

Groundwater and PFAS: State of Knowledge and Practice

Fate and Transport Section 4

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

Fate and Transport

INTRODUCTION

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

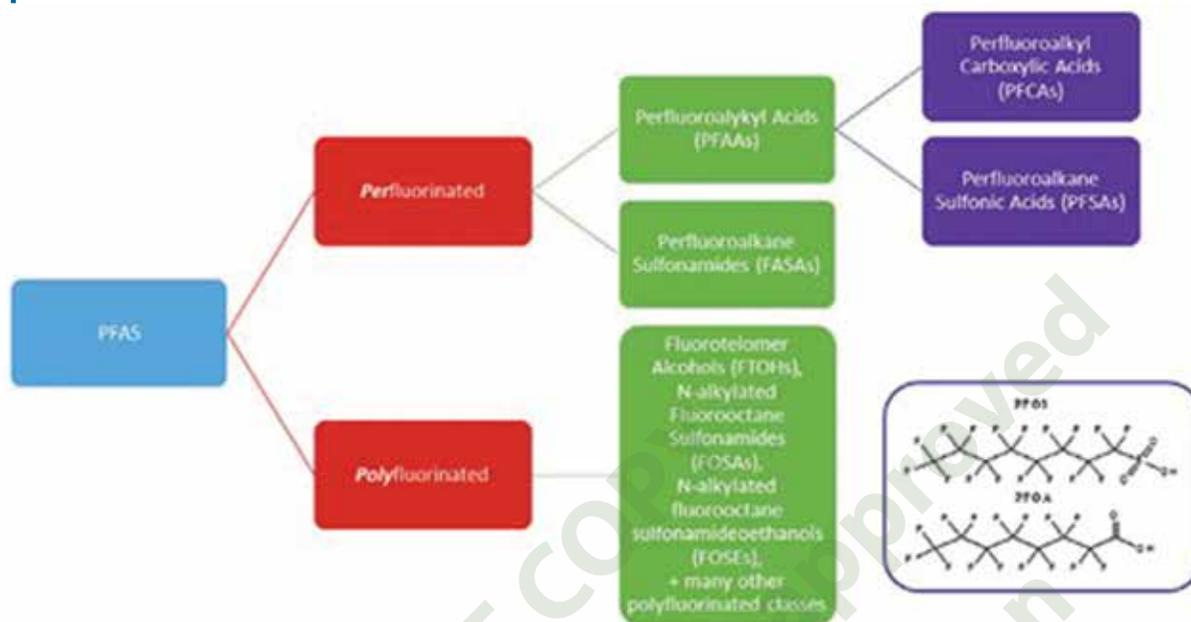
This section presents relevant properties of PFAS and current understanding of PFAS environmental fate and transport. Information is presented on PFAS chemistry, sources, mobility, fate and mass balance, distribution in the subsurface, and exposure points.

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

Key Takeaways of This Section

- There are multiple potential sources of PFAS to groundwater. Recognized sources of PFAS include (a) storage, transfer, and use of AFFF for firefighting and fire training; (b) disposal/land application of municipal biosolids; (c) discharge of effluent from municipal wastewater treatment systems; (d) release of landfill leachate; and (e) release from a variety of commercial and industrial sources. Some of these release mechanisms differ from typical leaks, drips, spills, and ruptures associated with many other contaminants, and may contribute to broader distribution in the environment and groundwater, rivaling migration via advective flow.
- PFAS exhibit hydrophobic, lipophobic, and surfactant¹ properties. These factors combine to confer unique transport considerations.
- PFAS molecules are miscible in water. They will readily exist in the aqueous phase and will not exist as separate non-aqueous phase liquids (NAPLs) in the subsurface. PFAS surfactant characteristics enhance infiltration due to reduction in surface tension.
- The polar “head” of many PFAS molecules tends to ionize in aqueous environments. Consequently, PFAS molecules are prone to sorption via electrostatic attraction to charged surfaces.
- PFAS also sorb to organic carbon owing to their hydrophobic and lipophilic C-F “tail.” PFAS molecules exhibit relatively high K_{oc} values compared to other common groundwater contaminants. However, K_{oc} and degree of sorption is site-specific, contingent upon the sorptive medium (e.g., surface charge, mineralogy, and organic carbon content) and solution chemistry, especially ionic strength, pH, and Ca²⁺ activity. Petroleum-based NAPL that may be present as a co-contaminant

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



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

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can lead to accumulation of PFAS at the oil-water interface due to the strong hydrophobic nature of the carbon-fluorine tail.

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

UNIQUE CHEMISTRY OF PFAS

The term PFAS includes both **poly**fluorinated alkyl substances, in which only some of the carbons in the alkyl chain have fluorines bound to them, and **per**-fluorinated alkyl substances, in which the alkyl-chain is fluorine-saturated (Buck et al. 2011). Figure 4.1 is a simplified depiction of poly- and perfluorinated alkyl substances.

A substantial reason for the unique chemistry of PFAS is that the carbon-fluorine (C-F) bond is the

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

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

strongest known carbon single bond (Table 4.1).

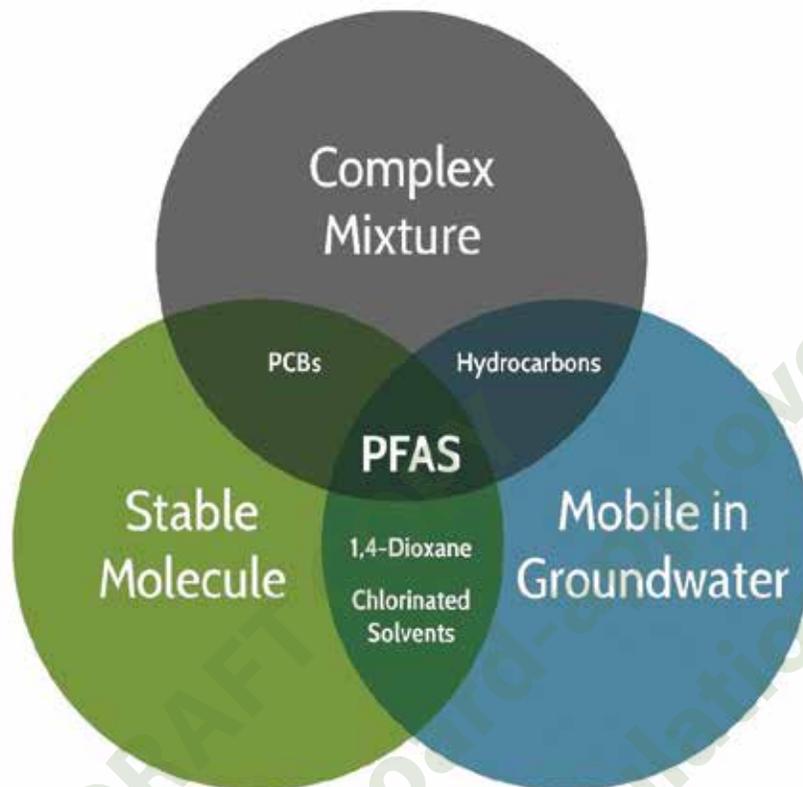
Fluorine atoms on a PFAS molecule act as a shell that protects the C-C bonds and other bonds and renders the PFAS molecule resistant to cleavage. The combination of (1) strong C-F bond; and (2) protective shell of F atoms renders some PFAS especially stable and particularly resistant to degradation by biological or chemical means.

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

- Anions are negatively charged.

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

Figure 4.2. PFAS comparison to other contaminant classes.



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

Zwitterionic PFAS have both anionic and cationic branches, and this makes them useful in creating surfaces that are both hydrophobic and lipophobic (i.e., non-stick). But this characteristic also complicates fate and transport.

Certain properties of many PFAS are similar to better-understood contaminants such as PCBs, chlorinated solvents, and hydrocarbons (Figure 4.2). For example, PFAS (especially originating from AFFF) tend to be present in complex mixtures, as is typical of hydrocarbons and PCBs. However, PFAS are much more soluble than PCBs, and are therefore more prone to forming dissolved-phase plumes. Unlike hydrocarbons and chlorinated solvents, the PFAS molecules are not considered biodegradable; precursors may be transformed via biodegradation into other PFAS species, but the total quantity of PFAS molecules is preserved. Some PFAS have similarities to chlorinated solvents in terms of mobility via advection and dispersion in groundwater, although there are limitations to this comparison. Chlorinated solvents and PFAS are both known to produce contaminant

plumes of extended lengths. However, in situ biodegradation is a commonly applied remedy for chlorinated solvents but, to date, has not been shown to be effective for PFAS. In terms of recalcitrance, PCBs are a more apt comparison to PFAS; PCB congeners may biologically transform, but the number of PCB molecules typically remains unchanged.

UCMR3 List, and PFOS and PFOA Chemistry

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

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

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

PFAS Listed in UCMR3	CAS RN	Chemical Formula	MW g/mol	pKa at 25oC (USNLM 2017)	Solubility, g/L at 25oC (Concawe 2016)	Log Kow (Concawe 2016)	Log Koc (USNLM 2017)	USEPA Health Advisory Level for drinking water
Perfluorooctane-sulfonic Acid (PFOS)	1763-23-1	CF ₃ (CF ₂) ₇ SO ₃ H	500	<1.0	0.52 – 0.57	6.43	2.4 – 4.7	Individual or Combined 70 ng/L*
Perfluorooctanoic Acid (PFOA)	335-67-1	CF ₃ (CF ₂) ₆ COOH	414	-0.5 – 4.2	3.4 – 9.5	5.30	1.92 – 2.59	
Perfluorononanoic Acid (PFNA)	375-95-1	CF ₃ (CF ₂) ₇ COOH	464	-0.21	9.5	5.92	5.08	No Standard
Perfluorobutane-sulfonic Acid (PFBS)	375-73-5	CF ₃ (CF ₂) ₃ SO ₃ H	300	-3.31	46.2 – 56.6	3.90	2.26	
Perfluoroheptanoic Acid (PFHpA)	375-85-9	CF ₃ (CF ₂) ₅ CO ₂ H	364	-2.29	4.2	4.67	1.52 – 2.82	
Perfluorohexane-sulfonic Acid (PFHxS)	355-46-4	CF ₃ (CF ₂) ₅ SO ₃ H	400	-6 – -5	2.3	5.17	1.78	

CAS RN = Chemical Abstracts Registry Number

MW = molecular weight

ng/L = nanograms per liter

g/L = grams per liter

g/mol = grams per mole

Kow = octanol/water partition coefficient

Koc = organic carbon partition coefficient

*The USEPA Health Advisory Level for drinking water is 70 ng/L for PFOS and PFOA as individual analytes, but EPA guidance recommends application of the 70 ng/L level to the combined concentrations.

the most information is available for these molecules. Practitioners interested in other PFAS molecules (as described above) can use this description as a general guide, but may need to look into the most current research for particular molecules.

PFOS has a sulfonate end (“head”) comprised of three oxygens, a sulfur, and a hydrogen. PFOA exhibits a similar “head” comprised of two oxygens and a

hydrogen with no sulfur. The hydrogen dissociates in aqueous systems, making PFOS and PFOA acids. When the hydrogen dissociates in water, the “head” of these molecules take on a negative charge, which contributes to sorption by electrostatic attraction.

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

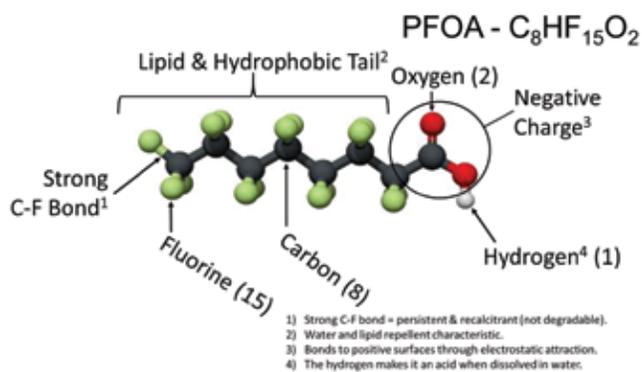
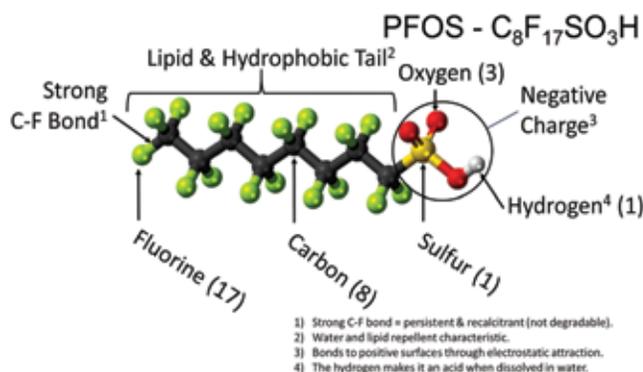


Table 4.3. Comparison of PFOA and PFOS properties to other organic compounds.

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

Key takeaways about PFAS chemistry include:

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

SOURCES

AFFF Composition, Release, Emplacement, and Migration

The presence of per- and polyfluoroalkyl substances (PFAS) in drinking water has emerged as a widespread concern. A recent survey estimated the EPA HA values are exceeded in drinking water supplies for 6 million people (Hu et al. 2016). Much of the PFAS contamination in drinking water originates from groundwater that has been affected by environmental releases. According to Hu et al. (2016), there are 290 military fire training areas and 533 civilian airports certified for the use of aqueous film-forming foam (AFFF) throughout the United States; the presence of military fire training areas was shown to be positively correlated to aqueous concentrations of PFAS in the environment, but civilian airports were not positively correlated.

Formulations of PFAS used in AFFF have changed substantially, with variable manufacturing methods employed by different suppliers and at different times. The dominant PFAS-producing process prior to 2001 was electrochemical fluorination, which resulted in PFOS as a prevalent component of firefighting foams (Concawe 2016). This process was largely replaced by fluorotelomerization that produces fluo-

rotelomers as molecular components of firefighting foams (Concawe 2016). Fluorotelomer chains contain 6, 8, or 10 carbons (e.g., 6:2 FtS, 8:2 FtS, and 10:2 FtS). According to the Western Australia Department of Environment Regulation (2017), "Legacy AFFF (such as 3M Light Water™ 3 per cent and 6 per cent) contains PFOS and PFOA; newer AFFF formulations (such as Ansulite™) contain fluorotelomers such as 6:2 FtS to 10:2 FtS. Longer-chain fluorotelomers (C8 and above) may degrade in the environment to produce PFOA homologues including perfluorohexanoic acid (PFHA)." The shorter-chain C6 fluorotelomers (6:2 FtS) cannot degrade to PFOS or PFOA (Concawe 2016); however, shorter-chain PFAS including end products still require consideration.

Discharge of AFFF, containing PFAS, differs from typical mechanisms of contaminant release to the environment, such as inadvertent drips, leaks, and spills. Mechanisms of AFFF release to the environment include: (1) low volume spills of foam concentrate during storage or transfer; (2) one-off, high-volume, broadcast application of foam solution for firefighting; (3) periodic, moderate to high volume, broadcast application of foam solution for apparatus testing or training. AFFF is applied by mixing foam concentrate and water to make foam solution that is aerated when sprayed from a nozzle to produce finished foam. Thousands of gallons of foam solution may be applied for a fire or training event (Guzzi 2011; Vyas and Patel 2013). Foam solution drains from the finished foam as an aqueous film with low surface tension that floats on fuel (http://www.davidsfire.com/foam_basics.htm). These characteristics facilitate vertical infiltration of foam solution through soil to groundwater and potential interaction with subsurface LNAPL, especially beneath fire training areas where fuel LNAPL may have accumulated. Surfactant properties of PFAS, such as PFOS and PFOA, can reduce interfacial tension, potentially affecting the mobility and solubility of petroleum hydrocarbon LNAPL. In addition to subsurface transport, AFFF may be prone to aerial dispersion and redeposition prior to infiltration (Guzzi 2011).

Considering PFOS as an indicator constituent, higher PFOS concentrations (e.g., > 1,000 µg/L) may occur beneath fire training and AFFF bulk storage areas. Lesser PFOS concentrations (e.g., <50 µg/L) in groundwater may occur beneath satellite AFFF storage areas, historic fire locations, apparatus testing

locations, and where infiltration of distal runoff occurs (Hale 2016).

In some instances, concentrations of PFAS in shallow soil correlate to underlying shallow groundwater concentrations by location. In these instances, shallow soil concentrations represent a residual fingerprint (perimeter and internal spatial concentration pattern) of past infiltration to groundwater that has been impacted by the direct infiltration of foam solution or foam concentrate (Hale 2016). As such, shallow soil analytical results may be used to guide intrusive groundwater investigation activities. In this instance, leaching of residual PFAS from the soil column to groundwater would not increase groundwater concentrations (i.e., dilute leachate will not increase the concentration of groundwater impacted by past infiltration of foam concentrate or foam solution). Under other circumstances, for instance if PFAS-impacted soil was excavated and placed above unimpacted groundwater, or if groundwater remediation occurred without soil remediation, leaching of residual PFAS from soil could exacerbate groundwater conditions.

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

Biosolids

PFAS have been widely detected in municipal biosolids (Venkatesan 2013). In one nationwide survey of biosolids, PFOS and PFOA were the most prevalent of 13 PFAS and were detected at about 403 and 34 ng/g respectively. Although Venkatesan and Halden (2013) demonstrated a significant presence of PFAS in biosolids, their work was done on biosolids from a 2001 inventory. PFOS and PFOA have been largely phased out since 2001, indicating biosolids might currently have lower PFAS concentrations, especially of PFOS

and PFOA. Approximately 50% of biosolids produced in the U.S. are applied to agricultural land as fertilizer (Sepulvado et al. 2011), providing a potential pathway for PFAS contamination of soil and groundwater.

Sepulvado et al. (2011) report that PFAS can transport to groundwater via leaching, and leaching rates decrease with increasing chain length. This finding is consistent with reported K_d values which increase with chain length for C5-C10 PFAS. This suggests although PFOS and PFOA are the most prevalent PFAS in biosolids, shorter-chain PFAS might be more mobile in biosolid-affected groundwater. Further work regarding the transport of PFAS from municipal biosolids to groundwater is needed to better understand the possible transport of PFAS from land application sites throughout the U.S.

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

Regardless of the concentration of PFAS in the applied biosolids, transport principles are consistent. Perfluorocarboxylates (PFCAs) in soil have been found to be correlated with the total mass of applied biosolids. Long- and short-chain PFCAs exhibit some differences in that longer-chain PFCAs are more strongly correlated with total biosolid mass applied while shorter-chain PFCAs are more subject to decreasing as the time since application increases (Washington et al. 2010). This demonstrates the effect of chain length and leaching potential on the transport of PFAS in biosolids to groundwater and soils.

Landfill Leachate

The reported Σ PFAS concentrations measured in landfill leachates range from below the reporting limit to 36 $\mu\text{g/L}$ (Beskin 2012; Ahrens 2011). Although results may reflect the selected analytes (there are many PFAS while only a small portion are individually quantifiable), referenced studies reported similar quantities of PFAS analytes. Typically landfill leachate is either recirculated through the landfill or treated. If

treated, typically a municipal wastewater treatment plant (WWTP) receives the leachate and may be ill equipped to remove or treat PFAS (see Wastewater Treatment Systems below). The estimated 8.5–25 kg/yr of Σ PFAS (Beskin 2012) to leave a landfill via leachate has the potential to have significant impacts to WWTPs and surface water bodies that receive WWTP effluent. This may also be a significant source of PFAS to biosolids. If leachate recirculation is employed, there is a risk of contaminating the surface water and an increased likelihood of leachate leaking into the aquifer (due to the increase in leachate head).

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

Wastewater Treatment Systems

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

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

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

Onsite wastewater treatment systems, specifically septic systems, can be a source of PFAS to groundwa-

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

The presence of PFAS in WWTPs can mostly be attributed to consumer products, industrial impacts, and AFFF. Changes in the composition of these as a result of the shift in manufacturing toward shorter-chain PFAS has been noted to affect PFAS concentrations at WWTPs (Houtz et al. 2016). As the composition of PFAS in consumer products and industrial uses shift, and as impacts from historical releases decrease, the composition of WWTP effluent will likely continue to shift in the future.

Air Deposition

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

In addition to air deposition near industrial sources, PFAS have been widely detected in precipitation in the form of rain and snow (Codling et al. 2014). Studies have shown urban regions which are strongly affected by wintertime snowfall are impacted by atmospheric deposition of PFAS.

MOBILITY

PFAS are far less volatile and may be more prone to sorption than other common contaminants (e.g., benzene, PCE, MtBE), based on comparison of organic carbon partition coefficients (K_{oc}) and vapor pressure. As an example, values of K_{oc} for PFOS range from 229 to 6310 (Franz et al. 2013). The sorption of PFOS and its K_{oc} vary depending on site-specific factors (Higgins and Luthy 2006; Chen et al. 2009; Tang et al. 2010; Chen et al. 2012; Wang and Shih 2012). Generally, shorter PFAS are more mobile in groundwater and will leach from soil to groundwater at a faster rate. This results in shorter-chain PFAS at the leading edge of a groundwater plume. Other factors affecting PFAS sorption in the subsurface include:

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

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

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

MASS BALANCE

The chemical bond between carbon and fluorine is short, strong, and difficult to break thermally, chemically, or biologically. The enzymes produced by environmental bacteria can attack the longer, weaker bonds between carbon and other elements in poly-

Figure 4.3.

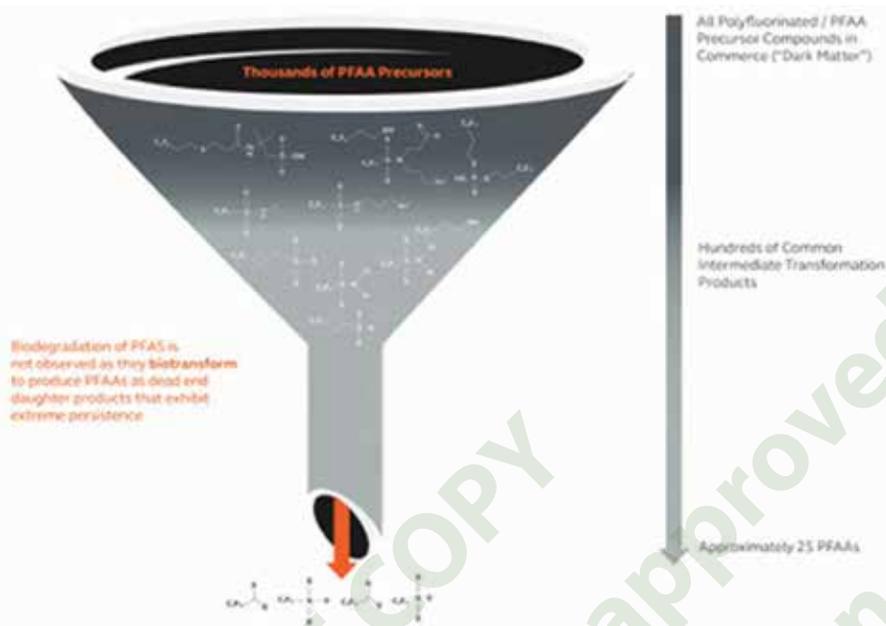


Figure 3. Aerobic biotransformation funnel: There are potentially thousands of PFAA precursors, which can biotransform under aerobic conditions to make hundreds of common polyfluorinated intermediate products. The terminal aerobic biotransformation products of all of these PFAA precursors are the perfluorinated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

Suthersan et al. 2016 (NGWA copyrighted)

fluorinated precursors, leaving stable perfluorinated chemicals in the environment, particularly the longer-chained PFOA, PFOS, and PFNS, but also PFBS, PFHxS, and PFHpA. Suthersan et al. (2016) call the stable perfluorinated chemicals formed from PFAS precursor degradation “dead-end daughter products.” The transformation of a wider range of PFAS species into the smaller number of dead-end daughter products has been termed “biological funneling” (Figure 4.3).

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

precursors have moieties that can biotransform, they are typically less water-soluble and less mobile than their dead-end perfluorinated daughter products (Bhatarai and Gramatica 2011).

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

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

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

These factors need to be considered when evaluating PFAS sites, as they can lead to underestimates of contaminant nature and extent and consequently misspent remediation dollars. Difficult-to-detect polyfluorinated compounds can be carried by advection with groundwater flow (Houtz et al. 2013). As these compounds enter the biodegradation “funnel” (Figure 4.3, Suthersan et al. 2016), they can degrade to extremely persistent perfluorinated end products, leading to increased downgradient abundance of persistent compounds. Section 5, Field Sampling and Analyses, lists specialty analytical methods for soil and groundwater that can be used to quantify the bulk amount of precursors in the funnel. These analyses, along with laboratory methods for quantifying individual compounds, can be used to estimate the mass balance at a site.

In one sense, the generation of persistent, bioaccumulative PFAS downgradient from the source is akin to the generation of the more toxic vinyl chloride from PCE and TCE. However, a key distinction is that with chlorinated solvents, the parent compounds are relatively easily measured and the degradation pathways are well understood, leading to a comprehensible mass balance. The enormous variety of PFAS parent compounds and precursors—that critically can be difficult to detect and quantify—and degradation pathways complicates mass balance estimation significantly. Additionally, unlike PCE and TCE, atmospheric deposition of PFAS can be an offsite input to the mass balance that is unrelated to a site-specific discharge or source. PFAS surfactants used to prepare fluorinated polymers can travel great distances from their source before they enter groundwater and surface waters (Stemmler and Lammel 2010; Taniyasu et al. 2013; Wang et al. 2014).

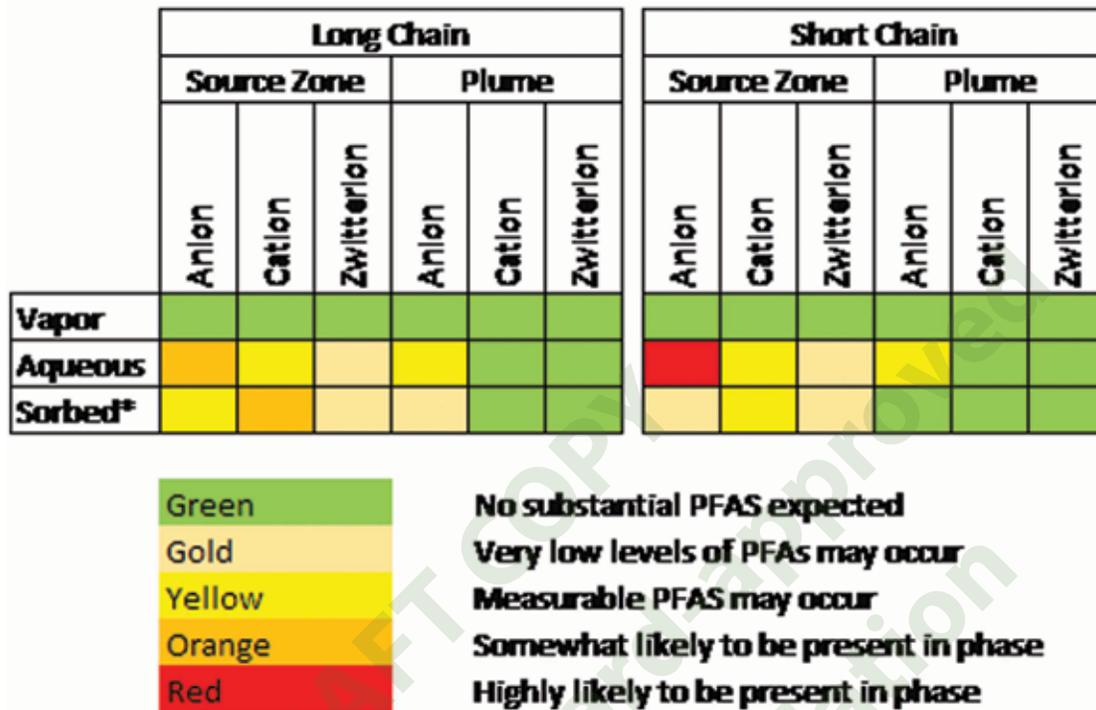
DISTRIBUTION IN THE SUBSURFACE

Previous sections have illustrated that PFAS in the subsurface can originate from several types of sources, and the nature of the distribution follows from the method of release and subsequent transport. As noted previously, post-release surface transport of AFFF can result in a widely dispersed initial footprint. Although PFAS extent and distribution in groundwater associated with AFFF use may predominantly be associated with runoff and infiltration of foam solution around the time of the release, subsequent transport in groundwater can also be significant, and has resulted in plumes extending downgradient for extended distances (e.g., greater than one mile) at many documented sites.

When considering the distribution of PFAS in the subsurface, the “source” can encompass the footprint of the original release, including post-release surface transport; “plume” can refer to the area downgradient of the release that has only been impacted due to groundwater transport. Unlike source zones impacted with non-aqueous phase liquids (NAPLs), such as chlorinated solvents or hydrocarbons, there is unlikely to be an easily defined boundary between source and plume for PFAS. Soil sampling, however, can be helpful in resolving the source footprint and differentiating it from the advective plume. In general, and depending on the age of the site, unless groundwater flow is particularly rapid, the source zone is more likely to be affected by a relatively higher concentration of precursors while the plume is likely to be enriched in the dead-end products, which include PFOA, PFOS, and the other UCMR3 PFAS.

As a means to present typical distribution of PFAS in the subsurface, an adapted 14-compartment model (ITRC 2011) was utilized. The 14-compartment model provides a means to identify contaminant mass distribution in various phases on a relative basis. The modified compartment model shows distribution between aqueous, sorbed, and vapor phases. The “NAPL” phase was removed from the standard 14-compartment model, as PFAS are unlikely to be present as a non-aqueous phase liquid, and partitioning of PFAS into a NAPL phase is a complicated process that is beyond the scope of this analysis. For this analysis, the model compartments were further subdivided into the various ionic species of PFAS molecules: anions, cations, and zwitterions (i.e., molecules that exhibit both positively and negatively

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



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

charged groups). All six of the UCMR3 PFAS compounds, and dead-end products discussed previously, are anions (specifically, these compounds are acids that dissociate into anionic form at near-neutral pH values). The compartmental model is shown in Figure 4.4 for both short-chain PFAS (C-F chains of six or less carbon atoms) and long-chain PFAS (C-F chains of seven or more carbon atoms). Color-coded ratings are assigned to each compartment with the intent of illustrating PFAS distribution at a typical site. The color-coding presented herein is based on expected behavior under hypothetical circumstances; actual presence and distribution of the PFAS compounds is highly site-specific.

Substantial knowledge gaps exist in terms of our general understanding of the subsurface distribution of PFAS. Three primary factors behind the knowledge gaps include: (1) the complex mixture of molecules comprising PFAS; (2) the lack of simple analytical methods to identify specific molecules; and (3) the combined hydrophobic/hydrophilic nature of the PFAS molecules that strongly affects sorption and mobility. Specific knowledge gaps that have been

identified by the NGWA PFAS team, regarding PFAS distribution, include the following.

- Limited data on transport-related properties PFAS aside from PFOA and PFOS, including precursors and other dead-end products.
- Limited understanding of sorption mechanisms; e.g., conditions under which a linear organic-carbon sorption model is applicable, and recommendations for alternative sorption models.
- The role of precursors in sustaining a downgradient contaminant plume.
- The role of precursors in maintaining a contaminant plume is also not well understood. Precursor identification and quantification has largely been due to academic studies to date.
- The potential role of non-aqueous phase liquids is also not well understood. The surfactant properties of the molecules complicate the interaction between PFAS and hydrophobic/hydrophilic substances.

EXPOSURE POINTS

Non-occupational human exposure to per- and polyfluorinated compounds typically occurs through food, drinking water, and air. Food accounts for 90% of non-occupational exposure (Fromme 2009). Groundwater used for drinking water supplies is also considered a dominant exposure pathway for some PFAS to humans because water treatment technologies do not efficiently remove these persistent compounds (Weiss et al. 2015). Even if not used for drinking water, groundwater contaminated with PFAS can be discharged to surface water. Surface water has additional exposure points including drinking water, recreational use, and fish consumption.

Due to the bio-accumulative properties of PFAS, fish from impacted surface water bodies are domi-

nant exposure to PFOS and other long-chain PFAS (Haug 2010). Other sources of PFAS to food include livestock drinking contaminated water, crops fertilized with biosolids containing PFAS, and crops irrigated with contaminated water.

The prevalence of PFAS in drinking water was surveyed as part of the USEPA Unregulated Contaminant Monitoring Rule. This study analyzed for six PFAS (PFOA, PFOS, PFHxS, PFNA, PFBS, and PFHpA). It was found 66 public water supplies contain PFOA and PFOS concentrations greater than the current health advisory of a combined PFOS and PFOA concentration of 70 ppt (Hu 2016). Despite the low concentrations of PFAS (relative to other studied emerging contaminants) in public water supplies, the USEPA health advisory concentrations indicate that water with very small amounts of PFAS can be a health concern.

REFERENCES

- Ahrens, L., M. Shoeib, T. Harner, S.C. Lee, R. Guo, and E.J. Reiner. 2011. Wastewater treatment plant and landfills as sources of polyfluoroalkyl compounds to the atmosphere. *Environmental Science and Technology* 45, no. 19: 8098-8105.
- Beskin, J.P., B. Li, M.G. Ikononou, J.R. Grace, and L.Y. Li. 2012. Per- and polyfluoroalkyl substances in landfill leachate: Patterns, time trends, and sources. *Environmental Science and Technology* 46, no. 21: 11532-11540.
- Bhatarai, B., and P. Gramatica. 2011. Prediction of aqueous solubility, vapor pressure and critical micelle concentration for aquatic partitioning of perfluorinated chemicals. *Environmental Science & Technology* 45, no. 19: 8120-8128.
- Buck, R.C., J. Franklin, U. Berger, J.M. Conder, I.T. Cousins, P. De Voogt, A.A. Jensen, K. Kannan, S.A. Mabury, and S.P.J. van Leeuwen. 2011. Perfluoroalkyl and polyfluoroalkyl substances in the environment: Terminology, classification, and origins. *Integrated Environmental Assessment and Management* 7, no. 4: 513-541.
- Chen, H., S. Chen, X. Quan, Y. Zhao, and H. Zhao. 2009. Sorption of perfluorooctane sulfonate (PFOS) on oil and oil-derived black carbon: Influence of solution pH and [Ca²⁺]. *Chemosphere* 77, no. 10: 1406-1411.
- Chen, H., C. Zhang, Y. Yu, and J. Han. 2012. Sorption of perfluorooctane sulfonate (PFOS) on marine sediments. *Marine Pollution Bulletin* 64, no. 5: 902-906.
- Codling, G., C. Halsall, L. Ahrens, S. Del Vento, K. Wiberg, M. Bergknut, H. Laudon, and R. Ebinghaus. 2014. The fate of per- and polyfluoroalkyl substances within a melting snowpack of a boreal forest. *Environmental Pollution* 191: 190-198.
- Concawe. 2016. *Environmental fate and effects of poly- and perfluoroalkyl substances (PFAS)*. Report No. 8/16. Auderghem, Belgium: Concawe.
- Engineering ToolBox. 2017. "Vapor Pressure Common Liquids." http://www.engineeringtoolbox.com/vapor-pressure-d_312.html (retrieved January 7, 2017)
- Ferrey, M., and J.T. Wilson. 2009. Extent of Sorption and Biodegradability of Perfluorooctanoic Acid (PFOA) and Perfluorooctanesulfonic acid (PFOS) in Aquifer Sediment (Maryland). *10th International In Situ and On-site Bioremediation Symposium, Baltimore, MD*.
- Franz, T., A. Dawe, L. McDonald, C. Levicki, and J. Miller. 2013. Modelling of PFOS fate and transport. In *Real Property Institute of Canada Federal Contaminated Sites National Workshop*. June 19-20, Halifax, Nova Scotia.

- Fromme, H., S.A. Tittlemier, W. Völkel, M. Wilhelm, and D. Twardella. 2009. Perfluorinated compounds – Exposure assessment for the general population in western countries. *International Journal of Hygiene and Environmental Health* 212, no. 3: 239-270.
- Guelfo, J.L., and C.P. Higgins. 2013. Subsurface transport potential of perfluoroalkyl acids at aqueous film-forming foam (AFFF)-impacted sites. *Environmental Science & Technology* 47, no. 9: 4164-4171.
- Guzzi, Armand. 2011. "Basic Foam Operations – Part 5." <http://www.firehouse.com/article/10462559/basic-foam-operations-part-5> (retrieved January 7, 2017)
- Hale, J.R. 2016. Distribution of PFOS in Groundwater from AFFF Storage, Handling, and Use. Submitted to NGWA *Groundwater Solutions: Innovating to Address Emerging Issues in Groundwater Resources Symposium*.
- Haug, L.S., C. Thomsen, A.L. Brantsæter, and H.E. Kvalem. 2010. Diet and particularly seafood are major sources of perfluorinated compounds in humans. *Environment International* 36, no 7: 772-778.
- Higgins, C.P., and R.G. Luthy. 2006. Sorption of perfluorinated surfactants on sediments. *Environmental Science & Technology* 40, no. 23: 7251-7256.
- Houtz, E.F., C.P. Higgins, J.A. Field, and D.L. Sedlak. 2013. Persistence of perfluoroalkyl acid precursors in AFFF-impacted groundwater and soil. *Environmental Science & Technology* 47, no. 15: 8187-8195.
- Houtz, E.F., R. Sutton, J.-S. Park, and M. Sedlak. 2016. Poly- and perfluoroalkyl substances in wastewater: Significance of unknown precursors, manufacturing shifts, and likely AFFF impacts. *Water Research* 95: 142-149.
- Hu, X.C., D.Q. Andrews, A.B. Lindstrom, T.A. Bruton, L.A. Schaider, P. Grandjean, R. Lohmann, C.C. Carignan, A. Blum, S.A. Balan, C.P. Higgins, and E.M. Sunderland. 2016. Detection of poly- and perfluoroalkyl substances (PFAS) in US drinking water linked to industrial sites, military fire training areas, and wastewater treatment plants. *Environmental Science & Technology Letters* 3, no. 10: 344-350.
- ITRC (Interstate Technology & Regulatory Council). 2011. *Integrated DNAPL Site Strategy*. ITRC Integrated DNAPL Site Strategy Team. Washington DC: Interstate Technology & Regulatory Council.
- Lindstrom, A.B., M.J. Strynar, A.D. Delinsky, S.F. Nakayama, L. McMillan, E.L. Libelo, M. Neill, and L. Thomas. 2011a. Application of WWTP biosolids and resulting perfluorinated compound contamination of surface and well water in Decatur, Alabama, USA. *Environmental Science & Technology* 45, no. 19: 8015-8021.
- Lindstrom, A.B., M.J. Strynar, and E.L. Libelo. 2011b. Polyfluorinated compounds: Past, present, and future. *Environmental Science & Technology* 45, no. 19: 7954-7961.
- McKenzie, E.R., R.L. Siegrist, J.E. McCray, and C.P. Higgins. 2016. The influence of a non-aqueous phase liquid (NAPL) and chemical oxidant application on perfluoroalkyl acid (PFAA) fate and transport. *Water Research* 92: 199-207.
- Richardson, S.D., and S.Y. Kimura. 2016. Water analysis: Emerging contaminants and current issues. *Analytical Chemistry* 88, no. 1: 546-582.
- Schaider, L.A., J.M. Ackerman, and R.A. Rudel. 2016. Septic systems as sources of organic wastewater compounds in domestic drinking water wells in a shallow sand and gravel aquifer. *Science of the Total Environment* 547: 470-481.
- Sepulvado, J.G., A.C. Blaine, L.S. Hundal, and C.P. Higgins. 2011. Occurrence and fate of perfluorochemicals in soil following the land application of municipal biosolids. *Environmental Science & Technology* 45, no. 19: 8106-8112.
- Sinclair, E., and K. Kannan. 2006. Mass loading and fate of perfluoroalkyl surfactants in wastewater treatment plants. *Environmental Science & Technology* 40, no. 5: 1408-1414.
- Stemmler, I., and G. Lammel. 2010. Pathways of PFOA to the Arctic: Variabilities and contributions of oceanic currents and atmospheric transport and chemistry sources. *Atmospheric Chemistry and Physics* 10, no. 20: 9965-9980.
- Suthersan, S.S., J. Horst, I. Ross, E. Kalve, J. Quinnan, E. Houtz, and J. Burdick. 2016. Responding to emerging contaminant impacts: Situational management. *Groundwater Monitoring & Remediation* 36, no. 3: 22-32.
- Tang, C.Y., Q. Shiang Fu, D. Gao, C.S. Criddle, and J.O. Leckie. 2010. Effect of solution chemistry on the adsorption of perfluorooctane sulfonate onto mineral surfaces. *Water Research* 44, no. 8: 2654-2662.

- Taniyasu, S., N. Yamashita, H.-B. Moon, K.Y. Kwok, P.K.S. Lam, Y. Horii, G. Petrick, and K. Kannan. 2013. Does wet precipitation represent local and regional atmospheric transportation by perfluorinated alkyl substances? *Environment International* 55: 25-32.
- TAMU (Texas A&M University). 2017. "Selected Bond Energies and Bond Lengths." <http://www.chem.tamu.edu/rgroup/connell/linkfiles/bonds.pdf> (retrieved January 18, 2017)
- USEPA (U.S. Environmental Protection Agency). 2014. *Emerging Contaminants – Perfluorooctane Sulfonate (PFOS) and Perfluorooctanoic Acid (PFOA)*. EPA 505-F-14-001. Washington, DC: United States Environmental Protection Agency Office of Solid Waste and Emergency Response.
- USEPA (U.S. Environmental Protection Agency). 2016. Fact Sheet: PFOA & PFOS Drinking Water Health Advisories. EPA 800-F-16-003. Washington, DC: United States Environmental Protection Agency.
- USNLM (U.S. National Library of Medicine). 2017. "Hazardous Substances Data Bank (HSDB)." <https://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB> (retrieved January 17, 2017)
- Venkatesan, A.K., and R.U. Halden. 2013. National inventory of perfluoroalkyl substances in archived U.S. biosolids from the 2001 EPA National Sewage Sludge Survey. *Journal of Hazardous Materials* 252–253: 413-418.
- Vyas, K., and P. Patel. 2013. Foam concentrates application rate and their flow rates: An overview on floating roof tank fire extinguishment. *International Journal of Research in Engineering and Technology* 2, no. 12: 167-172.
- Wang, F., and K. Shih. 2012. Influence of solution chemistry on adsorption of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) on boehmite. *World Academy of Science, Engineering & Technology* 69: 1287-1291.
- Wang, Z., I.T. Cousins, M. Scheringer, R.C. Buck, and K. Hungerbühler. 2014. Global emission inventories for C4–C14 perfluoroalkyl carboxylic acid (PFCA) homologues from 1951 to 2030, Part I: Production and emissions from quantifiable sources. *Environment International* 70: 62-75.
- Washington, J.W., H. Yoo, J.J. Ellington, T.M. Jenkins, and E.L. Libelo. 2010. Concentrations, distribution, and persistence of perfluoroalkylates in sludge-applied soils near Decatur, Alabama, USA. *Environmental Science & Technology* 44, no. 22: 8390-8396.
- Weiss, J., J. de Boer, U. Berger, D. Muir, T. Ruan, A. Torre, F. Smedes, B. Vrana, F. Clavien, and H. Fiedler. 2015. PFAS analysis in water for the Global Monitoring Plan of the Stockholm Convention: Set-up and guidelines for monitoring. Chemicals Branch United Nations Environment Programme (UNEP) Division of Technology, Industry and Economics.
- Western Australia Department of Environment Regulation. 2017. Interim Guideline on the Assessment and Management of Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS). Contaminated Sites Guidelines. Version 2.1.