

# **Per and polyfluoroalkyl substances (PFAS) in groundwater and soil: A review**

**By**

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## Acronyms

|        |  |
|--------|--|
| PFAS   | Per-and polyfluoroalkyl substances         |
| CEC    | Contaminates of emerging concern           |
| PFOA   | Perfluorooctanoic acid                     |
| PFOS   | Perfluorooctane sulfonate                  |
| EPA    | Environmental Protection Agency            |
| PFAA   | Perfluoroalkyl acids                       |
| PFCA   | Perfluoroalkyl carboxylic acids            |
| PFSA   | Perfluoroalkyl sulfonic acids              |
| FTOH   | Fluorotelomer alcohols                     |
| PTFE   | Polytetrafluoroethylene                    |
| ECF    | Electrochemical fluorination               |
| POP    | Persistent organic pollutants              |
| SDWA   | Safe Drinking Water Act                    |
| UCMR 3 | Unregulated Contaminant Monitoring Rule    |
| PWS    | Public water system                        |
| PFHpA  | Perfluoroheptanoate                        |
| PFNA   | Perfluorononanoate                         |
| PFBS   | Perfluorobutane sulfonate                  |
| PFHxS  | Perfluorohexane sulfonate                  |
| WWTP   | Wastewater treatment plant                 |
| FTP    | Fluorotelomer polymers                     |
| FTCA   | Fluorotelomer carboxylic acids             |
| FTUCA  | Unsaturated fluorotelomer carboxylic acids |
| PFHxA  | Perfluorohexanoic acid                     |
| PFDA   | Perfluorodecanoic acid                     |
| FSBF   | Fluorosurfactant-based foams               |
| NAPL   | Non-aqueous phase liquids                  |
| FOSA   | Perfluorooctane sulfonamide                |
| PFUnDA | Perfluoroundecanoate                       |
| PFDoDA | Perfluorododecanoate                       |
| GAC    | Granular activated carbon                  |
| NF     | Nanofiltration                             |
| RO     | Reverse osmosis                            |
| IX     | Ion-exchange resin                         |

## 1. Introduction

Per- and polyfluoroalkyl substances (PFAS) is the general term used for a group of more than 4000 manmade chemicals. These chemicals have unique chemical and physical properties that convey oil and water repellency, resist temperature extremes, and reduce friction.<sup>1,2</sup> Because of these properties they have been widely used in consumer products and industry processes. For example PFAS are found in nonstick coatings (Teflon™), fast food wrappers, stain and water repellants (Scotchgard™, Gore-Tex™), polishes, textile coatings, paper products, cosmetics, pesticides, herbicides, and fire fighting foams.<sup>1,2,7</sup> They are also used in the photographic, automotive, semiconductor, aerospace, construction, electronics, and aviation industrial manufacturing.<sup>3,5</sup> PFAS compounds can have multiple structures and functional groups that vary in molecular weight and are ubiquitous in the environment, they are found all around the world in remote and urban environments. They have been detected in surface water, groundwater, rainwater, seawater, landfill leachates, soil, sediment, wastewater treatment plant influent/effluent and biosolids, wildlife, the atmosphere, and in human blood.<sup>1,2,3</sup> There is evidence of possible health effects from PFAS exposure and they are considered to be contaminants of emerging concern (CEC).<sup>1,2</sup> Certain PFAS have been linked to adverse effects including hepatic toxicity, reproduction and developmental toxicity, suppression of immune system and some cancers (Thyroid and liver).<sup>1,2</sup> Because of their toxicological characteristics PFAS are also an emerging

drinking water contaminate with widespread occurrence in groundwater and surface water resources.

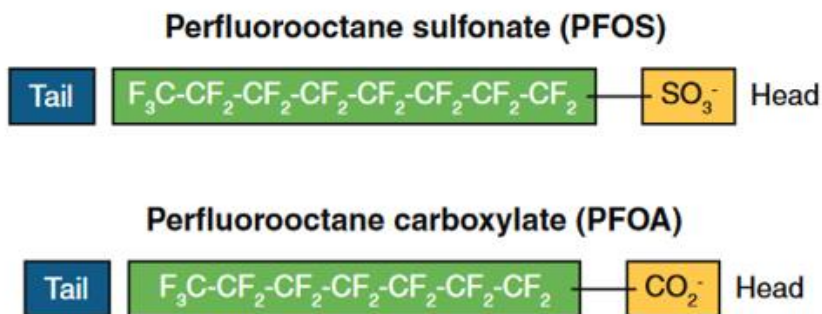


Figure 1. The tail and head structure of PFOS and PFOA molecules.

Figure from ITRC website<sup>5</sup>

The diverse family of fluorinated synthetic chemicals called PFAS have a hydrophilic functional group (head) and a hydrophobic and lipophilic fluorinated chain (tail) as shown in figure 1.<sup>5,22</sup> The PFAS molecular structure which consist of an aliphatic chain or multiple chains with either all (perfluoroalkyl) or part (polyfluoroalkyl) of the hydrogen's replaced with fluorine so they have one or more fluoroalkyl moiety ( $C_nF_{2n+1}$ ) with a terminal functional head.<sup>7,21</sup> The functional group can be a carboxylates, sulfonates, sulphonamides, phosphonates, or alcohols.<sup>29</sup> This high-energy carbon fluorine bond called the strongest bond in nature has a strong stability rendering these compounds stable in the environment and resistant to photodecomposition, hydrolysis, microbiological degradation and vertebrate metabolism.<sup>24</sup> Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) are the most commonly found and studied of the many PFAS.<sup>14</sup> At environmental pH PFOA and PFOS exist in their anionic form and have high aqueous solubility and

lower sorption potential.<sup>1,2</sup> However, ionized PFAS are more likely to sorb to particles because of electrostatic interactions especially the sulfonate functional group.<sup>8,9</sup> The Chemical structures of PFOS and PFOA are seen in figure 1. The Environmental Protection Agency (EPA) estimates the half-life of PFOA and PFOS in water at 92 and 41 years respectively.<sup>22,35</sup> Environmental studies of PFAS concentrate on the perfluoroalkyl acids (PFAA) that include perfluoroalkyl carboxylic acids (PFCAs) such as PFOA and perfluoroalkyl sulfonic acids (PFSAs) such as PFOS.<sup>18</sup> Short chain PFCAs have seven or fewer carbons, six or less of which are perfluorinated and long chain PFCAs have eight or more carbons where seven or more are perfluorinated.<sup>29</sup> Short chain PFSAs have five or fewer carbons all being perfluorinated and the long chain PFSAs having six or more carbons all perfluorinated.<sup>29</sup> Shorter chained perfluoroalkyl and polyfluoroalkyl substances sometimes called precursors such as fluorotelomer alcohols (FTOH) are gaining attention because they are much more mobile in the environment.<sup>3,5</sup> FTOH can be volatile and has been found in stack emissions, they have been identified as the cause of wide spread environmental distribution by atmospheric transport where they have been found in the arctic and antarctic<sup>1,5,8</sup> PFOA and PFOS have a long history and are no longer produced they have been replaced by shorter chain PFAS that are less bioaccumulative but potentially just as toxic.<sup>28,29</sup> Figure 2 illustrates the breakdown of the basic PFAS family tree, which is comprised of polymer and non-polymer groups. The polymer group will not be discussed because the non-polymer group is most commonly detected in the environment. The non-polymer group consists of two groups the perfluorinated and polyfluorinated substances.<sup>5</sup>

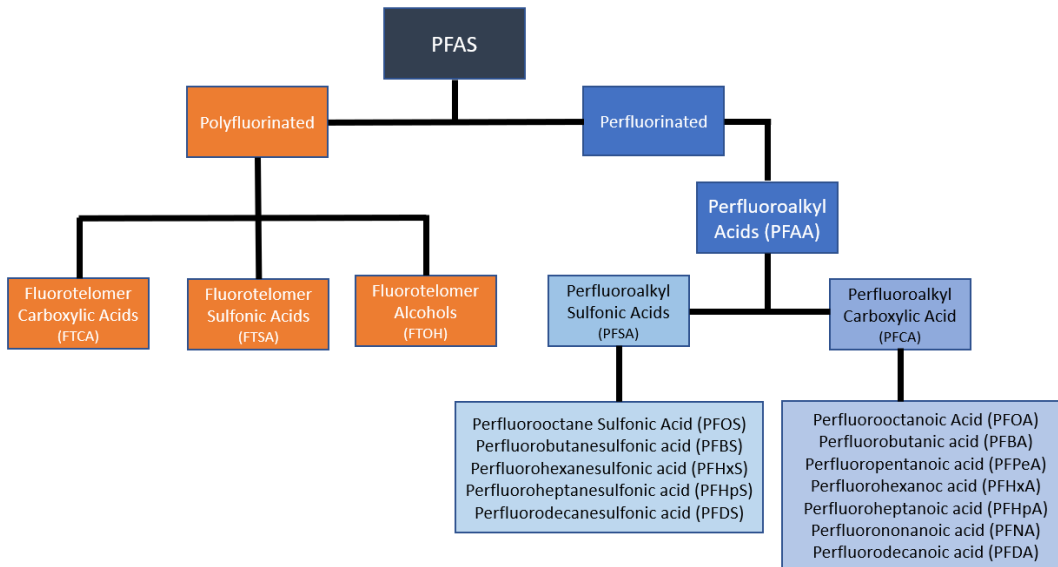


Figure 2: Basic family tree of PFAS

## 2. History

PFAS was accidentally discovered in 1938 by DuPont in a failed refrigerant experiment.<sup>43</sup> By 1945 DuPont used this failed refrigerant known as polytetrafluoroethylene (PTFE) to create a new line of nonstick cookware named Teflon. Not until 1952 with the help of the Minnesota Mining and Manufacturing Company (3M) and the chemical called C8, now known as PFOA, Teflon was commercialized.<sup>5</sup> In 1963 the US Navy and 3M developed Aqueous Film Forming Foam (AFFF) for extinguishing hydrocarbon fires.<sup>5</sup> AFFF consist of very high concentrations of PFOS, which is produced using electrochemical fluorination (ECF), a process licensed by 3M in the 1940's and used until 2001.<sup>5</sup> Production of these two PFAS declined in the 2000's due to growing concerns about ecological and human health effects.<sup>22</sup>

In the early 2000's several countries established regulations on PFOA and PFOS and in 2002, the only U.S. manufacturer of PFOS agreed to phase out its production.<sup>1,14</sup> PFOA was voluntarily phased out by all major U.S. manufacturers by 2015 due to concerns about health effects.<sup>2</sup> In 2009, PFOS was added to the Stockholm Convention's list of persistent organic pollutants (POP) with the goal to reduce or eliminate the production, use, and release.<sup>6,12</sup> Due to their wide use in many house hold products PFAS is believed to be in blood serum of 99% of the general U.S. population.<sup>1</sup> In 2012 the EPA under the Safe Drinking Water Act (SDWA) included six PFAS in its third Unregulated Contaminant Monitoring Rule (UCMR 3), which required almost 5000 public water systems (PWS) to monitor for PFAS.<sup>2</sup>

UCMR 3 screened the following six PFAS nationwide from 2013 to 2015; perfluoroheptanoate (PFHpA), perfluorononanoate (PFNA), perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), PFOA and PFOS. UCMR 3 monitoring provided a dataset of 36,977 samples from approximately 4900 public water systems of which PFAS were detected in 4%.<sup>5,17</sup> In 2016, EPA set a lifetime drinking water health advisory (HA) for PFOS and PFOA of 0.07 micrograms per liter (ug/L).<sup>1,2</sup> UCMR 3 monitoring results showed 64 PWS exceeded the HA, three of which are in Florida.<sup>17</sup> Approximately 50% of detectable PFAS samples contained mixtures of 2 or more PFAS.<sup>17</sup> Co-occurrence of PFAS could reflex source of contamination. The highest PFAS concentrations have been recorded near PFAS manufacturing facilities, landfill sites, firefighting training areas, and wastewater treatment plants (WWTP).<sup>14</sup> UCMR 3 revealed that these sources have contaminated



potable water supplies with PFAS.<sup>3</sup> Figure 3 developed from the UCMR 3 results shows the aquifers with PFOA and PFOS detections. Delineating these different sources of PFAS in groundwater is important for effective contaminate management and limiting environmental and human health risks.<sup>22</sup>

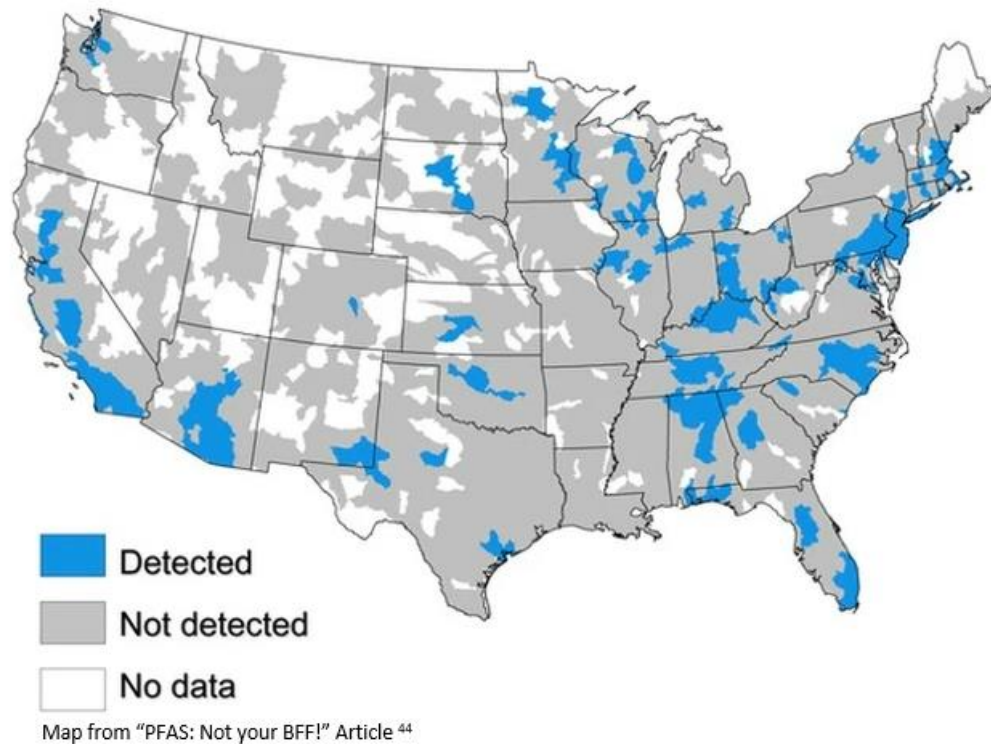


Figure 3: Hydrological units with detectable PFASs

### 3. Ecological and Human Health Impacts

PFAS have been found in biota, specifically plants, fish, and humans, through the process of bioaccumulation. Studies have found evidence of uptake and accumulation of PFAAs in plants which may be introduced by soil, water, or air.

PFAA uptake by plants was found in irrigated crops, crops in biosolid amended soil,

natural environment near PFAS sources, and aquatic plants in constructed wetlands.<sup>1,2,5</sup> Studies found the longer chain PFAAs especially PFSAs partition to the roots and the shorter more soluble PFAAs especially PFCAs partition to other parts of the plant.<sup>5</sup> This evidence leads to concerns of introducing PFAAs into livestock and crops. PFAS have been detected in the tissues of invertebrates, fish, birds, and mammals where PFOS was generally the dominate PFAS detected.<sup>5</sup> PFAS accumulation in fish have been found particularly PFOS and longer chain PFCAs where PFOS in fish partition to the tissue with highest protein density, including the liver, blood serum, and kidney.<sup>1,2,5</sup> Because of the historically high use of PFOS, it is generally found in the highest concentration of PFAS in fish. PFSAs are generally more bioaccumulative than PFCAs with the same number of carbon chains where concentrations of PFOS have been found 10 to 20 times greater in predatory fish than in their prey species.<sup>5</sup> The weight of evidence for trophic magnification was great enough for PFOS to be considered bioaccumulative by the Stockholm Convention POP Review Committee.<sup>1</sup>

Human exposure to PFAS can occur through ingestion, direct contact, inhalation, and occupational exposure.<sup>1,2</sup> The greatest portion of chronic intake is from ingestion of contaminated foods and drinking water.<sup>5</sup> PFAAs are not metabolized and half-lives of PFAS in humans are several years leading to long chain PFAAs being excreted very slowly in humans.<sup>5</sup> Therefore, PFAS will accumulate over time with continued exposure. As mentioned before PFAS generally binds to proteins and will accumulate in the blood liver and kidneys of humans.<sup>1,2</sup> Epidemiology studies suggest links between PFAS exposure and several health outcomes including

hepatic, cardiovascular, endocrine, immune, reproductive, and developmental effects.<sup>45</sup> Studies of PFOA, PFOS, and PFNA suggest links between PFAS exposure and increases in total cholesterol and LDL cholesterol.<sup>45</sup> Epidemiological studies of PFOA and PFOS exposure show evidence of pregnancy-induced hypertension and pre-eclampsia.<sup>45</sup> Studies show links between PFOA and PFOS exposure and an increase risk of thyroid disease.<sup>45</sup> Studies show evidence of a link between PFOA, PFOS, and PFHxS and decreased antibody responses to vaccines.<sup>45</sup> A risk of decreased fertility was found with exposure to PFOA and PFOS.<sup>45</sup> Also, evidence from epidemiology studies and cancer bioassays suggest Carcinogenetic Potential for PFOS and PFOA.<sup>1,2</sup> A wide range of regulatory screening levels for soil and water exist throughout the United States but there is not a consensus on a safe level for PFAS in soil and water.

## **4. PFAS Contamination Sources**

### **4.1 Landfills**

Legacy landfills are considered landfills that accepted waste from the 1950s to the 1990s, these landfills mostly lacked modern engineering controls such as liners, gas and leachate collection systems.<sup>22</sup> Landfills with these systems in place have limited leachate and groundwater interactions. Unlined landfills have a much greater potential of PFAS contamination to groundwater where release rates vary with waste age and time with the apparent driving force being rainfall.<sup>5,15,22</sup> Studies on landfill leachate found sources of PFAAs include consumer products (paper, textile, packaging, food contact paper, and carpet), building materials, and

electronics.<sup>15,20</sup> Also polyfluoroalkyl substances commonly known has precursors found in these products can transform once disposed in landfills abiotically and biologically into PFAAs.<sup>5,20</sup> This is because polyfluorinated compounds (precursors) contain carbon-hydrogen and carbon-oxygen bonds within the carbon chain that are subject to reactions, unlike the fully fluorinated PFAA compounds.<sup>29</sup> An example includes fluorotelomer alcohols (FTOH) a material in fluorotelomer polymers (FTP), which is a surface protectant used in textile, upholstery, paper, and carpets that are commonly found in landfills. The FTOH degrades by abiotic and biotic hydrolysis to fluorotelomer carboxylic acids (FTCA), unsaturated fluorotelomer carboxylic acids (FTUCA). These then can biodegrade further to PFCAs such as PFBA, PFHxA, in soil and WWTP sludge under both aerobic and anaerobic conditions.<sup>5,15,20</sup>

Landfill leachate studies have found PFCA concentrations of 10 to 8900 nanograms per liter (ng/L) and PFSA concentrations of 50 to 3200 ng/L.<sup>15</sup> Though PFSA is detected in most landfill leachate it is PFCA that is generally the dominant PFAS accounting for 20 to 90% of total PFAS detected in landfills.<sup>15,20</sup> The wide range in concentrations could be from variation in waste composition, age of landfill and or climate condition.

Municipal landfill leachate indicators of impacted groundwater quality include elevated concentrations of ammonia/ammonium, bicarbonate, potassium, total organic carbon, and dissolved methane.<sup>20,22</sup> Using these indicators and comparing the ratio of PFOA to the sum of PFAA was found to be useful in identifying PFAS impacts from municipal legacy landfills in groundwater. Industrial/construction waste landfills showed high concentrations of PFSAs mostly

PFHxS, PFOS with relatively low concentrations of PFCAs.<sup>22</sup> This can be a good reference for non-municipal landfill source identification when found with low concentrations of municipal landfill leachate indicators.<sup>22</sup>

E. Hepburn et al. (2019) developed a framework for identifying PFAS impacted groundwater from legacy landfills. Figure 4 is the troubleshooting tree developed, which systematically outlines which landfill indicators to analyze. After which the use of PFOA/ $\Sigma$ PFAA ratio can be used like a PFAS fingerprint to trace the sample to the possible source.<sup>20,22</sup>

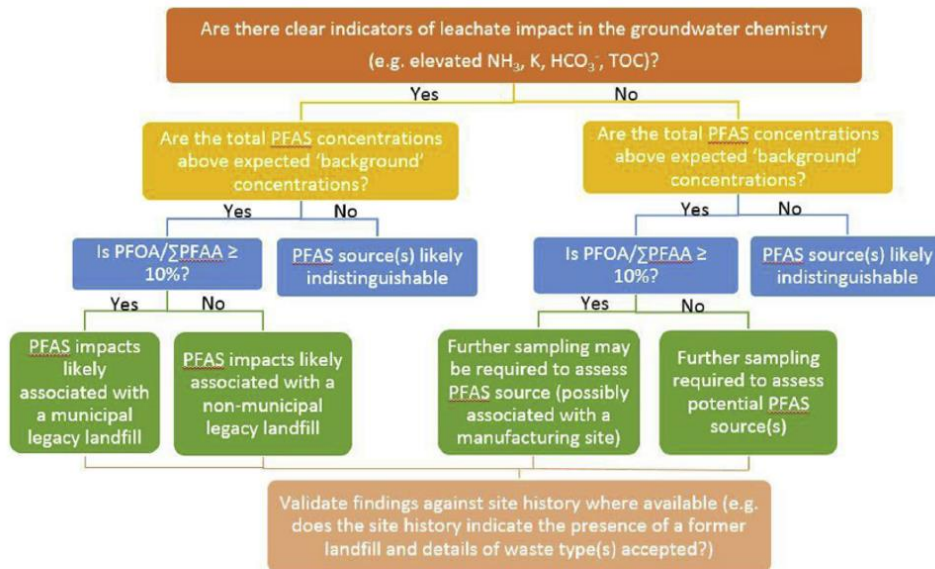


Figure 4: New framework for assessing legacy landfill PFAS impacts to groundwater.

Figure taken from Hepburn et. al.<sup>22</sup>

## 4.2 Wastewater

As the demand for water resources increase world wide, treated wastewater applications become encouraged by regulators and the water industry. However, treated wastewater also known as reuse water or reclaimed water along with treatment process byproducts known has biosolids can contain PFAS of significant

concentrations.<sup>27</sup> This increase in irrigation by use of treated wastewater and the land application of biosolids are a potential for long-term impacts on soil, surface, and groundwater.<sup>21</sup>

Studies have shown that WWTP do not remove PFAS but instead found PFAA concentrations increase between influent and final effluent due to oxidation of polyfluorinated precursors and transformation pathways such as microbial degradation during the treatment process.<sup>15,26,33</sup> Compounds of PFCAs such as PFOA, perfluorohexanoic acid (PFHxA), perfluorodecanoic acid (PFDA), and PFHpA increase in the aqueous phase of a WWTP from processes already described involving biodegradation of precursors such as FTOH.<sup>18</sup> Concentrations of longer chained PFAS compounds including PFOS and PFOA are most abundant in biosolids.<sup>1,2,18,26</sup>

WWTP can be significant point sources of PFAS depending on influent concentrations to the treatment plant. Concentrations of PFAS especially the PFAAs can become elevated when the WWTP receives industrial wastes from paper, textile or furniture manufactures.<sup>18,33</sup> Agricultural areas are most affected by wastewater biosolids when used for fertilizer soil amendments and also areas that use reclaimed water for landscape irrigation such as golf courses.<sup>18</sup> These lands become sources for uptake of PFAS by plants and soil organisms. Studies have found biosolids amended soil can contribute PFAAs to the food chain<sup>5,18,34</sup> Treated wastewater discharged to streams and wetlands can expose aquatic and terrestrial organisms to PFAS.<sup>27</sup> Considering these organisms bioaccumulate PFAS Rostkowski et al. calculated a safe water concentration for avian wildlife for PFOS at 50 ng/L.<sup>34</sup>

Studies have found PFAS totals in wastewater effluents up to 520 ng/L.<sup>26</sup> The presence of PFOA and PFOS in WWTPs can indicate they are also in the drinking water.<sup>25</sup> WWTPs effluent discharged to surface water and possibly to groundwater through irrigation and infiltration through soil could cycle back to drinking water, recirculating PFAS in the water cycle.

### **4.3 AFFF (Fire Training/ Fire Response Sites)**

Mixtures of many PFAS are often found in environmental samples from contaminated areas. PFOS and PFHxS have been known ingredients of fluorosurfactant-based foams (FSBF) or AFFF.<sup>12,16</sup> Legacy PFAS pollution hot spots are the result of the extensive use of AFFF at firefighting training facilities.<sup>7</sup> These foams were produced by 3M in the United States from the 1960s to 2002 under the name “Lightwater”.<sup>1,3,5</sup> PFAS are added to AFFF because of their surfactant properties, which gives better spreading of AFFF on water and oil resulting in rapid fire suffocation. Some of the highest PFAS concentrations in groundwater have been found at firefighting training sites in the milligram per liter level (mg/L).<sup>7,18</sup> AFFF contaminated ground water is usually dominated with higher PFOS concentrations compared to other PFAS.<sup>7,12,18</sup>

One of the main AFFF used around the world was 3M’s Lightwater, which had different formulations.<sup>16</sup> Lightwater contained very high concentrations of PFOS along with PFHxS and PFAA precursors.<sup>16</sup> In 2002 3M ceased global production but lightwater AFFF can still be found in use. Today AFFF based on 6:2 fluorotelomers and short chain PFAAs such as PFBS are produced.<sup>28</sup> These short

chain PFAAs and precursors present in modern AFFF formulations are considered less bioaccumulative, but are more mobile and they may be just as persistent in the environment as long chain substances.<sup>16,28</sup> Similar to all PFAS contamination sources AFFF impacted sites can impact drinking water sources and the environment by transport processes such as advection, dispersion and diffusion.<sup>5,6,10,19</sup> PFAS infiltration through soils to groundwater sources is also of concern. Figure 5 below illustrates these modes of transport.<sup>5</sup>

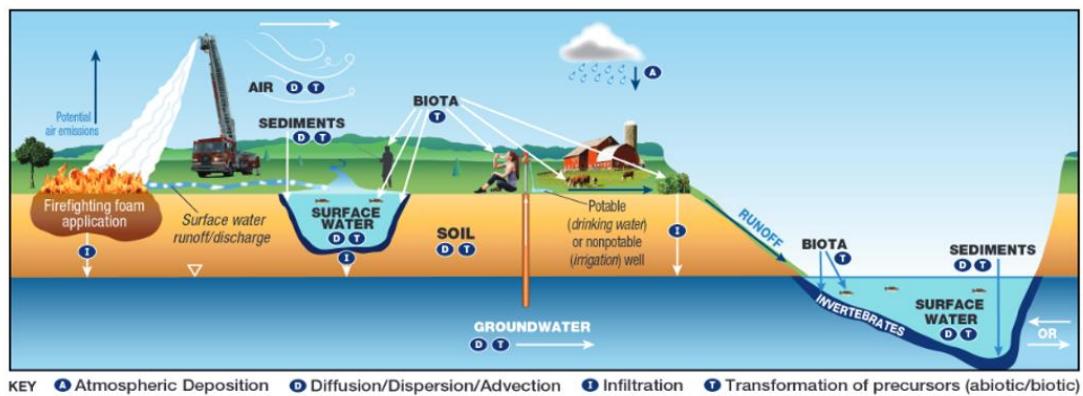


Figure found at ITRC website<sup>5</sup>

Figure 5: Conceptual model for AFFF impacted sites

#### 4.4 Industrial/Manufacturing Sites

PFAS are produced by two main processes, ECF and telomerization.<sup>1,2,3,5</sup> ECF was used by 3M until 2001 and created even and odd carbon chain lengths with 70% and 30% branched substances.<sup>1,2,3,5</sup> Today PFAS are mostly produced by telomerization, which creates even numbered straight chain isomers and was developed in the 1970s.<sup>5</sup> Manufacturing sites either produce PFAS or use them in their processing for coating applications or finished products. PFAS are also used to

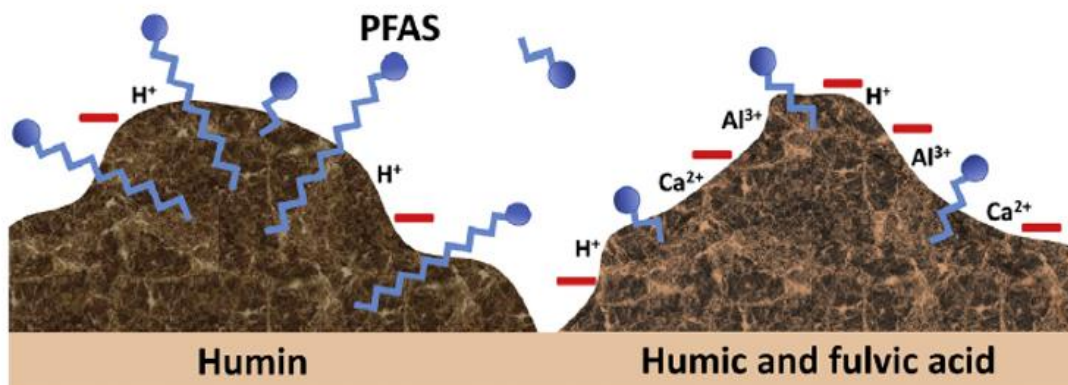


create a safer work environment by reducing harmful mists during some coating manufacturing processes.

Industries with the greatest potential for PFAS releases to the environment are textiles, paper mills, metal finishers, plating facilities, and manufacturers that use surfactants, molds, plastics, photolithographs and semiconductors.<sup>3,5</sup> Pathways for release include wastewater discharge, waste disposal, accidental releases and stack emissions.<sup>31</sup> Composition of PFAS release from these facilities depend on type of products used. Industrial sites are less likely to co-release contaminants so PFCA or PFSA dominated detections can most likely be traced to a manufacturing source.<sup>31</sup>

## **5. Soils**

Because PFAAs are mobile in soil and groundwater they can be expected to form large plumes in aquifers. Sorption and partitioning can restrict leaching rates in the vadose zone and reduce advection transport in groundwater.<sup>5,6,19</sup> Understanding fate and transport of PFAS is essential for an accurate risk assessment, which can determine the migration potential for source to groundwater and the potential health risks. Multiple processes such as partitioning, transport by advection, dispersion, and diffusion and transformation of precursors complicate source zone transport of PFAS.<sup>8-10</sup> Hydrophobic and lipophobic effects, electrostatic interactions and interfacial behaviors are important PFAS partitioning mechanisms.<sup>6,10</sup> Because the PFAS head and tail compete, partitioning to the soil/water, air/water and water/ non-aqueous phase liquids (NAPL) can occur.<sup>8,36</sup>



Graphic taken from Pereira et al. 2018<sup>9</sup>

Figure 6: Sorption of long and short chain perfluoroalkyl substance (PFAS) to organic compounds.

Biosolids and reclaimed water irrigation sites, fire fighting training sites with AFFF use, waste disposal and spillage sites will likely have PFAS contamination in the vadose zone. Downward leaching is expected during precipitation and irrigation due to dissolution of the soil bound PFAS.<sup>30</sup> PFAS structural and soil media properties effect leaching potential but the most important appears to be soil organic carbon.<sup>6</sup> Figure 6 above from H.C. Pereira et al. shows most long chain PFAS sorb to humin fractions while shorter chained PFAS bind to humic and fulvic acid due to cation effects.<sup>9</sup> Other factors that affect PFAS solid-phase adsorption include ionic strength, chain length, pH, redox condition and presence of co-contaminants.<sup>8</sup> Longer chained PFAS have a greater binding strength, which is attributed to PFAS hydrophobicity increasing with each additional CF<sub>2</sub> moiety.<sup>13, 36</sup> Decreasing pH was observed to increase PFAS sorption for the following; PFHxA, PFHpA, PFOA, PFNA, PFDA, Perfluoroundecanoate (PFUnDA), Perfluorododecanoate (PFDoDA),

Perfluorooctane sulfonamide (FOSA), and PFOS.<sup>9</sup> This is consistent with other sorption studies and is explained by de-protonation of the adsorbent surface, leading to more positive sites on the sorbent.<sup>15</sup> Studies also agree that PFSA sorb more strongly than PFCAs, due to PFSA containing one more C-F bond resulting in stronger hydrophobic properties and thus increased sorption.<sup>8-13</sup> Retention of long chained PFAS was observed in shallow soils after extended irrigation and precipitation events.<sup>12</sup> This retention can lead to reduce exposure by leaching to drinking water sources such as groundwater but may also lead to extended detection in groundwater due to long term persistence of PFAS in the soil source.<sup>6,8,10</sup>

Conceptual and mathematical models are used to predict fate and transport of PFAS. To assist with transport potential, models use organic carbon partitioning coefficient known as  $K_{oc}$ , which measures the mobility of a substance in soil.<sup>4</sup> A very high value indicates the substance is strongly adsorbed and prevented from moving through the soil and a low value means the substance is mobile.<sup>4</sup> Table 1 lists log  $K_{oc}$  values for select PFAS from many studies. This table is a combination of similar tables found at ITRC website and from H.C. Pereira et al.<sup>5,9</sup> Compared to other common groundwater contaminants, PFAS log  $K_{oc}$  is relatively high. Increasing PFAS log  $K_{oc}$  values correspond with increasing chain length and increasing sorption potential.<sup>29</sup>

**Table 1: Field and laboratory derived soil/sediment organic carbon normalized partitioning coefficients (log K<sub>oc</sub>) for target PFAS**

| PFAS Chemical  | Log K <sub>oc</sub> (L/kg) | Data Sources              |
|--|----------------------------|---------------------------|
| Perfluorobutanoate (PFBA)                                      | 1.88                       | 36                        |
| Perfluoropentanoate (PFPeA)                                    | 1.37                       | 36                        |
| Perfluorohexanoate (PFHxA)                                     | 1.31                       | 36, 39                    |
| Perfluoroheptanoate (PFHpA)                                    | 1.63                       | 36, 39                    |
| Perfluorooctanoate (PFOA)                                      | 1.89 to 2.63               | 6, 30, 32, 36, 37, 38, 42 |
| Perfluorononanoate (PFNA)                                      | 2.36 to 3.69               | 30, 32, 36, 38, 39, 42    |
| Perfluorodecanoate (PFDA)                                      | 2.96 to 4.6                | 30, 36, 38, 39            |
| Perfluoroundecanoate (PFUnDA)                                  | 3.3 to 5.1                 | 30, 36, 38, 39            |
| Perfluorobutane sulfonate (PFBS)                               | 1.22 to 1.79               | 6, 36                     |
| Perfluoroheptane sulfonate (PFHxS)                             | 2.5 to 3.7                 | 30, 36, 39                |
| Perfluorooctane sulfonate (PFOS)                               | 2.4 to 3.7                 | 6, 36, 37, 38, 42         |
| Perfluorodecane sulfonate (PFDS)                               | 3.53 to 3.66               | 38                        |
| Perfluorododecanoate (PFDoDA)                                  | 5.6                        | 39                        |
| Perfluorooctane sulfonamide (FOSA)                             | 4.2-4.5                    | 30, 37                    |
| Perfluorooctanesulfonamide (PFOSA)                             | 4.10                       | 37                        |
| 4:2 Fluorotelomer alcohol (4:2 FTOH)                           | 0.93                       | 32, 40, 41                |
| 6:2 Fluorotelomer alcohol (6:2 FTOH)                           | 2.43                       | 32, 40, 41                |
| 8:2 Fluorotelomer alcohol (8:2 FTOH)                           | 4.13                       | 32, 40                    |
| 10:2 Fluorotelomer alcohol (10:2 FTOH)                         | 6.20                       | 32, 40, 41                |
| 2-(N-ethylperfluorooctanesulfonamido) acetic acid (N-EtFOSAA)  | 3.23 to 3.49               | 38                        |
| 2-(N-methylperfluorooctanesulfonamido) acetic acid (N-MeFOSAA) | 3.11 to 3.35               | 38                        |

This table is a combination of similar tables found at ITRC website and from H.C. Pereira et al. <sup>5,9</sup>

PFAS was designed has a surfactant to form films at the water interface. It exhibits this very well with its hydrophobic tail orienting toward the air and the hydrophilic head dissolving in water. <sup>8,10,11</sup> Because of these properties PFOA and PFOS transport is greatly inhibited in unsaturated zones due to the impact of adsorption at the air-water and NAPL-water interface. <sup>11</sup> These retention processes should be accounted for in models to better predict the behavior of PFAS transport

in source zones. M.L. Brusseau also found that PFAAs at high concentrations with the head group interacting with water the tail can interact with each other forming aggregates.<sup>8</sup> This tendency could also enhance adsorption on carbon and minerals in the environment.<sup>11</sup> Studies have shown that the vadose zone may serve as a significant long-term PFAS source to groundwater.<sup>8,10,11</sup> Since PFOA and PFOS have been phased out of production they continue to be detected in drinking water sources due to these soil retention processes in the vadose zone.

## **6. Water Treatment**

Drinking water and dietary intake are the main exposure routes of PFAS to humans.<sup>19,20,23</sup> After the results of UCMR 3 revealed that drinking water was contaminated with PFAS, water utilities began to seek treatment technologies for PFAS removal. The more commonly used technologies include granular activated carbon (GAC), membrane filtration such as nanofiltration (NF) and reverse osmosis (RO), and ion-exchange resin (IX). All of these treatment technologies have their advantages and disadvantages depending on the source water quality and PFAS concentration. These technologies have high operation and maintenance costs when compared to conventional treatment.

Activated carbon has been widely investigated and accepted for PFOS and PFOA removal, which relies on the hydrophobic and electrostatic interactions of PFAS for removal by adsorption on the carbonaceous material.<sup>35</sup> GAC consistently removes PFOA and PFOS with greater than 90% efficiency.<sup>35</sup> Removal of short chain PFAS are less effective.<sup>5</sup> Activated carbon removal efficiency decreases with

increasing dissolved organic carbon (DOC) concentration in source water.<sup>29</sup> GAC requires thermal regeneration after which may have reduced removal rates compared to virgin GAC.<sup>1,2,3</sup> Exhausted carbon waste requires disposal and could be considered hazardous.<sup>29</sup>

The common methods of membrane filtration used for drinking water treatment are NF and RO. These methods use high pressure to force water through a semi permeable membrane with pore sizes of 1-10 nm and less than 1 nm respectively.<sup>35</sup> Membrane filtration has excellent broad range PFAS removal with efficiencies of 99%.<sup>35</sup> RO is preferred to NF because of better removal efficiency but does have higher operating costs.<sup>3</sup> Membrane filtration in general have high capital costs with high energy demands.<sup>3</sup> pretreatment of source water may be required because filtration is susceptible to fouling.<sup>3</sup> Membrane filtration is not destructive and the brine solution generated can consist of high PFAS concentration which will require disposal. Disposal methods are costly and include hazardous waste landfill or incineration. The temperature required to destroy PFAS is greater than 1000°C.<sup>35</sup>

IX resins which are beginning to gain popularity for drinking water treatment because they perform similar to GAC but have shorter empty bed contact time (EBCT) and have better removal rates of short chain PFAS.<sup>3</sup> IX also have a smaller footprint than GAC vessels, which can make installation easier. IX resins consist of polystyrene or polyacrylic beads, which can be selectively charged by either cation but mostly anion for target PFAS removal.<sup>29</sup> Removal efficiencies vary but are similar to GAC with 90 to 99% PFOS removal.<sup>3</sup> The presence of competing

ions can decrease efficiency.<sup>15</sup> Regeneration of IX resins is by chemical treatment which generates a brine of high PFAS concentration.<sup>29</sup>

## **7. Conclusion**

PFAS are a unique class of emerging contaminants and have shown widespread occurrence in groundwater and surface water resources. They have become the focus of environmental protection agencies worldwide because of their toxicological characteristics. PFAS contamination can be present at landfills receiving waste since the 1950s and at areas using AFFF such as firefighting training facilities and airports. Other potential sources of PFAS to groundwater and soils include disposal and land application of municipal biosolids, discharge of effluent from WWTP along with a variety of commercial and industrial manufacturing sources.<sup>3,5</sup>

PFAS are stable and resistance to degradation because of the very strong carbon fluorine bond of the PFAS molecule chain tail. PFAS molecules are prone to sorption especially organic carbon and oil. PFAS exhibit relatively high Koc values however Koc and the degree of sorption is site specific, depending on the sorptive medium and solution chemistry.<sup>8,10</sup>

Currently there are three treatment technologies that can provide effective PFAS removal from contaminated water. Removal efficiencies for GAC, RO, NF, IX depend on the properties of the source water but each has demonstrated up to 95% removal of PFAS.<sup>3,5</sup> Additional research is needed on environmental fate, transport, and chemical transformations of PFAS to better understand potential risks and for better management of contamination.

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