath a source area can volatilize, be absorbed by biota, accumulate at media interfaces, adsorb to media solids and NAPL via hydrophobic or electrostatic interactions, transform, or leach to groundwater ([Sharifan et al., 2021](#)).

These processes are influenced by competitive inhibition of adsorption, ion exchange, and the presence of both dissolved and NAPL⁴ co-contaminants.

Although mixtures of PFAS with varying chain lengths and branching have been observed in shallow soil horizons (Sepulvado et al., 2011; Xiao et al., 2015; Hale et al., 2017; Nickerson et al., 2020) there are trends in vertical stratification. Generally, longer chain, linear, and cationic or zwitterionic PFAS are retained more strongly and occur at greater concentrations shallow in the vadose zone. In contrast, shorter-chain, non-linear, and anionic PFAS are more mobile, occur deeper in the vadose zone, and can more easily migrate into the phreatic zone (Backe et al., 2013; Hatton et al., 2018; Li et al., 2018; Wang et al., 2021; Adamson et al., 2022). Also, precursors tend to be more common in shallow soils (Sharifan et al., 2021) and their end products tend to be more common in groundwater. However, groundwater concentrations of intermediate products are sometimes comparable to concentrations of end products (Nickerson et al., 2021).

Most work characterizing the retardation of PFAS in soil has focused on anionic species that exist in a charged state within the normal range of subsurface pH. However, Xiao et al., (2019) characterized the subsurface behavior of cationic and zwitterionic PFAS relative to that of anionic PFAS. They found:

- Cationic and zwitterionic PFAS were more retarded than anionic and neutral PFAS, although the differences diminished as concentrations increased.
- Hydrophobicity was a poorer predictor of sorption for cationic and zwitterionic PFAS than anionic PFAS.
- Sorption of cationic and zwitterionic PFAS was highly nonlinear.
- Sorption of cationic and zwitterionic PFAS apparently increased as their concentrations decreased.
- Sorption of cationic and zwitterionic of PFAS at low concentrations is dominated by electrostatic interactions with negatively charged soil constituents.
- Sorption of cationic and zwitterionic of PFAS at high concentrations is dominated by hydrophobic interactions.
- Sorption of cationic PFAS is highly correlated to OC and is reversible.
- Sorption of zwitterionic PFAS at low OC showed concentration-dependent hysteresis, indicative of adsorption irreversibility.

⁴ Although adsorption at NAPL interfaces is significant, recent work indicates partitioning into bulk NAPL is probably not a significant concern (Glubt and Brusseau, 2021).

- The maximum electrostatic potential of PFAS ions, computed using density functional theory, was found to be a useful predictor of the sorption of ionic PFAS species.

Phreatic Zone

Many PFAS fate and transport processes of the vadose zone are of less concern in the phreatic zone. Volatilization is primarily a concern in vadose soils within the source area. Accumulation at fluid interfaces (Lyu et al., 2018) including any NAPL interfaces (Glubt and Brusseau, 2021) is important in unsaturated soils but probably less so in groundwater plumes (Brusseau et al., 2019), although possible in the capillary zone. Adsorption and solvation interactions with co-contaminants and NAPLs are thought to be complex and not yet well understood (Chen et al., 2009; Guelfo et al., 2013). However, they are apparently a function of the media OC and surface charges, PFAS chain length, and PFAS concentration. Competitive inhibition of sorption amongst PFAS is a function of the differences in physiochemical properties of individual PFAS, which are generally not available because existing laboratory methods can only identify a small fraction of the known PFAS.

Groundwater transport of individual PFAS is predominantly retarded by electrostatic interactions and adsorption to organic carbon, likely with extended concentration decay due to matrix diffusion in compositionally heterogeneous materials (Adamson et al., 2022). The degree of retardation is a function of the ambient geochemistry and the physiochemical properties of the PFAS and the porous medium (Brusseau, 2018).

electrostatic interactions

PFAS with ionizable functional groups can undergo electrostatic interactions with other materials such as charged mineral surfaces and ions in solution (ITRC, 2022). Electrostatic interactions are greatly affected by geochemical conditions because they predominantly determine whether polar materials are in a neutral or charged state.

The pH affects the ionization state of polar materials and interacts with other geochemical parameters (Nguyen et al., 2020). For example, organic matter has the effect of increasing CEC as pH increases. Also, Tang et al., (2010) found that PFOS adsorption to the mineral goethite increased with decreasing pH, which they attributed to increased electrostatic interactions between anionic PFOS and increased net positive charges on goethite.

Retardation of ionic PFAS by electrostatic interactions is a function of the availability of suitably charged surfaces. Both positively charged and negatively charged surfaces are always present in the subsurface, but negative charges predominate. The density of negatively charged sites on subsurface particles is measured using CEC and the density of positively charged sites on subsurface particles is measured using AEC. Negative charge sites are associated with materials such as organic matter, humic substances, and

most clays (e.g., smectite/montmorillonite). Positive charge sites are associated with materials such as kaolinite clay, and hydrous oxides of iron and aluminum (Al) such as goethite. However, some materials such as kaolinite have “variable” charge states affected by pH; kaolinite takes on a negative charge at high pH and a positive charge at low pH.

Dissolved ions may alter retardation of charged PFAS via direct competition for complementary charged sites on mineral surfaces. However, there is also evidence that dissolved ions may interfere with hydrophobic interactions, but the interference is probably dependent on the valence state or species of ion ([Adamson et al., 2022](#)).

hydrophobic interactions (adsorption to organic carbon)

PFAS hydrophobic interactions are strongly influenced by the conformation of their carbon-chain backbone. Hydrophobicity increases with backbone lengthening and decreases with backbone branching ([Park et al., 2019](#)). Branching can also be associated with increased hydrophilicity because there are more heads to which polar functional groups can be attached. Consistent with these relationships, PFAS adsorption to OC decreases with decreasing backbone chain-length ([Sepulvado et al., 2011](#)) and increasing backbone branching ([Schulz et al., 2020](#)). Also, individual PFAS may have significant differences in their propensity for interacting with individual fractions of OC based on the length of their backbone. [Pereira et al., \(2018\)](#) found that longer-chain PFAS may preferentially interact with humin and shorter-chain PFAS may preferentially interact with humic and fulvic acids.

combined effects

Although hydrophobic interactions are generally insensitive to solution chemistry, PFAS adsorption to organic matter is known to be affected by factors that influence electrostatic interactions including solution pH, the ionization state of PFAS functional groups, and the ionic strength of the solution ([Sima and Jaffé, 2021](#)). There is a general trend for adsorption of anionic organic contaminants to increase with decreasing pH and increasing cation concentration ([Jafvert, 1990](#)). Anionic PFAS exhibit a similar but modified behavior, whereby sorption to organic carbon increases with decreasing pH but increasing concentration of only divalent cations ([Higgins and Luthy, 2006](#); [Johnson et al., 2007](#); [You et al., 2010](#); [Wang and Shih, 2011](#); [Kwon et al., 2012](#); [Kwadijk et al., 2013](#); [Zhou et al., 2013](#); [Du et al., 2014](#); [Pereira et al., 2018](#)). It has been suggested that divalent cations function as bridges between negatively charged surfaces in soil and negatively charged heads of anionic PFAS ([Higgins and Luthy, 2006](#); [Du et al., 2014](#)). Interestingly, [Pereira et al., \(2018\)](#) found that the presence of divalent cations was important to increase adsorption to organic carbon of intermediate-chain but not long-chain anionic PFAS.

PFAS adsorption to OC via hydrophobic interactions is widely thought to have a stronger effect on retardation than electrostatic interactions ([Higgins and Luthy, 2006](#); [Fabregat-Palau et al., 2021](#)). For example, OC carries a net negative charge within the normal

range of subsurface pH because its carboxylic and phenolic acid groups are dissociated (Kinniburgh et al., 1999). Also, anionic PFAS such as PFOA and PFOS exist in the subsurface in their (negatively) charged state because the pH of groundwater is almost always greater than the acid dissociation constant (pKa) of their functional groups. Despite the electrostatic repulsion, however, anionic PFAS still adsorb to the organic carbon (Higgins and Luthy, 2006; Zhang et al., 2019). Further, the widely observed greater retardation of PFOS than PFOA is due to stronger adsorption to OC conferred by the additional C–F unit in the PFOS backbone, rather than differences in electrostatic interactions between the soil matrix and the respective functional groups (Zhou et al., 2010; Milinovic et al., 2015).

Modeling

Site characterization and risk assessment rely in part on estimates of the subsurface transport of individual contaminants. However, there is not yet a reliable method to provide these estimates for PFAS because the standard equations for retardation of hydrophobic organic chemicals do not perform satisfactorily (Brusseau, 2018; Anderson et al., 2019; Silva et al., 2020). A primary concern is that these equations estimate retardation solely as a function of adsorption to OC (US EPA, 1990; 1996; 2020a) whereas PFAS are also significantly retarded by electrostatic interactions, and (primarily in the vadose zone) at fluid interfaces (Sharifan et al., 2021; Wang et al., 2021). US EPA, (1996) discusses modifying the standard calculation of the retardation coefficient (Kd) by adding a term for adsorption to inorganic materials, but problems remain. Many of the assumptions underlying the standard retardation calculations are violated by PFAS. Any mechanistic model must be provided coefficients specific to each process, but these are not yet available, and available laboratory analytical methods can only identify a small fraction of individual PFAS.

Contaminant retardation equations based on matrix organic carbon content have been successfully used for decades to model subsurface transport of many organic chemicals, but they are based on several caveats and assumptions that are problematic for PFAS. US EPA, (1996) enumerated the assumptions, including: within the range of OC present there was not significant sorption of the organic contaminant to other materials, such as minerals or clays; the organic chemical was nonionizing and therefore did not require use of separate coefficients for the pH-dependent fractionation between its ionized and neutral forms; there was no contaminant source loss due to volatilization or degradation; adsorption was linear with concentration; the system was in equilibrium with respect to adsorption, such that adsorption and desorption kinetics could be ignored; and sorption was reversible (rather than accounting for the facts that desorption is usually slower than adsorption and adsorption is sometimes irreversible). These assumptions are problematic for PFAS because the transformation of PFAS precursors is not fully characterized; some PFAS may volatilize; PFAS are often ionizing and interact with minerals such as clays and metal-oxides; their affinity for media interfaces is nonlinear, their adsorption may be faster than desorption and their sorption may exhibit hysteresis; they have slow sorption kinetics; and they exhibit some irreversible adsorption (Pignatello and Xing, 1995; Milinovic et al., 2015; Zhi and Liu, 2018; Xiao et al., 2019; ITRC, 2022). Further, there

has been increasing recognition over several decades that estimates of organic contaminant concentrations in groundwater frequently do not decrease as rapidly as predicted by sorption equilibrium models (US EPA, 1990). Desorption is recognized as frequently being a slower process than adsorption, and slow adsorption kinetics are now widely recognized as a significant process, attributable to effects such as pore diffusion and matrix diffusion⁵ (Sudicky et al., 1985; Pignatello and Xing, 1995; Li et al., 2018; You et al., 2020). These processes result in slower decreases in contaminant concentrations than models based on reversible, equilibrium adsorption to organic carbon predict.

Although the challenges of modeling subsurface transport of PFAS are considerable, ongoing research is progressing toward developing suitable models. For example, Higgins and Luthy, (2007) had encouraging results with a mechanistic model that estimated the contributions of hydrophobic and electrostatic interactions using Gibbs free energy terms. More recently, compartment models have been developed for modeling PFAS retardation in different environments where the relative influences of retardation mechanisms differ, such as between the vadose and phreatic zones (Brusseau et al., 2019; Silva et al., 2020). However, adequate information to populate the parameters of these models for site-specific application is not yet available.

Chemometric research is being conducted to provide the process-specific retardation parameters needed for mechanistic PFAS transport models. Recent studies have used methods that assume independent, additive linear relationships to identify the individual contributions of various processes to observed retardation. Li et al., (2018) compiled a dataset from the available literature and based on linear regression identified OC, pH, and clay fraction as significant predictors of retardation. They also noted field based Kd values were biased high relative to those calculated using laboratory batch method. Knight et al., (2019) used linear regression on soil properties and partial least squares regression on infrared spectra of soils to predict sorption of PFOA with some success using OC, silt + clay content, and pH. Rovero et al., (2021) found that soil sodium and calcium ions were significant predictors of retardation, but OC was only a significant predictor at a relatively high (>5%) fraction. They noted a tremendous range in Kd values in the literature and that Kd from field samples were biased high relative to those from synthetic laboratory samples. They also cautioned that use of a single Kd value might not be appropriate for estimating retardation of PFAS and that the standard equations for estimating subsurface transport of organic chemicals (US EPA, 1996; 2020a) might not be appropriate for PFAS. As suggested by Rovero et al., (2021), Fabregat-Palau, (2021) compiled a dataset from the literature but augmented it with their own results to expand the ranges of the predictive variables, particularly that of OC. They found that PFAS sorption onto both organic and mineral fractions increased with chain length and that sorption could be predicted using a parametric method suggested by US EPA (1996) as a function of PFAS chain length, soil organic content, and silt + clay content.

⁵ Matrix diffusion typically results from contaminants having differing adsorption propensities for constituents of compositionally heterogeneous media.

SITE CHARACTERIZATION

This document focuses on management PFAS contamination in groundwater. However, planning characterization and remediation of contaminated groundwater require a wholistic understanding of the context in which it exists.

Conceptual Site Model (CSM)

Characterization of a PFAS site starts with the development of a preliminary CSM, and sampling data are used to refine the CSM. While developing the CSM and planning site characterization the input of US EPA Regional risk assessors should be sought in addition to that from hydrologists, hydrogeologists, ecologists, and engineers, so the information gathered is adequate to support risk assessment.

A CSM usually includes information on hydrogeology, contaminant sources and concentrations, fate and transport, and geochemistry. CSMs for PFAS should incorporate all environmental phases encountered at a site, including liquid (groundwater, soil water, surface water, and atmospheric water vapor), solid (saturated and unsaturated bedrock, unconsolidated materials, soil, and sediments), and gas (soil gas and the atmosphere). Potential contaminant transport pathways and receptors (such as humans, wildlife, and vegetation) are also important components of the CSM. A CSM for a PFAS site may also require characterization of plants because PFAS are known to bioaccumulate in them.

Release Sites

All potential sources of PFAS releases to the environment need to be considered when developing a CSM. Several PFAS source areas are often present on the same site. For example, AFFF source areas other than fire training areas on U.S. Air Force sites have been documented by [Anderson et al., \(2019\)](#). They found the most common PFAS in groundwater at these sites were PFOS and PFHxS followed by PFOA. Frequencies of detection for most PFAS were similar at high-volume “testing and maintenance” and medium-volume “hangars and buildings” locations but lower at the low-volume “emergency response” locations where only a one-time release of AFFF occurred.

Site Classifications

The four commonly recognized major PFAS sites are fire training sites, industrial sites, landfills, and WWTPs, but metal treatment operations, runoff to surface water contaminated by atmospheric deposition, recharge to groundwater by surface water, or off-site upgradient locations are examples of sources that are sometimes overlooked ([Hu et al., 2016](#); [Meegoda, 2020](#); [ITRC, 2022](#)). Examples of concerns typical for characterizing each of these types are provided by [ITRC \(2022\)](#). However, fire-fighting practice areas are briefly described herein to provide an example of the information needed to develop a CSM for PFAS sites, because of their relative frequency and complexity of contaminant mixtures ([Schultz et al., 2004](#); [Place and Field., 2012](#); [Houtz et al., 2013](#); [D’Agostino and Mabury, 2014](#); [Nickerson et al., 2021](#)). Although the aspects

of development of a CSM for a fire training site can be extended to other types of PFAS sites, significant differences from other “major” PFAS site types exist. Releases at industrial and manufacturing sites are associated with atmospheric deposition, stormwater and wastewater discharges, disposal of solid wastes, leaks, spills, and potentially fire training. Leachate from landfills directly enters surface water or groundwater. Releases associated with WWTP include effluent discharges, inadvertent releases from liquid containment structures, air emissions, and biosolids disposal or use as soil amendment.

Fire Pits

Fire pit PFAS source areas and their characteristic contaminants are described by Meegoda et al., (2020) and ITRC, (2022) (Figure 2). Fire training pits are often located at chemical manufacturing facilities, refineries, airports, and military installations. During fire training, an aircraft carcass has often placed in a bermed area, dowsed with a flammable liquid, ignited, and then extinguished using AFFF. The range in flammable liquids applied to the fire training pits has been broad and includes fuels such as aviation gasoline, jet fuel 4 (JP4), diesel, etc., all of which could contain BTEX compounds. In addition to hydrocarbon fuels and the relatively broad range of materials included in AFFF, other organic compounds measured in groundwater beneath and downgradient of fire pits include the chlorinated volatile organic compounds (CVOCs) perchloroethylene (PCE) and trichloroethylene (TCE) (Meegoda et al., 2020). Transport of contaminants into the subsurface from fire training areas occurs by infiltration of precipitation and water used during fire training.

Subsurface Characterization

Although not the focus of this document, sampling and analysis of soil and solid aquifer media during development of the CSM provides critically important information for assessment of groundwater plumes. In addition to providing data needed to biogeochemically characterize the subsurface media, these samples provide contaminant concentration data that is necessary to understand the horizontal and vertical distribution of contaminants in both the source area and the downgradient plume. They are also useful for assessing the potential for source area soils to continue to leach contaminants to groundwater and for back-diffusion to prolong the presence of PFAS in groundwater after source removal. This information contributes to the technical basis for assessing risk and developing, designing, and deploying remedial technologies to address PFAS contamination. However, each solid media sample only characterizes conditions at discrete points, or if vertically composited, over selected depth intervals at discrete points. Also, these samples cannot be practicably replicated at later times to discern the mobility of contamination in the solid phase materials.

Unlike analyses of solid media, including vertically composited samples, analyses of groundwater provide a vertically and aerially integrated measure of contamination in the subsurface that can readily be repeated through time to assess plume stability. Groundwater samples integrate the effects of time-varying groundwater flow directions such as those frequently observed intra-annually within water-table (e.g., overburden)

aquifer matrices containing fine-grained materials. Lack of sufficiently frequent groundwater monitoring to detect all significant shifts in groundwater flow direction can result in inflated estimates of hydrodynamic dispersion (and therefore diffusion) relative to advection in groundwater flow models. Such a mis-estimation can significantly alter projected cleanup times that are influenced by matrix diffusion.

Analytical Suite

In addition to PFAS, analyses of samples from PFAS sites should include possibly co-occurring contaminants such as hydrocarbon fuels, organic solvents, and non-PFAS surfactants. Analyses for both individual and total PFAS should be performed and include precursors and intermediates. Example precursor and intermediate PFAS include chemicals such as 6:2 FTSA, 7:3 Fluorotelomer carboxylic acid (7:3 FTCA), and N-MeFOSAA⁶. Precursors and PFAS intermediates are not monitored as frequently as PFAAs, but these chemicals may have concentrations similar to those of PFAAs (Houtz et al., 2013; Robel et al., 2017; Martin et al., 2019; Liu and Avendaño, 2013). It is also important to include geochemical parameters in the sampling and analysis program because subsurface geochemistry can influence PFAS distribution and treatment (Weber et al., 2017). Due to the evolving understanding of PFAS transport (Rovero et al., 2021) the authors recommend that at a minimum, supplementary soil and sediment sample analyses should include pH, foc, clay content, and CEC, and field screening during surface and groundwater sampling should include pH, ORP, SC, turbidity, and DO.

Data Reduction

Forensics for identifying and unconfounding PFAS release sources are rapidly developing but not yet comparable in capability to those in use for contaminants such as hydrocarbons and CVOCs (Charbonnet et al., 2021). Current methods include comparisons of analytes to those expected for manufacturing process, comparisons of analyte distributions between samples using bar charts and radar plots, diagnostic ratios, ordinal methods principal component analysis (PCA), and machine learning methods such as clustering, neural networks, and Bayesian inference (Kibbey et al., 2020; Ruyle et al., 2021; ITRC, 2022). Commercial packages are already available to support forensic analysis, but ongoing research is exploring the utility of modern data reduction techniques such as machine learning methods.

Regardless of the environmental media analyzed, presentation of the PFAS contaminant concentration data should also include mapping and contouring in both plan-view and cross-sectional views. For a better understanding of PFAS presence, fate, and transport, it may be necessary to map and contour the contamination by individual target compound (e.g., PFOA, PFOS, Benzene, TCE), by sums of PFCAs and PFSAs, by PFAS precursors, and/or by total organic fluorine. Mass-flux calculations may be useful (e.g., Adamson et al., 2020).

⁶ 6:2 FTS and N-MeFOSAA are measured by 8327/3215. N-MeFOSAA is measured by 537. All 3 are measured by ASTM D7979.

ANALYTICAL METHODS

A common challenging problem with PFAS release sources is analytical characterization. Source materials and release areas contain multiple PFAS for which available analytical methods do not provide full coverage for individual analytes. Species-specific analytical methods for PFAS include EPA methods 537.1 ([US EPA, 2020b](#)), 533 ([US EPA, 2019a](#)), 3512 ([US EPA, 2021b](#)), 8327 ([US EPA, 2021c](#)), and 1633 ([US EPA, 2021d](#)) (**Table 2**), ASTM D-7979 ([ASTM, 2019](#)), and ASTM D-7968 ([ASTM, 2017](#)). Information regarding the origins of analytical techniques for PFAS is provided by [Kissa, \(2001\)](#); [Schultz et al., \(2004\)](#); and [Higgins et al., \(2005\)](#). US EPA provides a reference webpage for analytical methods at [PFAS Analytical Methods Development and Sampling Research | US EPA](#). Summary tables for a wide range of analytical methods are provided on the web by the ITRC at: [ITRC PFAS Section11.2 AnalyticalMethods Jan2022.xlsx \(live.com\)](#).

Methods for Individual Analytes

Currently four analytical methods are recognized by the US EPA for the detection of specific PFAS in water. If other methods are approved for use at a site, then the laboratory should provide the most recent Demonstration Of Capability (DOC) and Limit Of Quantitation (LOQ) or Lower Limit Of Quantitation (LLOQ) for US EPA review. The DOC should include all target analytes as well as isotopic surrogates.

US EPA Method 537.1

US EPA Method 537.1 ([US EPA, 2020b](#)) is a method for the determination of 18 selected PFAS in drinking water. PFAS sampled from several classes are included in this analysis, including PFCAs, PFSAs, analytes with ether linkages (Adona, GenX/HPFO-DA), analytes containing both fluorine and chlorine atoms, and PFOS intermediates. The method was multi-lab validated and includes data demonstrating performance in reagent water, groundwater, and surface water.

US EPA Method 533

US EPA Method 533 ([US EPA, 2019a](#)) complements EPA Method 537.1 and is a method for the determination of 25 selected “short chain” PFAS (i.e., those with carbon chain lengths of 4 to 12) in drinking water, 11 of which are not included in the analyte list for US EPA Method 537.1.

US EPA SW-846 Methods 3512/8327

US EPA SW-846 Method 3512 ([US EPA, 2021b](#)) is a rapid sample preparation method. US EPA SW-846 Method 8327 ([US EPA, 2021c](#)) is a direct injection method that detects

24 individual PFAS in various environmental waters (i.e., non-potable water). The PFAS analytes are drawn from several classes, including sulfonic acids (e.g., PFOS), carboxylic acids (e.g., PFOA), and precursors and intermediates such as fluorotelomer sulfonic acids (e.g., 6:2 FTSA), and N-MeFOSAA. The method was multi-lab validated and includes data demonstrating performance in four matrices of reagent water, groundwater, surface water, and wastewater effluent.

US EPA Method 1633

US EPA draft Method 1633 (US EPA, 2021d) was developed in conjunction with the U.S. Department of Defense (US DoD) and is a liquid chromatography and mass spectrometry (LC-MS/MS) method in the multiple reaction monitoring (MRM) mode in wastewater, surface water, groundwater, soil, biosolids, sediment, landfill leachate, and fish tissue. This method quantifies 40 individual PFAS compounds sampled from families including perfluoroalkyl carboxylic acids, perfluoroalkyl sulfonic acids, 6:2 FTSA, perfluorooctane sulfonamides, perfluorooctane sulfonamidoacetic acids, perfluorooctane sulfonamide ethanols, per- and polyfluoroether carboxylic acids, ether sulfonic acids, and 7:3 FTCAs.

ASTM D-7968 and D-7979

Two additional methods for analyzing PFAS in environmental media have been accepted by the American Society for Testing and Materials (ASTM) but not the US EPA. These are ASTM D7968 for soil and D7979 for water, sludge, influent, effluent, and wastewater (ASTM, 2017; ASTM, 2019). These methods are single lab validated. ASTM D-7979 includes data demonstrating performance in reagent water, surface water, and WWTP influent and effluent. ASTM D-7968 includes data demonstrating performance in four ASTM soils. Both ASTM D7968 and D7979 quantitate the same 21 individual PFAS compounds.

Other Analytical Methods in Development

Various methods are in different stages of development that are intended to provide additional data regarding the presence of PFAS compounds in environmental media. The US EPA maintains a webpage that tracks the status of method research:

<https://www.epa.gov/chemical-research/status-epa-research-and-development-pfas>

Methods in development include the total oxidizable precursors assay (TOP), extractable organic fluorine (EOF) and adsorbable organic fluorine (AOF) assays, the total organofluorine assay (TOFA), the particle-induced gamma emission (PIGE) spectroscopy method, Nuclear Magnetic Resonance (NMR), and the fluorine specific electrode (FSE). These methods provide general quantification of PFAS including unknown PFAS that are most likely derived from precursor compounds in aqueous or solid phase samples. They may be used to evaluate the potential presence of polyfluorinated compounds as precursors to perfluorinated compounds (NGWA, 2017), or as a measure of the total fluorine content of a sample (Suthersan et al., 2016).

Total Oxidizable Precursors Assay

PFAAs commonly present in PFAS formulations, including PFOS and PFOA, can be measured using US EPA methods 537.1, 533, 8327, and 1633, but PFAS precursors used to formulate PFAS products and PFAS intermediates formed during oxidation of precursors may also be present in environmental matrices. Some PFAS precursors and intermediates are measured with these methods, but others are not. The TOP assay, sometimes referred to as TOPA, was designed to estimate precursor concentrations present and the potential for the PFAS mixture to eventually degrade into PFAAs. When using the TOP assay, at least two samples are collected. One is analyzed for PFAS without an oxidation treatment. The second sample is subjected to oxidation with hydroxide, persulfate, and heat. After oxidation, the second sample is analyzed for PFAS (Houtz and Sedlak, 2012; Houtz et al., 2013, and 2016; Martin et al., 2019). The difference between the unoxidized and oxidized sample measurements represents the precursor and intermediate PFAS present in a sample. During oxidation, the backbone of some PFAS react to form shorter chain length compounds. For example, 6:2 FTSA may form perfluoropropanoic acid (PFPrA), PFBA, and perfluorooctane sulfonamide (PFPA) (Martin et al., 2019). Consequently, TOP assay data must be interpreted carefully. Precursor and intermediate amounts can be estimated but the chain length or specific species cannot be identified. When analyzing post-oxidation TOP samples PFPrA should be included to effectively estimate precursor and intermediate concentrations (Martin et al., 2019). Unfortunately, this compound is not included in many PFAS analytical methods.

Combustion Ion Chromatography Methods

In remediation studies the unique properties of PFAS can make it difficult to distinguish sorption and other losses from transformation and mineralization. Total organic fluorine assessment (TOFA) methods attempt to address these concerns. TOFA is not specific to precursors chain length or of the end point compounds; it is an estimate of the total organic fluorine content in a sample. TOFA can be used where there is uncertainty as to whether a US EPA method adequately measures all the PFAS likely to be present. TOFA considers the total mass of fluorine which may be present as PFAS chemicals. Fluorine mole balances are often used to describe the performance of remedial systems, and Combustion Ion Chromatography (CIC) methods are often used to measure fluoride (Miyake et al., 2007).

TOFA methods include EOF and AOF assays. EOF is a capture and combust technique. It uses CIC to measure organic fluorine and fluoride. The EOF assay is synonymous with TOF-CIC assay and has been applied to seawater, blood, freshwater, sediments, soils, protein pellets, fish tissue, and liver tissue (McDonough et al., 2019). The total organic fluorine can be calculated by subtracting the total inorganic fluoride from the total fluoride (D'Agostino and Mabury, 2017).

An adsorbable organic fluorine (AOF) assay has been described that uses elution through polystyrene-divinylbenzene based organic carbon rather than combustion. Residual fluoride is then removed using sodium nitrate and the sample is analyzed using CIC (Wagner et al., 2013). This method has only been applied to water (McDonough et al., 2019). USEPA draft method 1621 (USEPA, 2022b) is an AOF based on CIC that is intended for detection of organofluorines in water at the parts-per-billion level. In addition to PFAS, this method can detect fluorinated pesticides and pharmaceuticals. Organic fluorine is removed via a nitrate wash. Reliance on contaminant adsorption to GAC introduces a dependence on the size of the PFAS molecules that can be detected, however, given the propensity of GACs to preferentially adsorb to longer-chain PFAS.

PIGE spectroscopy is a new, rapid, and effective AOF method to quantify total fluorine in aqueous samples and consumer products such as papers and textiles (Ritter et al., 2017; NGWA, 2017). This method relies on adsorption of PFAS to GAC. Due to the high concentrations of fluoride in natural waters, there is some skepticism that this approach will be useful in measuring total organic fluorine attributed to PFAS in water samples, unless methods are developed to differentiate between inorganic and organic fluorine in a manner compatible with PIGE (Hoque et al., 2002).

Nuclear Magnetic Resonance

Nuclear Magnetic Resonance (NMR) is being developed to detect a greater proportion of total PFAS than detected by LC/MS methods (e.g., Gauthier and Mabury, 2022). NMR is being explored as both a screening and PFAS class-specific analysis. The method can differentiate between PFASs, non-PFAS, and fluoride ions, eliminating the need for sample clean-up even for complex samples (e.g., Camdzic et al., 2021; McDonough et al., 2019).

Fluorine Specific Electrode

The fluorine specific electrode (FSE) can be used as an independent measure of the degradation of per- and polyfluoroalkyl substances (PFAS) at contaminated sites. This is because it can be used to measure the concentration of the fluoride anion (F^-) in groundwater and increased aqueous fluoride concentrations are a strong indicator of PFAS degradation (Vecitis et al., 2009). Measurements of fluoride concentration have been used as an indicator of PFAS treatment in treatability studies (Park et al., 2016; Santos et al., 2016; Yin et al., 2016) but should be used with a full understanding of the limitations of the method.

Retention of fluoride by solid phase media (i.e., soil, aquifer materials) indicates that measurements of fluoride in groundwater samples may underestimate the total amount of fluoride present (Stonebridge et al., 2020). Further, interferences in solution, including oxidants and reagents to neutralize oxidants, should be taken into consideration. The need for low detection levels is also a major constraint.

Experimental FSE methods are under development ([Stonebridge et al., 2020](#)) but require ion-specific electrodes. Ion-specific electrodes are needed because fluorine precipitates with calcium so fluorine could be misrepresented in hard water using some electrodes. Nonetheless, in general ion specific electrodes are portable and inexpensive and may be used for aqueous samples in the field or the lab.

SAMPLING

General guidance and standard operating procedures (SOPs) for sampling PFAS in groundwater have been provided by the US EPA and others ([US EPA, 2019b, and 2019c](#); [NGWA, 2017](#); [Zintek et al., 2017](#); [MDEQ, 2018, and 2020](#); [Proffitt, 2020](#)). [Field et al., \(2021\)](#) summarized commonalities and discrepancies between existing U.S. PFAS sampling guidelines.

Equipment

Modifications of procedures for collecting samples of subsurface contaminated media are necessary when sampling them for PFAS. As with other contaminants, analytical interferences can result from cross-contamination by inadequately decontaminated drilling tools or well purging and sampling equipment. However, special care is required because PFAS may be incorporated into the composition and coatings of sampling equipment and supplies. The summary of sampling guidelines below is intended to help prevent PFAS contamination of samples in the field but is intended to be used in conjunction with an approved program- and site-specific sampling SOP.

- All equipment and supplies used for sampling should be scrutinized for potential PFAS contamination. Equipment should ideally be tested prior to use for PFAS and fluorine leaching. A soak test in water has been advocated for this determination ([Field et al., 2021](#)) but equipment blanks must be performed regardless of whether soak test data are used.
- Fluorocarbon or fluorotelomere materials such as Teflon™ PTFE, fluorinated ethylene-propylene (FEP), ethylene tetrafluoroethylene (ETFE), and polyvinylidene fluoride (PVDF) must be avoided when sampling because they contain PFAS and could inadvertently contaminate samples.
- Aluminum foil, fast food wrappers and containers may contain PFAS and should be avoided on-site, but if present should not be brought into the sampling areas and hands should be washed after contact. Applied products such as sunscreens and insect repellent may also contain PFAS. If uncertain about any applied products used, include them in equipment blank sampling.

- PPE, including chemically resistant Tyvek® or any other materials made of Teflon™, Viton®, FEP, etc., should be avoided (uncoated Tyvek is acceptable). Also, waterproof, water-resistant, or stain-resistant clothing may contaminate the sample with PFAS used in these products; verify whether these products contain PFAS (for example, waterproofing using natural rubber, or some waxes may be acceptable). It is recommended that new clothes are washed 6-10 times to remove PFAS products used in the textile industry.
- PFAS-free pens such as grease pencil or (if allowed by a mandatory SOPs) ball-point pen or Sharpee® should be used when recording information in the field and labeling samples.
- Decontamination should be done with Alconox®, Citrinex®, or Liquinox®.
- Excluding sample bottleware, sampling equipment constructed with stainless steel, polyvinyl chloride (PVC), polypropylene, and high-density polyethylene (HDPE) or possibly low-density polyethylene (LDPE) is recommended (NGWA, 2017).
- US EPA analytical method 537.1, 533, 8327, and 1633 descriptions explicitly specify permissible sampling containers. Glass sampling equipment or sample containers should not be used due to PFAS sorption to the glass and because of the presence of Teflon™ liners in glass volatile organic compound (VOC) sample vial caps.
- Bailers should not be used for well purging or sampling because they unacceptably turbidate the water. Rather, low-flow sampling methods should be used.
- Peristaltic pumps are acceptable for performing low flow well purging and sampling. Peristaltic pumps can collect groundwater samples at water table depths of about 23 feet or less. The flexible tubing used in conjunction with the peristaltic pump should be silicone; it should not be made of Teflon™, Viton®, FEP, or chemically related materials as this could impart PFAS or fluorine into the groundwater sample.
- Downhole positive displacement pumps (e.g., Grundfos, Monsoon®) are also acceptable for performing low flow well purging and sampling. However, these pumps may contain internal parts and components made of Teflon™, Viton®, FEP, etc. that could contaminate groundwater samples. PFAS-free water should be pumped through these pumps and tubing and analyzed as an equipment blank. It is preferable however to use equipment that does not contain materials that potentially could leach PFAS.
- If feasible, single use tubing, etc., should be used when well purging or water sampling for PFAS. Otherwise, decontamination protocols are needed between sampling events.
- Probes or field meters should be used to track chemical stabilization of the water purged from the wells. Preferably, the pump outflow should pass through a cell

equipped with a multiparameter probe such as a YSI Pro Series. However, some field instruments such as a nephelometer (turbidity meter) will require sampling from the cell outlet.

- Field screening should be performed at a minimum for alkalinity, turbidity, pH, ORP, SC, and DO⁷. Field screening should be intermittently conducted during well purging until the site-specific sampling plan criteria for parameter stabilization are satisfied, after which sampling may begin.
- If possible, avoid field filtration of water samples if turbidity is below 50 nephelometric turbidity units (NTU). Instead, attempt to obtain stable field screening turbidity no greater than 10 NTU. If water sample filtering is deemed necessary, use polypropylene or glass fiber filters. Avoid nylon and PTFE filters.
- If collecting samples for different contaminant classes (PFAS, CVOCs, BTEX, etc.), collect samples for PFAS first to avoid cross-contamination by other sample containers or supplies. Place the PFAS samples in an individual sealed plastic bag and physically separate them from other sample types. If site-specific procedures permit the use of LDPE, Ziploc® bags can be used.
- PFAS samples should be transported in coolers and stored at less than 6°C. Coleman® or Igloo® coolers (or other PFAS-free brands) can be used to transport the samples. If site-specific procedures permit the use of LDPE, Ziploc® bags can be used to organize samples for shipment.

Quality Assurance/Quality Control

For US EPA sampling events, specific quality assurance/quality control (QA/QC) activities that apply to the implementation of these procedures will be listed in the US EPA Uniform Federal Policy for Quality Assurance Plan (UFP-QAPP) or sampling and analysis plan (SAP) as prepared for the applicable sampling event ([US EPA, 2019c](#)). A detailed description of QA/QC samples and the steps involved in their collection is also available from [NGWA \(2017\)](#). Laboratory reporting limits should be checked against needed detection limits specified by these documents. Individual US EPA Regions will require QC samples to be collected to assure the quality of the data and might include or be equivalent to, but are not necessarily limited to, the following:

- *temperature blank* – a temperature blank is provided by the laboratory and accompanies the samples throughout the sampling program and back to the laboratory. One temperature blank should be included in each sample cooler.

⁷ Note that if sediment or soil samples are collected for PFAS analysis they should also be analyzed for geochemical parameters including at a minimum pH, foc, CEC, and clay content.

- *trip blank* – a trip blank is provided by the laboratory and accompanies the samples throughout the sampling program and back to the laboratory. One trip blank should be included in each sample-filled cooler.
- *field reagent blank* – this sample should be collected in the field to evaluate the potential for contamination from the overall sample collection process. Two containers are supplied, one filled with water from the laboratory. The field staff transfer the water from the filled container into the empty container. One field blank should be collected on each day of groundwater sampling.
- *field duplicate* – These are duplicates of samples collected in the field that are blinded to the laboratory by using some alternative name.
- *matrix spike / matrix spike duplicate* – these are collected in the field, and the laboratory adds known amounts of contaminants to them before analysis.
- *equipment blank* – an equipment blank is collected in the field to determine if contamination to samples has come from any equipment used during sampling. Water is poured over or run through equipment into the equipment blank bottle. One equipment blank should be collected on each day of groundwater sampling.

US EPA Approved Analytical Methods

Method 537.1

US EPA Method 537.1 explicitly lists required sampling containers and sampling protocol in Section 8 of the Standard. Samples should be collected in 250 mL polypropylene bottles with polypropylene caps and pre-preserved by the laboratory with dry Trizma®. Samples do not have to be headspace free. All compounds listed in US EPA Method 537.1 have adequate stability for 14 days when collected, preserved, shipped, and stored as described in the method. Water samples should be extracted as soon as possible but must be extracted within 14 days, and the extracts must be analyzed within 28 days.

Method 533

US EPA method 533 explicitly lists required sampling containers and sampling protocol in Section 8 of the Standard. Samples should be collected in polypropylene bottles with polypropylene caps and pre-preserved by the laboratory or in the field with dry ammonium acetate. Samples do not have to be headspace free. All compounds listed in US EPA Method 533 have adequate stability for 28 days when collected, preserved, shipped, and stored as described in the method. Water samples should be extracted as soon as possible but must be extracted within 28 days, and the extracts must be analyzed within 28 days.

Method 8327

US EPA method 8327 explicitly lists required sampling containers and sampling protocol in Section 8 of the Standard. Samples should be collected in polypropylene bottles with polypropylene caps. Samples do not have to be headspace free. All compounds listed in US EPA Method 8327 have adequate stability for 14 days when collected, preserved, shipped, and stored as described in the method. Water samples should be extracted as soon as possible but must be extracted within 30 days, and the extracts must be analyzed within 30 days.

Draft Method 1621

US EPA draft method 1621 explicitly lists required sampling containers and sampling protocol in Section 8 of the Standard. Samples should be collected in polypropylene bottles with polypropylene caps, and aqueous samples must be collected in triplicate but do not have to be headspace free. Extractions should be performed as soon as possible but samples may be maintained in the laboratory up to 90 days prior to analysis.

Draft Method 1633

US EPA draft method 1633 explicitly lists required sampling containers and sampling protocol in Section 8 of the Standard. All sample containers must have linerless HDPE or polypropylene caps. Other sample collection techniques, or sample volumes may be used, if documented.

- Aqueous samples: Automatic sampling equipment should be used to collect free-flowing samples as grab samples. Excepting landfill leachate, two aliquots should be collected, one in a 500 mL HDPE bottle and one in a 250-mL or 125-mL HDPE bottle. Use smaller bottles if adequate sample is not available. Landfill leachate also requires two aliquots, but both may be collected in 100 mL HDPE bottles. Maintain the samples at 0 - 6 °C from the time of collection until shipped to the laboratory. Samples must be protected from light in the laboratory. Samples may be held in the laboratory for up to 90 days from collection if stored at ≤ -20 °C or 28 days if stored at 0 - 6 °C, but issues may then occur with certain PFPA, perfluorooctane sulfonamide ethanols and perfluorooctane sulfonamidoacetic acids after 7 days.
- Soil, sediment, and biosolid samples: These should be collected as grab samples in wide-mouth HDPE jars filled to no more than $\frac{3}{4}$ capacity. The samples should be maintained at 0 - 6 °C from the time of collection until receipt at the laboratory. Solid samples (soils and sediments) and tissue samples may be held for up to 90 days, if stored by the laboratory in the dark at either 0 - 6 °C or ≤ -20 °C, with the caveat that samples may need to be extracted as soon as possible if nonafluoro-3,6-dioxaheptanoic acid (NFDHA) is an important analyte.
- Sample extracts: Sample extracts should be stored in the dark at less than 0 - 4 °C until analyzed. If stored in the dark at less than 0 - 4 °C, sample extracts may be

stored for up to 90 days, with the caveat that issues were observed for some ether sulfonates after 28 days. These issues may elevate the observed concentrations of the ether sulfonates in the extract over time. Samples may need to be extracted as soon as possible if NFDHA is an analyte of interest.

REMEDICATION

This section addresses PFAS remediation methods applicable to groundwater, which remain a topic of active research. For the interested reader, however, a review of PFAS treatments specific to drinking water is provided by [Crone et al., \(2019\)](#), a review of soil remedial technologies for PFAS is provided by [Mahinroosta and Senevirathna, \(2020\)](#), and review of technologies to potentially address back-diffusion is provided by [Brooks et al., \(2021\)](#).

The outlook for successful management of PFAS in groundwater has been assessed by [Newell et al., \(2020\)](#). They conducted a study comparing PFAS to other groundwater contaminants for the purpose of assessing remediation potential. They compared PFAS to CVOCs, benzene, 1,4-dioxane, and MTBE. They evaluated nine metrics for comparison: production quantities, number of potential sites, detection frequency, required destruction/removal efficiency, median plume length, hydrophobic sorption, regulatory criteria, in-situ remediation capability, and research intensity. They also conducted five qualitative comparisons: low-level detection capabilities, methods to assess risk of complex mixtures, nonaqueous phase dissolution, plume length prediction, and monitored natural attenuation (MNA) protocols. They found that production quantities, number of potential sites, detection frequency, and required destruction/removal efficiency indicated that PFAS might be a lesser challenge; that median plume length was comparable to chlorinated solvent plume lengths; that adsorption was not definitive; and that regulatory criteria, in-situ remediation, and research intensity indicated that PFAS might be more troublesome than the comparison contaminants. Their assessment of the qualitative metrics was that while remediating PFAS sites will be challenging the groundwater community has the experience to accomplish the task.

Comparative Reviews

Comparative reviews of established and developing remediation processes for PFAS in water are provided by [Merino et al., \(2016\)](#), [Kucharzyk et al., \(2017\)](#), [Ross et al., \(2018\)](#), [Trojanowicz et al., \(2018\)](#), [Nzeribe et al., \(2019\)](#), [Meegoda et al., \(2020\)](#), and [Wanninayake \(2021\)](#). These reviews discussed remedial processes including adsorption using activated carbon (AC) including colloidal (CAC), powdered (PAC), and granular (GAC) forms; IXR) and non-ionic exchange resins (XR); biopolymers; molecularly imprinted polymers (MIP); RO; microfiltration, ultrafiltration (UF), and nano-filtration (NF); ozonation; Fenton processes; microwave hydrothermal treatment; incineration; heat-activated persulfate; permanganate oxidation; advanced oxidation processes (AOP) including electrochemical oxidation (EO) and plasma; advanced reduction processes

(ARP) including use of aqueous iodide or dithionite and sulfite, vitamin-B12 and Ti(III)-citrate reductive defluorination; zerovalent iron (ZVI); photolysis; photocatalysis; sonochemical degradation, sub- or supercritical water; bioremediation using microbes and fungi; ozonation under alkaline conditions; radiolytic processes using ionizing radiation; and treatment-train approaches.

Dominant Remedial Methods

Presently, GAC, IXR or less commonly XR, RO, and NF are the commonly available and demonstrably implementable primary technologies for removal of PFAS from water (Tang et al., 2006; Espana et al., 2015; Meegoda et al., 2020). Ex-situ GAC with incineration of the spent GAC is the most common treatment technology. It performs well for removal of long-chain PFAS but does not perform well on short-chain PFAS or PFAS precursors. IXR can remove a wider range of PFAS, but older versions of IXR do not perform well for the shortest chain PFAS and had not yet been evaluated for precursors. RO and NF have been more successful than GAC and IXR for complete or nearly complete removal but are considerably more expensive. New GAC and IXR have recently been developed, however, that are now commercially available and purportedly are better able to sequester wider ranges of PFAS.

Although many applications of PFAS treatment technologies to date have been ex-situ, in-situ treatment is also being explored. A current topic of interest is in-situ colloidal activated carbon (CAC) emplaced either by injection on a grid or as a carbon-based permeable reactive barrier (PRB). The performance will likely be a function of the ability of the subsurface injections to infiltrate all migration pathways of significant permeability so that the contaminant plume fully interacts with the emplaced AC. Sorption capacity and competition for surface sites between PFAS and other groundwater solutes are site-specific issues that will likely determine long-term treatment performance. Like other sorption-based technologies, saturation capacity of the treatment material and contaminant rebound via matrix diffusion will likely be issues.

Developing Remedial Methods

Methods of PFAS removal from water other than GAC, IXR, RO, and NF are still in various stages of development or have drawbacks that presently make them less attractive than the presently dominant methods. Some promising methods have progressed to pilot testing or small-scale (often mobile) implementation. Others, however, were conducted at the laboratory bench scale under idealized, sometimes extreme conditions (e.g., temperature), and using relatively high PFAS concentrations. They also variously required uncompetitive residence times, or were less energetically favorable than currently used technologies, or were likely to increase toxicity of non-target materials that are common in environmental media. Some examples of such problems are provided by Horst et al., (2020). For example, plasma, electrochemical treatment, and sonolysis are expected to be more energy intensive than incineration. Also, in the presence of non-target materials such as chloride, bromide, arsenic, and trivalent chromium, the hydroxyl

radical created by some oxidative technologies can react with these to form problematic materials such as perchlorate, bromate, arsenate, or hexavalent chromium.

Short-chain PFAS

Most research on the remediation of PFAS has focused on relatively long-chain species. However, [Ateia et al., \(2019\)](#) reviewed remediation of short-chain (four to seven carbons) and ultra-short-chain (two to three carbons) PFAS. Removal of short-chain PFAS is more challenging than for longer chain PFAS using carbonaceous sorption. Short-chained PFAS are hydrophilic and less likely to form aggregates, yet adsorption mechanisms for carbonaceous materials such as AC are hydrophobic and rely partly on electrostatic interactions. Electrochemical oxidation (EO), an AOP, has been shown to degrade short-chain PFAS less efficiently than longer chain PFAS ([Niu et al., 2012](#)) and again, can create undesirable by-products from non-target constituents in the water to be treated. Previous studies of WWTPs have found higher PFAS in the effluent than the influent, indicating transformation of precursors occurs at a greater rate than that of endmember PFAA ([Lee et al., 2010a](#); [Pan et al., 2016](#)), and at the time of writing there was no evidence of reactions of short chain PFAS to the knowledge of the authors. Also, WWTPs did not treat short-chain PFAS, but it was suggested that hybrid sorption systems might be effective. It was concluded that at least some of these degradation methods were promising but further development was needed, including new sorbents for short chain PFAS and decreased costs such that upscaling costs would not be cost prohibitive.

Handling of Remedial By-Products

Remediation of PFAS often does not result in complete defluorination or mineralization. Consequently, management of remedial by-products containing residual or recalcitrant PFAS is necessary. Therefore, existing literature was reviewed by [Horst et al., \(2020\)](#) to identify the potential remedial by-products that will require management. Current and developing remedial methods rely on either thermal destruction or sequential defluorination. Current technologies typically concentrate PFAS prior to disposal or attempts at thermal destruction. Treatment technologies such as aerobic or anaerobic digestion in WWTP or digestion of sludges also transform PFAS precursors to more recalcitrant species such as PFAAs, but it is likely that some precursors or intermediary PFAS remain. In addition, PFAS treatment technologies in development can create problematic by-products when applied to waters from the natural environment in which non-target materials are typically present. For example, [Horst et al., \(2020\)](#) list perchlorate, bromate, and hexavalent chromium formed from chloride, bromide, and trivalent chromium.

Adsorbents

Some reviews of adsorption-based remedial processes for PFAS in water are provided by [Wang et al., \(2019\)](#); [Zhang et al., \(2019\)](#); [Gagliano et al., \(2020\)](#); [Vu and Wu, \(2020\)](#); and [Dixit, \(2021\)](#). [Wang et al., \(2019\)](#) summarized treatment of PFAS in groundwater

using carbonaceous materials, numerous IXR, zeolites, minerals, and alumina (commonly used in water treatment). [Zhang et al., \(2019\)](#) reviewed the technical feasibility of PFAS adsorption by several materials in solution, including AC, IXR, minerals, MIP, carbon nanotubes (CNTs), and a wide range of biosorbents. [Gagliano et al., \(2020\)](#) focused their review on relative performance of adsorbents including AC, biochar, MIP, IXR, nanoparticles, CNT, and mineral materials, the effect of organic matter, and adsorbent regeneration. [Vu and Wu, \(2020\)](#) reviewed sorbents including carbonaceous materials, resins, minerals, biomaterials, and polymers but included somewhat older literature in their review. [Dixit et al., \(2021\)](#) reviewed PFAS removal by IXR for water treatment plants but based their review only on the most recent applied developments.

Sorption Materials

Ex-situ adsorption by GAC is presently the dominant remedial technique for PFAS in water ([Schroder et al., 2010](#)) and is considered as providing the best combination of reliability and cost-effectiveness for PFAS removal ([Hansen et al., 2010](#)). As previously stated, GAC from most sources is known to be more effective at removing long-chained PFAS than short-chain PFAS ([Appleman et al., 2014](#)). GAC is susceptible to earlier breakthrough of (potentially unmonitored) shorter-chain PFAS and adsorbs PFOS better than PFOA ([Yu et al., 2009](#)), although continuing research on developing GAC with better performance for short-chain PFAS is promising. PAC is used in potable water treatment plants but compared to GAC has the disadvantage of limited percent removals and being difficult to regenerate, so it is typically disposed of as a constituent of spent treatment sludges. PAC could be used for modest removal needs.

Like GAC, resins are frequently used for PFAS removal. Both anionic and non-anionic resins have been studied for the remediation of PFAS. An advantage of resins over carbon-based sorption materials such as GAC is that it can have greater effectiveness at removing shorter-chain PFAS, particularly for newer resins developed specifically to adsorb PFAS, but the efficiency of resins varies greatly and background water quality has an influence ([Gagliano et al., 2020](#)). Most PFAS at ambient groundwater pH values are usually anions so strong base IXR are indicated for their treatment ([Gagliano et al., 2020](#))⁸. [Deng et al., \(2010\)](#) reported that polyacrylic resins have shown a higher efficiency for PFAS removal than polystyrene resins. Also, [Dixit et al., \(2021\)](#) indicated that polystyrenic resins have a higher affinity for PFAS than NOM, whereas polyacrylic resins have a higher affinity for NOM than PFAS. Older resins were apparently relatively specific to PFAS species, and this was considered problematic ([Vu and Wu, 2020](#)), but newer resins (e.g., A592E) have been reported to capture a wide range of PFAS ([Dixit et al., 2021](#)). Several resins developed for PFAS removal are now commercially available (e.g., Amberlite™, PSR2 Plus, CalRes 2301, Sorbix PURE LC, Resin Tech SIR-110-HP) but they are intended for single-use rather than regeneration and thus lack one of the key advantages of most resins, regeneration. In addition, in contrast to the generally observed trends, at least one supplier (Calgon™) indicates that PFAS-specific GACs can now be more successful than IXR in removing short-chain PFAS.

⁸ Obviously, if a mixture of ionic forms of PFAS were present then treatment using a single charge-dependent material would require augmentation, likely in a treatment-train approach.

Adsorption alternatives have been thought to be more limited for the newer, shorter-chain PFAS that have replaced the older PFAS because of their lower hydrophobicity. [Vu and Wu, \(2020\)](#) in their review of literature, that included some comparatively older resins, concluded that most sorption studies were conducted in synthetic solutions using AC or an IXR with rather high specificity, and consequently were successful only in removing PFOA and PFOS. [Dixit et al., \(2021\)](#) after reviewing the most recent and applied literature indicated that newer resins were able to remove a broad range of PFAS, but to restate, lacked the usual advantage of regeneration.

Many sorbents other than AC and IXR have been investigated but are considered impractical or unsuitable for various reasons. As previously mentioned, certain PACs may have higher adsorption capacity than certain GACs ([Hansen et al., 2010](#)) but is normally not regenerated for practical reasons including difficulty in separation from other constituents of treatment sludges ([Crone et al., 2019](#)). Biochar and multiwalled CNTs were found to be incapable of adequate short-chain PFAS removal ([Inyang and Dickenson, 2017](#); [Deng et al., 2010](#)). [Chen et al., \(2011\)](#) found that maize-straw-origin ash and single-walled CNTs were both effective adsorbents for PFOS but did not investigate their capability for removal of other PFAS. [Ochoa-Herrera and Sierra-Alvarez, \(2008\)](#) found that AC showed superior sorption for PFAS than a zeolite and activated sludge, and [Du et al., \(2014\)](#) illustrated that activated alumina, silica, zeolite, and montmorillonite were inferior to AC (as well as IXR) for PFAS removal. Other materials that have been shown to adsorb PFAS have the drawback of not being available on an industrial basis, including for example: synthesized materials (e.g., a porous aromatic framework constructed from benzene rings, covalent triazine-based framework, hexagonal boron nitride nanosheets, quaternized cotton and aminated rice husk, AC fibers from polyacrylonitrile fiber, and poly(ethylenimine)-functionalized cellulose microcrystals ([Gagliano et al., 2020](#)). Nanoparticle material oxides such as titania, iron oxides, alumina, and silica also have been shown to possess the ability to sorb to PFAS via electrostatic interaction and hydrogen bonds ([Wang and Shih, 2011](#); [Lu et al., 2016](#)). A study by [Zhou et al. \(2016\)](#) of magnetite nanoparticles used as a magnetic nanocomposite found that the material sorbed PFAS, and [Gong et al., \(2016\)](#) eliminated PFOA using starch-stabilized magnetite nanoparticles. Microplastics, common in some seawaters, have been shown to weakly sorb PFAS ([Llorca et al., 2018](#)).

Sorption Mechanisms

Sorption mechanisms vary by material. The mechanisms for sorption to AC and biochar are electrostatic and hydrophobic interaction ([Zhang et al., 2019](#)) and the hydrophobic effect has been found to increase with PFAS chain length ([Gagliano et al., 2020](#)). [Deng et al., \(2010\)](#) found that sorption rate and capacity of IXR were mainly a function of polymer matrix and porosity, but the functional group of the resin also impacts the rate of PFAS removal ([Dixit et al., 2021](#)). Recently available IXR were designed specifically for PFAS function via ion exchange and hydrophobic effects ([Dixit et al., 2021](#)). Other sorbing mechanisms for various materials include hydrogen and covalent bonding ([Gagliano, et al., 2020](#)) and at adequate concentrations, formation of micelles or hemi-

micelles as well as ligand and ion exchange and fluorophilic interaction (Vu and Wu, 2020).

Influence of Environmental Conditions and Co-contaminants

Geochemical conditions can significantly affect PFAS adsorption. Tang et al., (2010) found that PFOS adsorption onto silica was not greatly affected by pH, solution ionic strength, or calcium concentration. Wang and Shih, (2011) also found that adsorption of PFOS and PFOA on alumina decreased with increases of sodium, potassium, magnesium, and calcium cations. The efficacy of adsorbents for PFAS may be reduced by competitive effects. A review by Zhang et al., (2019) reported that dissolved organic carbon, NOM, HA, and WWTP effluent organic matter were known to reduce the adsorption affinity of sorbents for PFAS. However, a recent study by Siriwardena et al., (2019) found that co-contaminants including kerosene, TCE, and ethanol, and changes in pH, presence of sulfate, NOM, and iron oxides had little impact on the sorption of PFAS to GAC.

Regeneration of GAC and IXR

Both GAC and IXR can be regenerated for reuse but Gagliano et al., (2020) concluded that economical regeneration of adsorbents is challenging and in need of additional research. GAC has an economic advantage over many other treatment technologies because it can often be relatively inexpensively regenerated several times for re-use using heat (Baghirzade et al., 2021; Xiao et al., 2020). The GAC is dried at a relatively low temperature of about 105°C, thermally pyrolyzed at higher temperatures of about 650-850°C (or, according to some sources, in the range of 1000-1200°C for complete mineralization of PFAS) and then usually treated with steam or carbon dioxide. The amount of GAC active surface area recovered varies widely, however, because without fine control of the regeneration process the micropore structures of the GAC can be damaged. To date, although demonstrated at the bench scale and possibly completed without sampling for PFAS, GAC reactivation of PFAS-laden GAC has not been demonstrated at the full scale.

Regeneration of IXR is less economical than regeneration of GAC. Also, currently commercially available resins designed for PFAS removal are intended for single use although research and development continue. Chemical adsorbent regeneration, typically used for IXR, is usually done using methanol, sodium chloride, or sodium hydroxide. Stand-alone methanol or sodium chloride or their combination work very well for PFAS removal, but stand-alone sodium hydroxide performs very poorly. For some resins, a combination of a base (e.g., sodium hydroxide) with an inorganic (e.g., sodium chloride) is effective. Unfortunately, all these processes result in significant volumes of regeneration fluids for which there is no economical way to separate the contaminants, and the ultimate destruction of the PFAS requires unusually high (perhaps as high as 1600-2000 °C) temperatures (Bolam et al., 2021).

Reverse Osmosis (RO) and Nanofiltration (NF)

Pressure-driven membrane filtration processes such as RO or NF are well established separation technologies, which require hydraulic pressure of the feed stream exceeding the osmotic pressure to generate net flux of the clean water (i.e., the membrane permeate). RO membranes have lower molecular weight cut-off (MWCO) than NF membranes for superior rejection efficiencies of dissolved contaminants including monovalent ions (e.g., Na⁺, Cl⁻). NF membranes provide higher water permeability and thus higher energy efficiency than RO membranes due to the larger membrane pore size distribution. RO and NF have gained a foothold in various water treatment and desalination applications as a means of municipal water generation from seawater and as a potable water treatment technology. However, NF and RO have higher operating cost compared to other dominant remedial technologies for PFAS such as GAC or IXR.

Studies have shown that RO and NF thin-film composite (TFC) membranes with polyamide barrier layer have excellent rejection efficiencies for PFAS compounds. [Tang et al., \(2006, and 2007\)](#) found between 90% and 99% removal of PFOS by NF and >90% by RO membranes. [Patterson et al., \(2019\)](#) investigated point-of-use GAC and RO systems and found that RO removed about 100% of PFAS. [Appleman et al., \(2013\)](#) also reported rejection efficiency >93% by NF for 9 different PFAS compounds whose molar weight ranged between 214 g/mol – 500 g/mol (for PFBA and PFOS, respectively). Using water samples from water reuse plants in California, [Appleman et al., \(2014\)](#) also demonstrated superior rejection efficiencies of RO relative to GAC or IXR with 24 PFAS of various size and functional groups. In a more recent study ([Chow et al., 2021](#)) which investigated PFAS in bottled water products, it was also confirmed that RO-treated products contained significantly lower summed PFAS concentration than bottled water products without RO treatment. The above results demonstrated that RO and NF membranes are both effective for separation of long- and short-chain PFAS as the membranes reject solutes primarily by size-exclusion ([van der Bruggen et al., 2003](#)).

Although the amount of water produced/treated may largely differ depending on the system size, configuration, and application, NF and RO continuously generate the residual concentrate stream. However, disposal or management of a large volume of the membrane concentrate can be a major challenge. The presence of PFAS in the membrane concentrate may complicate the residual management process due to this concern ([Tow et al., 2021](#)). Accordingly, conventional concentrate management methods such as surface discharge, sewer, deep well injection, or evaporation ponds may be restricted. Regulations on PFAS are expected to rapidly increase, and accordingly, the effectiveness of maximum contamination levels (MCLs) set by different regulatory agencies will need to be evaluated. Thus, complex, stringent post-treatment or management processes may be necessary for PFAS-laden membrane concentrate.

Various operational strategies (e.g., concentrate recycling or closed-circuit desalination) and system configurations (e.g., multi-stage RO with interstage booster pump) have been explored to minimize the concentrate disposal ([Lee et al., 2019](#); [Efraty, 2012](#)). High-recovery systems, however, not only require costly components, but also increase the

energy consumption per unit volume of the permeate (i.e., specific energy consumption) to accommodate a higher concentration factor in the membrane feed channel.

RO and NF systems also suffer from fouling of the membrane due to accumulation of colloidal particles, scaling or inorganic salts, and growth of microorganisms: liu et al., 2018a found that PFAS adhere to membrane surfaces or complex with solutes resulting in surface adsorption via electrostatic or hydrophobic interactions. Formation of a thick fouled layer above the membrane surface may cause severe decline of the permeate flux, thereby requiring frequent replacement of the membrane element. Zhao et al., (2016) demonstrated 70% productivity loss due to membrane fouling induced by PFOS in the feed solution with magnesium and/or humic acid (HA). In a recent study by Boo et al., (2018), development of loose and negatively charged NF membrane was investigated to allow selective passage of salts to prevent formation of PFAS-salt bridging. To overcome the challenges from membrane fouling potentially induced by PFAS adsorption, continued research efforts are necessary to understand the behavior of PFAS under various fluid conditions and material properties of the membrane.

Biodegradation

Vertical stratification of PFAS species often observed at PFAS release sites could be explained by aerobic biodegradation of selected PFAS species, predominantly including PFAS precursors, in addition to differential mobility (Bekele et al., 2020; ITRC, 2022). At PFAS release sites generally more of the longer chain PFAS and PFAS precursors are observed in vadose soils than the underlying groundwater, where PFAAs and branched-chain isomers are more common (Schulz et al., 2020). This could be consistent with greater mobility of shorter chain PFAS, aerobic transformation of longer chain PFAS to shorter chain PFAS, and aerobic transformation of PFAS precursors to PFAAs. Thus, increased groundwater transport could be expected from perhaps common vadose-zone PFAS degradation to PFAAs. Available studies are congruent with biodegradation as the predominant mechanism for vadose zone PFAS degradation. Further, in groundwater, linear PFAS are often closer to the source area and branched isomers are further downgradient. This is an illustration of differential retardation between linear and branched PFAS.

WWTP PFAS studies are a good source of information for engineered biological treatment of groundwater. It is not uncommon for WWTPs, which rely on biodegradation to degrade incoming contaminants, to have higher concentrations of PFOS and PFOA in treated water than influent water. This suggests a higher rate of biotransformation of PFAS precursors to PFOS and PFOA than the rate of any destruction of PFOS and PFOA, which at present is assumed to not occur. Most WWTPs rely on aerobic digestion to treat wastewater, although a minority use anaerobic digestion, and both processes are microbially mediated. In summary, the degradation of PFAS precursors in WWTPs appears to primarily be biologically mediated and occur under both aerobic and anaerobic conditions (Lenka et al., 2021).

PFAS degradation processes are not universally observed in WWTPs and appear to be dependent on differences in the bacteria present in individual treatment plants. [Ochoa-Herrera et al., \(2016\)](#) investigated the microbial toxicity and biodegradability of PFOS and shorter-chain PFAS. They found that none of the tested compounds were toxic to methanogenic (anaerobic) activity of wastewater sludge up to 500 mg/L, but all the PFAS were highly resistant to microbial degradation under both aerobic and anaerobic conditions. In contrast, [Liu and Avendaño, \(2013\)](#) found that sources of activated sludge inoculant were critical to biodegradation. The same precursors that proved recalcitrant in the presence of one inoculum were degraded in the presence of another. The same outcome resulted when aerobic degradation was inoculated using soils. Bacteria cultured from contaminated groundwater was also able to degrade FTOHs (4:2, 6:2, and 8:2 FTOH) by oxidation, probably cometabolically, and 6:2 fluorotelomer sulfonate (6:2 FTS) by desulfonation and defluorination.

Present data do not show all PFAS can be mineralized using biological mechanisms ([Horst et al., 2020](#)). Aerobic biodegradation of precursors is commonly observed in several environmental media, and a review by [Shasavari et al., \(2021\)](#) noted that fungal and bacterial strains have been isolated that are capable of degrading PFAS. Based on a review of PFAA precursor degradation in the environment by microbes, activated sludge, plants, and earthworms, [Zhang et al., \(2021\)](#) concluded that environmental biotransformation mainly involves aerobic oxidation, dealkylation, and defluorination of non-fluorinated functional groups, and surprisingly the cleavage of carbon-fluorine (C-F) bonds, to form shorter-chained PFAAs. In a review of microbial degradation of PFAA precursors in microbial culture, activated sludge, soil, and sediment, [Liu and Avendaño, \(2013\)](#) found the lack of direct detection methods for precursors problematic and that there was a significant issue with bound residues in soils. Nonetheless, significant transformation of (FTOHs), fluorotelomer sulfonate, fluorotelomer stearate and citrate esters, fluorotelomer phosphate esters, fluorotelomer acrylate and methacrylate, fluorotelomer ethoxylates, and n-ethyl perfluorooctane sulfonamidoethanol were found in the literature. Noteworthy, some PFAS precursors were found to be anaerobically defluorinated during biotransformation. Examples of anaerobic bioactive environments include the less common anaerobic digestion WWTPs and treatment sludge piles.

Degradation of the PFAAs that result from PFAS precursor degradation has not been observed in the environment to the knowledge of the authors, and they have until recently been thought to be entirely recalcitrant. However, biodegradation of PFOA and PFOS were reported in a methodological study of sewage sludge by [Schroder, \(2003\)](#) under anaerobic but not aerobic conditions. Decreases in concentration of PFOA were much slower than and subsequent of those of PFOS in the study. Fluoride, indicative of mineralization, was not detected in either the aerobic or anaerobic reactors.

A study by [Yi et al., \(2016\)](#) sought to optimize degradation of PFOA by *Pseudomonas parafulva* and obtained a reduction of 32% after 96 hours, and 48% after 96 hours using supplemental glucose. A decrease of about 67% PFOS in 96 hours was observed in a study by [Kwon et al., \(2014\)](#) using *Pseudomonas aeruginosa*. It was shown by

[Chetverikov et al., \(2017\)](#) that *Pseudomonas plecoglossicida* was able to transform 75% of PFOS in soil to perfluoroheptanoic acid.

A microcosm study by [Huang and Jaffé, \(2019\)](#) investigated the microbial destruction of PFOA and PFOS using *Acidimicrobium* sp. strain A6 (A6) under iron-reducing conditions. A6 is an autotroph that under anaerobic conditions oxidizes ammonium (electron donor), known as the Feammox process. It is found in the environment where the pH is less than 7 in iron rich soil. A6 can also use hydrogen as an electron donor and has the practical benefit of being able to cometabolically degrade trichloroethene (TCE) and perchloroethene (PCE). The [Huang and Jaffé, \(2019\)](#) study included investigation of whether PFOA and PFOS can be biodegraded using either pure A6 culture or microbially enriched A6 culture (i.e., denitrifiers *Ralstonia* and *Bacillus*, iron reducers *Acidimicrobium* and *Aciditerrimonas*, and sulfate reducers *Desulfosporosinus*) using ammonium or hydrogen under iron-reducing conditions during 60 and 100-day incubations. They reported the defluorination of up to 60% PFOA and PFOS by *Acidimicrobium* sp. strain A6 (A6) during 100-day incubations, with the highest degradation percentages occurring for the A6 with microbial enrichment using ammonium as the electron donor. Significantly, there were concomitant evidentiary increases in fluoride and shorter chain perfluorinated products. Buttressing these results, [Huang et al., \(2022\)](#) performed anaerobic incubation of biosolids containing PFOA and PFAS-free lab samples spiked with PFOA. Samples were spiked with *Acidimicrobium* sp. Strain A6, or ferrihydrite, or both. Control samples were also used, and incubations lasted 150 days. The only samples that exhibited decreased concentrations of PFAS were those that were spiked with both *Acidimicrobium* sp. Strain A and ferrihydrite; PFOA concentrations decreased in excess of 50% in these samples, with concomitant increases of shorter-carbon-chain PFCAs and fluoride.

Oxidation

AOPs for PFAS degradation have been extensively tested ([Moriwaki et al., 2005](#)). AOPs are based on free radical oxidants such as hydroxyl that can be generated numerous ways ([Trojanowicz et al., 2018](#)). AOPs for some PFAS such as fluorotelomers and PFCAs usually proceed by sequential defluorination, but AOP apparently does not destroy PFASs ([Horst et al., 2020](#)). In fact, PFAS in general are recalcitrant to chemical oxidation. The resistance to oxidation is believed to be the result of the difficulty of the relatively large free radicals to access the C–C bonds in the fluorocarbon tails. This is due to the tight packing of the fluorine atoms around the C–C bonds as well as the strength of the C–F bonds.

[Wang et al., \(2019\)](#) found mixed results for PFAS treatment using AOPs. Examples of numerous AOP treatment permutations abound, and results are sometimes contradictory. Hydrogen peroxide activated using ultraviolet (UV) light, ozone, or ferrous iron were tested but these trials were unsuccessful in at least one study ([Schroder and Meesters, 2005](#)). Ozone with UV has also been trialed and was successful, but relatively slow ([Hori et al., 2004](#)). Ozone and hydrogen peroxide with ozone were successful under alkaline conditions and pretreatment under acid pH conditions ([Lin et al., 2012a](#)). Ozone, UV,

heat, and photolysis have also been successful, often variously combined with persulfate, Fenton's reagent, zerovalent metals, and subcritical water (Hori et al., 2005, and 2008a; Huang et al., 2005; Lee et al., 2010b and 2012; Qu et al., 2010; Tsitonaki et al., 2010; Lin et al., 2012a; Jin et al., 2014). Suthersan et al., (2016) noted that in-situ oxidation for PFAS remained a largely un-surmounted challenge. They described a nascent in-situ remedial technique for PFAS using activated persulfate that reportedly can mineralize PFOS. This technology is purportedly dependent on a specific activation method.

AOPs have several potential drawbacks. In general, it is problematic when AOPs are used to treat CVOC plumes that are comingled with PFAS (Merino et al., 2016). AOPs frequently create PFAS with shorter perfluorinated alkyl chains that are not degraded (Nzeribe et al., 2019; Trojanowicz et al., 2018), generally increasing PFAS transport. AOPs also have the liability of forming more toxic oxidized forms of non-target materials often present in environmental samples.

Reduction

PFAS should be less resistant to reduction than oxidation because the relatively smaller free radicals should have easier access to the C–C bonds in the fluorocarbon tails. This is a function of the tight packing of the fluorine atoms around the C–C bonds as well as the strength of the C–F bonds.

Chemical reduction shows some promise for in-situ destruction of PFAS in groundwater (Wang et al., 2019) but requires several hours for mineralization of PFAS (Horst et al., 2020). PFAS have been degraded using ZVI in sub- and super-critical water (Hori et al., 2006, and 2008b). Nanoscale ZVI has been shown to have improved efficacy due at least in part to the increased specific surface area and in the presence of stabilizing agents (Crane and Scott, 2012; Arvaniti et al., 2015) that prevent aggregation which reduces reactive surface area (Phenrat et al., 2007).

Cui et al., (2020) reviewed destruction of PFAS using ARPs and Trojanowicz et al., (2018) reviewed destruction of PFAS using ARPs and AOPs. ARPs have been understood to sequentially defluorinate the carbon backbone of PFAS; Bentel et al., (2019) provide detailed description of several degradation mechanisms. Cui et al., (2020) found that degradation pathways for PFAS vary as a function of their head groups and in at least some cases the length of their fluorocarbon chain. Degradation was highly influenced by solution chemistry factors, such as pH, concentration of sulfate or iodide, DO, HA, nitrate, and temperature. Degradation increased with increasing temperature, and nitrate slowed degradation with increasing concentration. Increasing pH favors reductive degradation, and the optimal pH is within the alkaline range evidently because there is less hydrogen/hydronium ion (H^+/H_3O^+) to scavenge aqueous electrons (e_{aq}^-). When using sulfite (SO_3^{2-}) or iodide (I^-) as a solute, degradation efficiency increased with dose because more e_{aq}^- becomes available until a critical level was reached, above which efficiency decreased because scavenging of the e_{aq}^- became dominant. The inhibiting effects of DO on destruction of PFAS are considerable due to scavenging of e_{aq}^- by DO. Also, water matrix constituents can affect destruction of PFAS in water by different

mechanisms. Humic acid for example is a constituent of dissolved organic matter (DOM) that can accelerate degradation below a threshold concentration, above which decomposition slows. The mechanism of action is uncertain.

Other Technologies

Several other groundwater remediation technologies for PFAS are in various stages of development including field trials, such as photocatalysis, electrochemical treatment, foam fractionation, plasma, and sonification. Several materials as photocatalysts have been investigated for the cost-effective treatment of PFAS in groundwater using light radiation (Xu et al., 2020a). Sahu et al., (2018) synthesized petitjeanite $\text{Bi}_3\text{O}(\text{OH})(\text{PO}_4)_2$ (BOHP) microparticles as a photocatalyst and used them with UV light to mineralize ~100% PFOA within one hour of treatment. Mineralization of PFAS also occurred in the presence of NOM. Liu et al., (2017) used nZVI and visible light, as a cheaper alternative to UV, and removed 69.7% and 89.7% PFOA in the absence and presence of hydrogen peroxide, respectively. Xu et al., (2020b) eliminated almost all PFOA using titanium dioxide with peroxymonosulfate (PMS) and visible light. All these trials required strong irradiance, however, which is relatively costly.

Electrochemical treatment destroys PFAS at the anode by electron transfer and by hydroxyl radical generation. Electrons are thought better able to attack chemical bonds in the fluorocarbon tail of PFAS than oxidants owing to their small size, which affords the electrons better access between the fluorine atoms tightly packed around the C–F and C–C bonds. Formation of the hydroxyl radical is likely problematic due to its propensity to transform relatively innocuous constituents of environmental waters to more toxic forms. The composition of the anode significantly affects efficiency (Lin et al., 2012b; Zhao et al., 2013; Schaefer et al., 2015) and boron-doped diamond anodes are often recommended. Nonetheless, other anode materials have been successful. Yang et al. (2016) mineralized 90% of PFOA using iron electrodes. Wang et al., (2016) eliminated 99.7% PFOA using zinc cathode and stainless-steel cathode. Liu et al., (2018b) used an Al-Zn electrode to degrade PFOA in groundwater and removed 79.4% PFOA within one hour. Lin et al., (2018) used porous Ti_4O_7 ceramic material as an anode for mineralization of PFOS and PFOA, and within three and two hours of reaction ~100% PFOA and 93.1% PFOS were removed.

Foam fractionation can successfully attain drinking water concentrations of PFAS in treated water (Meegoda et al., 2020). Air is bubbled through a column of water and foam fractionate is removed from the surface of the water column. Ozone has been used in place of air to simultaneously oxidize co-contaminants.

Plasma used in wastewater treatment can be generated using electricity, radiofrequency, or microwaves (Fridman and Kennedy, 2004; Locke and Thagard, 2017). Unlike traditional AOPs, plasma from electrical discharges can simultaneously oxidize and reduce organic molecules (Nzeribe et al., 2019). Efficiency is a function not only of the plasma source but also the conductivity, temperature, and pH of the water as well as the chemical structure of the contaminant. Stratton et al., (2017) found plasma was an

effective treatment technology, but again, oxidation can transform relatively innocuous constituents of environmental waters to more toxic forms.

Sonification is the use of soundwaves to create bubbles in water, the surface of which attract PFAS. When the bubbles cavitate extreme heat is generated, destroying PFAS without formation of by-products. The cavitation however also creates reactive species like those of ARP. These radicals usually remain within the bubble or on the bubble surface and include $\bullet\text{H}$ and $\bullet\text{OH}$, and if they escape the bubble may recombine to form hydrogen peroxide, or $\bullet\text{H}$ may react with oxygen to form the radical $\bullet\text{HO}_2$ (Wood et al., 2017). Nonetheless sonification has been effective at destroying PFAS (Moriwaki et al., 2005; Cheng et al., 2008), and can be enhanced by addition of sulfate (Lin et al., 2015). Co-contaminants can reduce efficiency, probably due to competition with PFAS to occupy the bubble surface, but Cheng et al., (2008) indicated that DOM has little deleterious effect.

Treatment Train Processes

Groundwater PFAS plumes often include CVOCs, petroleum hydrocarbons, dissolved organic carbon, and heavy metals. All these materials can reduce the efficiencies of PFAS treatment technologies. Consequently, a combined treatment approach including multiple processes may be advantageous for groundwater remediation (Horst et al., 2018).

Some current work on treatment train approaches includes an in-situ study by Crimi et al., (2017) and a successful approach used by Boonya-atichart et al., (2018). Crimi et al., (2017) used GAC for adsorption and heat-activated persulfate for in-situ oxidative degradation of PFAS and found persulfate was ineffective. Boonya-atichart et al., (2018) demonstrated a combined system of photocatalysis and membrane filtration to treat PFOA from groundwater. A concentrated stream of contaminants obtained from filtration was mineralized using photocatalysis with nZVI, and a UF system was utilized to eliminate the nZVI from the photocatalytic route. By this process, 99.6% PFOA was removed from groundwater, and 59.6% retentate was degraded using photocatalysis.

Lu et al., (2020) reviewed PFAS remediation treatment train approaches based on a sampling from 150 publications. They classified treatment trains as either tandem (removal followed by degradation) or parallel (simultaneous destructive mechanisms). The tandem treatment trains they reviewed included: NF and electrochemical anodic oxidation, biochar and ZVI, GAC and activated persulfate, GAC and thermal mineralization, NF, nZVI and UF, and IXR with electrochemical anodic oxidation. The parallel treatment trains reviewed included: electro-Fenton with electrochemical anodic oxidation, hydrogen peroxide and activated persulfate, thermolysis and photolysis degradation, ZVI/GAC micro-electrolysis with vacuum ultraviolet (VUV)-Fenton, and electron beam with activated persulfate. They found that many innovative technologies in laboratory development required extreme operating conditions that were not likely to be cost effective at scale-up. Based on their review they proposed a tandem combination of

NF with electrochemical anodic oxidation, and a parallel combination of electro-Fenton degradation with electrochemical anodic oxidation.

SUMMARY

PFAS are a family of thousands of chemicals defined as: *fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it)*. They have been used in a multitude of commercial, industrial, and consumer products but some have been discovered to be very toxic.

They have been synthesized using either ECF or telomerization and the impurities characteristic of each of these processes can be used for source forensics. A useful conceptual prototype is a fluorinated, linear carbon-chain backbone with a polar functional group attached to one end referred to as the head; the opposite end is referred to as the tail. The tail is hydrophobic and oleophobic and the head is hydrophilic, rendering the molecule an amphiphilic surfactant with a propensity to collect at media interfaces such as between air and water. The tail can undergo hydrophobic interactions with materials such as organic carbon particles in soil, and if the head is in a charged state, it can undergo electrostatic interactions with materials such as charged mineral surfaces or ions.

PFAS are commonly observed in environmental media including soil, surface water and groundwater. PFAS may enter the environment through releases from industrial and manufacturing facilities, the direct use of PFAS products such as AFFF at airports and military bases, landfill leachate, WWTP effluent, land application of WWTP biosolids and sludges for soil improvement, or irrigation using WWTP effluent. Multiple PFAS sources sometimes exist at a single site, and many releases include a mixture of different PFAS as well as co-contaminants such as hydrocarbons and CVOCs.

The movement of PFAS that enter the subsurface environment is retarded by their affinity for interfaces between media such as air and water, hydrophobic interactions, and electrophilic interactions. These retarding properties vary for individual PFAS and can contribute to a chromatogram-like redistribution of originally homogeneous PFAS mixtures. Redistribution can also be affected by the presence of co-contaminants and the transformation of classes of PFAS (termed precursors) into more stable classes of PFAS.

The complexity of PFAS retardation and transformation in the subsurface can make development of a CSM challenging. Conducting subsurface sampling is atypically difficult because PFAS may be incorporated into the composition and coatings of sampling equipment and supplies. Also, analytical methods are limited to either measuring only several dozen individual PFAS or relying on some strong assumptions to estimate a total amount of PFAS.

Some PFAS do not respond well to traditional remedial techniques due to properties such as hydrophobicity, oleophobicity, and exceptional chemical stability. Numerous

innovative remedial technologies are in development, but many have only been demonstrated at the laboratory bench scale or do not seem economically viable for scale-up to practical implementation. Treatment train approaches have been trialed to overcome some of the limitations of specific remedial methods but have been similarly criticized.

Currently GAC and IXR are the primary means of PFAS removal, although RO and NF may become more commonly used processes due to their greater removal efficiency if they can be made more economical. Both GAC and IXR have several advantages and disadvantages. Regeneration of GAC is relatively economical and therefore makes this technology more attractive, but IXR regeneration is somewhat costly due to the need for concentrate disposal, if regeneration is even possible. Until very recently a common problem with these materials was preferential adsorption of some PFAS relative to others, but this is reportedly less of a problem with newly developed GAC and IXR intended for the treatment of PFAS. Real-world issues such as groundwater co-contaminants, organic material, and geochemistry can affect the efficacy of GAC and IXR. The presence of co-contaminants and organic material can adversely affect the performance of GAC although this may be less of an issue with IXR, and both GAC and IXR performance can be affected by solution conditions such as pH and alkalinity.

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Table 1. Selected properties of example PFAS. Data downloaded on 07/07/2021 from the US EPA CompTox Chemicals Dashboard, available at: <https://comptox.epa.gov/dashboard>.

Property	Units	HFPO-DA	PFBA	PFBS	PFDA	PFHxS	PFNA	PFOA	PFOS
Boiling Point	°C	68.3 to 106	108 to 123	205 to 214	205 to 239	218 to 238	190 to 222	188 to 204	219 to 244
Density	g/cm ³	1.69 to 1.70	1.55 to 1.68	1.81 to 1.85	1.76 to 1.82	1.84	1.75 to 1.80	1.70 to 1.75	1.84 to 1.85
Flash Point	°C	18.7 to 20.3	18.0 to 47.3	#N/A	79.6 to 82.7	#N/A	72.6 to 74.0	62.1 to 73.9	#N/A
Henry's Law	atm- m ³ /mole	0.0201	0.0000501	2.95E-10	1.5E-10	1.94E-10	1.18E-09	1.92E-10	1.8E-11
Index of Refraction	unitless	1.27	1.29	1.32	1.29	1.31	1.29	1.29	1.3
LogKoa: Octanol-Air	unitless	2.29	3.46	4.16	4.28	4.27	4.2	4.16	4.75
LogKow: Octanol-Water	unitless	3.37 to 9.12	1.43 to 3.93	1.95 to 3.68	4.15 to 9.53	2.20 to 5.25	3.54 to 8.64	3.11 to 7.75	4.17 to 7.03
Melting Point	°C	-107 to -53.3	-17.9 to 13.5	20.4 to 106	5.98 to 90.0	26.7 to 190	4.71 to 68.5	-8.69 to 54.2	15.2 to 185
Molar Refractivity	cm ³	33.4	23.2	32	52.7	41.8	47.8	42.9	51.5
Molar Volume	cm ³	197	127	162	292	217	265	237	272
Polarizability	Å ³	13.2	9.19	12.7	20.9	16.6	19	17	20.4
Surface Tension	dyn/cm	14.7	15.4 to 18.7	23.4	16.4	21	16.6	16.8	19.6
Vapor Pressure	mm Hg	18.2 to 41.0	3.92 to 33.6	1.14e-8 to 0.208	1.46e-3 to 4.63e-2	8.19E-09	8.44e-3 to 0.171	0.111 to 0.345	0.00000248
Water Solubility	mol/L	4.81e-4 to 7.00	1.53e-3 to 1.37	-0.523 to 7.25e-3	2.62e-10 to 3.73	1.49e-6 to 0.853	4.06e-9 to 3.35	6.27e-8 to 2.98	6.25e-9 to 2.27

PFOA = Perfluorooctanoic acid

PFOS = Perfluorooctane sulfonic acid

PFBA = Perfluorobutanoic acid

PFBS = Perfluorobutane sulfonic acid

PFNA = Perfluorononanoic acid

PFDA = Perfluorodecanoic acid

PFHxS = Perfluorohexane sulfonic acid

HFPO-DA = Hexafluoropropylene oxide dimeric acid

#N/A = data not available from the source used

Table 2. Four US EPA Methods used to analyze PFAS analytes in environmental media. US EPA SW-846 Method 8327 addresses 24 PFAS analytes in four aqueous matrices of reagent water, groundwater, surface water, and wastewater effluent. US EPA Method 537.1 is a solid phase extraction (SPE) LC/MS-MS method for the determination of 18 selected PFAS in drinking water matrices. US EPA Method 533 addresses “short chain” PFAS (C4-C12) and can be used to test for 11 additional PFAS in drinking water matrices. US EPA Method 1633 addresses 40 PFAS analytes in wastewater, surface water, groundwater, soil, biosolids, sediment, landfill leachate, and fish tissue.

Target Analyte Name	Abbreviation	CAS Number	533	537.1	8327	1633
Perfluoroalkyl carboxylic acids						
Perfluorobutanoic acid	PFBA	375-22-4	+		+	+
Perfluoropentanoic acid	PFPeA	2706-90-3	+		+	+
Perfluorohexanoic acid	PFHxA	307-24-4	+	+	+	+
Perfluoroheptanoic acid	PFHpA	375-85-9	+	+	+	+
Perfluorooctanoic acid	PFOA	335-67-1	+	+	+	+
Perfluorononanoic acid	PFNA	375-95-1	+	+	+	+
Perfluorodecanoic acid	PFDA	335-76-2	+	+	+	+
Perfluoroundecanoic acid	PFUnA	2058-94-8	+	+	+	+
Perfluorododecanoic acid	PFDoA	307-55-1	+	+	+	+
Perfluorotridecanoic acid	PFTTrDA	72629-94-8		+	+	+
Perfluorotetradecanoic acid	PFTeDA	376-06-7		+	+	+
Perfluoroalkyl sulfonic acids						
Perfluorobutanesulfonic acid	PFBS	375-73-5	+	+	+	+
Perfluoropentanesulfonic acid	PFPeS	2706-91-4	+		+	+
Perfluorohexanesulfonic acid	PFHxS	355-46-4	+	+	+	+
Perfluoroheptanesulfonic acid	PFHpS	375-92-8	+		+	+
Perfluorooctanesulfonic acid	PFOS	1763-23-1	+	+	+	+
Perfluorononanesulfonic acid	PFNS	68259-12-1			+	+
Perfluorodecanesulfonic acid	PFDS	335-77-3			+	+
Perfluorododecanesulfonic acid	PFDoS	79780-39-5				+
Fluorotelomer sulfonic acids						
1H,1H, 2H, 2H-Perfluorohexane sulfonic acid	4:2FTS	757124-72-4	+		+	+
1H,1H, 2H, 2H-Perfluorooctane sulfonic acid	6:2FTS	27619-97-2	+		+	+
1H,1H, 2H, 2H-Perfluorodecane sulfonic acid	8:2FTS	39108-34-4	+		+	+
Perfluorooctane sulfonamides						
Perfluorooctanesulfonamide	PFOSA	754-91-6			+	+
N-methyl perfluorooctanesulfonamide	NMeFOSA	31506-32-8				+
N-ethyl perfluorooctanesulfonamide	NEtFOSA	4151-50-2				+
Perfluorooctane sulfonamidoacetic acids						
N-methyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA	2355-31-9		+	+	+
N-ethyl perfluorooctanesulfonamidoacetic acid	NEtFOSAA	2991-50-6		+	+	+
Perfluorooctane sulfonamide ethanols						
N-methyl perfluorooctanesulfonamidoethanol	NMeFOSE	24448-09-7				+
N-ethyl perfluorooctanesulfonamidoethanol	NEtFOSE	1691-99-2				+

Per- and Polyfluoroether carboxylic acids						
Hexafluoropropylene oxide dimer acid	HFPO-DA	13252-13-6	+	+		+
4,8-Dioxa-3 <i>H</i> -perfluorononanoic acid	ADONA	919005-14-4	+			+
Perfluoro-3-methoxypropanoic acid	PFMPA	377-73-1	+			+
Perfluoro-4-methoxybutanoic acid	PFMBA	863090-89-5	+			+
Nonafluoro-3,6-dioxaheptanoic acid	NFDHA	151772-58-6	+			+
Ether sulfonic acids						
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	9Cl-PF3ONS	-				+
11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	11Cl-PF3OUdS	-				+
Perfluoro(2-ethoxyethane)sulfonic acid	PFEESA	-				+
Fluorotelomer carboxylic acids						
3-Perfluoropropyl propanoic acid	3:3FTCA	-				+
2 <i>H</i> ,2 <i>H</i> ,3 <i>H</i> ,3 <i>H</i> -Perfluorooctanoic acid	5:3FTCA	-				+
3-Perfluoroheptyl propanoic acid	7:3FTCA	-				+

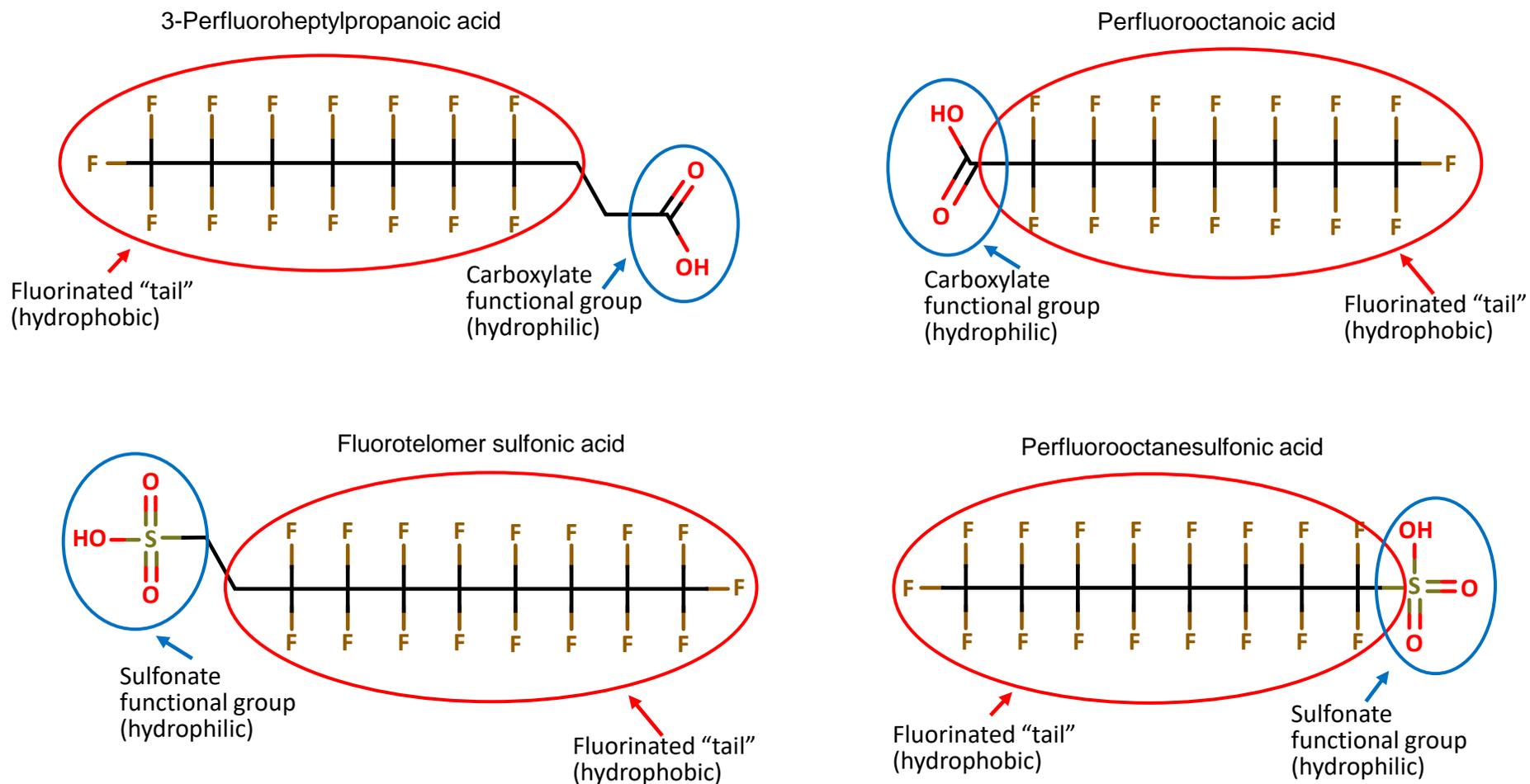


Figure 1. Examples of PFAS.

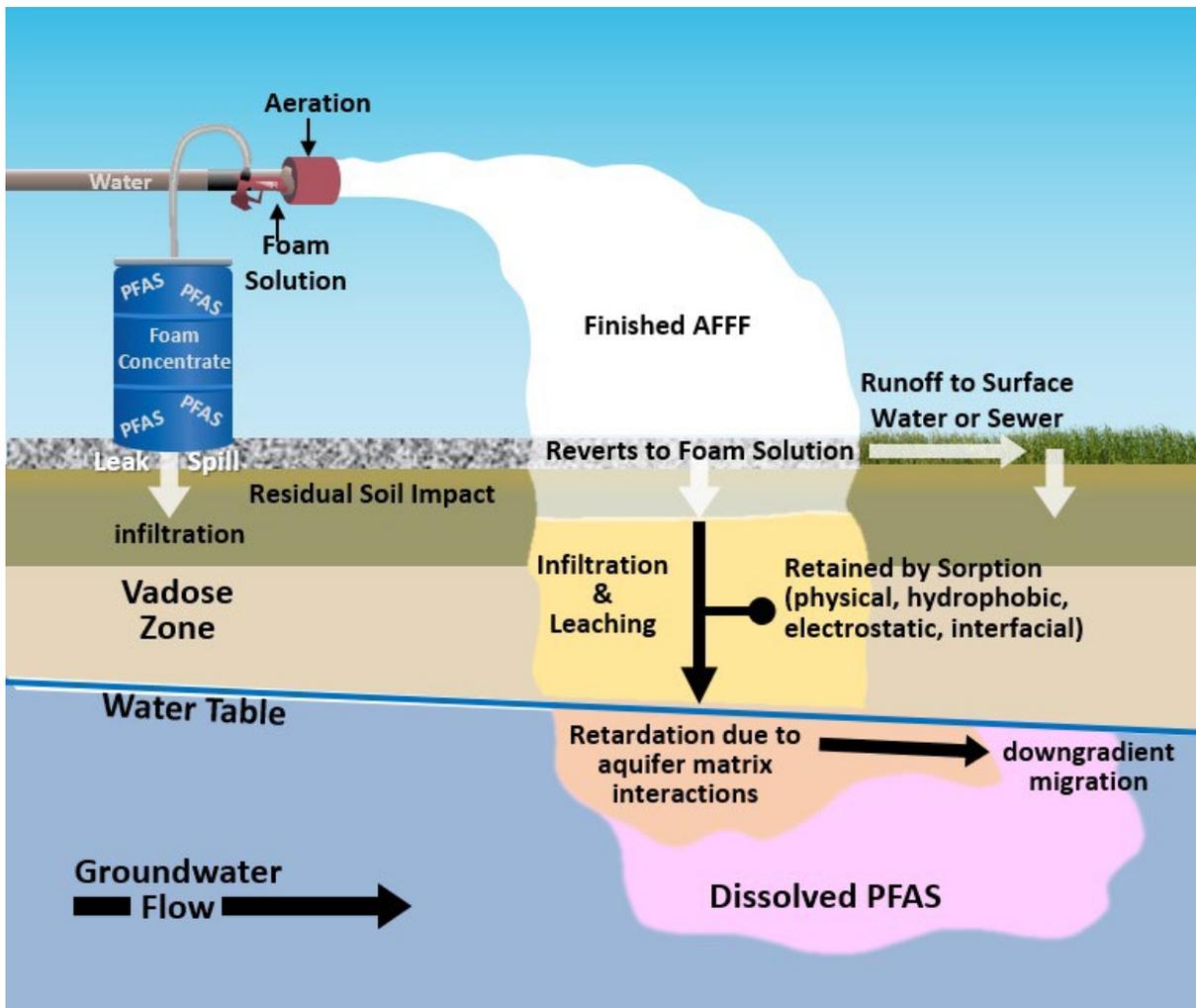


Figure 2. Conceptual site model for firefighter training source area. *Source: Adapted from figure by J. Hale, Kleinfelder and ITRC 2022. Used with permission.*



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