Review

Fate and Transport of Per- and Polyfluoroalkyl Substances (PFAS) at Aqueous Film Forming Foam (AFFF) Discharge Sites: A Review

Jeffery Tyler McGarr [1],*, Eric Gentil Mbonimpa [2], Drew Clifton McAvoy [3] and Mohamad Reza Soltanian [1,3]

[1] Department of Geosciences, University of Cincinnati, Cincinnati, OH 45221, USA
[2] Department of Systems Engineering and Management, Air Force Institute of Technology, Dayton, OH 45433, USA
[3] Department of Chemical and Environmental Engineering, University of Cincinnati, Cincinnati, OH 45221, USA
* Correspondence: mcgarrjt@mail.uc.edu

Abstract: Per- and polyfluorinated alkyl substances (PFAS) are an environmentally persistent group of chemicals that can pose an imminent threat to human health through groundwater and surface water contamination. In this review, we evaluate the subsurface behavior of a variety of PFAS chemicals with a focus on aqueous film forming foam (AFFF) discharge sites. AFFF is the primary PFAS contamination risk at sites such as airports and military bases due to use as a fire extinguisher. Understanding the fate and transport of PFAS in the subsurface environment is a multifaceted issue. This review focuses on the role of adsorbent, adsorbate, and aqueous solution in the fate and transport of PFAS chemicals. Additionally, other hydrogeological, geochemical, ecological factors such as accumulation at air–water interfaces, subsurface heterogeneity, polyfluorinated PFAS degradation pathways, and plant interactions are discussed. This review also examines several case studies at AFFF discharge sites in order to examine if the findings are consistent with the broader PFAS literature. We present the most crucial future research directions and trends regarding PFAS and provide valuable insights into understanding PFAS fate and transport at AFFF discharge sites. We suggest a more comprehensive approach to PFAS research endeavors that accounts for the wide variety of environmental variables that have been shown to impact PFAS fate and transport.

Keywords: PFAS; aqueous film forming foam; fire training areas; case studies

1. Introduction

Poly- and perfluoroalkyl substances (PFAS) are an environmentally persistent group of chemicals consisting of over 5000 chemical species [1,2]. The United States Environmental Protection Agency (USEPA) has selected 29 PFAS compounds to be included in their fifth Unregulated Contaminant Monitoring Rule, which identifies contaminants that should be monitored in drinking water but are not included in the Safe Drinking Water Act. PFAS are especially problematic as they can lead to detrimental health effects, including increased cancer risk, reproductive health issues, and birth defects [3–5]. Furthermore, setting PFAS-related health standards is problematic as sufficient toxicity data are unavailable [6].

PFAS have been used in a wide variety of industrial processes and consumer products [7–10]. Their widespread usage and utility can be attributed to a variety of properties, including but not limited to high thermal stability and amphiphilic properties (i.e., being simultaneously hydrophobic and hydrophilic) [11]. Properties that make PFAS attractive to manufacturers and inherently (perhaps unknowingly) attractive to consumers also make them a threat to human and environmental health [3,12,13]. PFAS-containing products have had the opportunity to spread around the world for nearly a century. As a result, PFAS as an environmental contaminant on regional and global scales also simultaneously

grew unchecked and unnoticed until the early 2000s. It was then that studies found long-chain PFAS in wildlife from remote habitats [14] and in human blood serum samples [15]. Today, PFAS contamination is a global issue, with the compounds being detected in water, sediments, animal and plant tissues, and humans on every continent [16,17].

Public awareness and fears of PFAS bioaccumulation led 3M, a prominent manufacturer of PFAS, to phase out production of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), as well as their longer-chain PFAS precursors in favor of shorter-chain PFAS, such as perfluorobutane sulfonate (PFBS) [18]. The transition to short-chain PFAS has not been matched in the literature, with few studies examining the presence, fate, transport, and potential impacts on the environment and human health of short-chain PFAS [19–21]. The same is true for regulations. For example, a lifetime health advisory issued by the USEPA in 2016 set a guidance of 70 parts per trillion (ppt) of PFOA and PFOS combined in drinking water [22]. As of March 2023, the USEPA has proposed federal regulation of six PFAS, including just 4 ppt of PFOA and 4 ppt of PFOS [23]. Such advisories are not available for many shorter-chained compounds at the federal level in the US. However, many states and other countries have regulations for many other PFAS compounds.

PFAS are aliphatic compounds related by a partially (polyfluorinated) or fully fluorinated (perfluorinated) alkyl chain consisting of carbon (C) and fluorine (F) atoms [11] (Figure S1). The C–F bond is one of the strongest chemical bonds, making PFAS incredibly resilient in typical environmental conditions. Furthermore, chain length (i.e., number of carbon atoms in the molecule) is a distinguishing factor between PFAS species that affects its environmental behavior [24–26]. PFAS chain lengths are typically described as long- (C > 7), short- (C = 4–7), or ultra-short-chain (C = 2–3) [17]. PFAS also differ in their functional group (e.g., sulfonates, carboxylates, phosphonates, and alcohols), which has been shown to affect environmental behavior [27]. Key groups of PFAS are perfluoroalkyl acids (PFAAs) and polyfluorinated compounds or fluorotelomers. PFAAs include perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs). Polyfluorinated compounds or fluorotelomers include fluorotelomer sulfonates (FTSAs), fluorotelomer carboxylates (FTCAs), and fluorotelomer alcohols (FTOHs) [11]. Polyfluorinated compounds are of critical importance as they are precursor compounds for PFAAs. As such, polyfluorinated compounds present a source of PFAAs in the environment long after initial PFAS contamination due to transformation and degradation [11,28,29]. Additionally, PFAS compounds can vary in their structure, with linear and branched isomers, with linear isomers being more mobile and bioaccumulative than branched ones [30].

Aqueous film forming foam (AFFF) is a surfactant solution that has long been used to fight hydrocarbon-fuel-based fires (i.e., jet fuel) in firefighter training areas (FTA) at military installations, airports, civilian fire departments, petroleum refineries, and other industrial sites [11,31,32]. Since their introduction in the 1960s, PFAS in AFFF formulations have been manufactured through electrochemical fluorination (ECF) and telomerization [11,33]. The ECF process results in the creation of long-chain PFAAs (primarily PFSAs and their precursors), and the telomerization process results in the creation of polyfluorinated fluorotelomers [11,34]. Both formulations consist of a proprietary and diverse group of PFAS consisting of known and widely unknown compounds, necessitating non-targeted analytical techniques to examine their compositions [33]. PFOS-based AFFF was phased out in the early 2000s, coinciding with 3M's decision to phase out production of long-chain PFAS [16]. Since the discontinuation of PFAA-based AFFF, fluorotelomer-based AFFF has been the only PFAS-containing AFFF manufactured in the United States. Fluorotelomer-based AFFFs are problematic because many fluorotelomers are precursor compounds of PFAAs [29].

Transport of AFFF constituents (and PFAS in general) within the environment is difficult to understand for a variety of reasons, including presence of co-contaminants and numerous PFAS species, degradation of precursors, variable saturation, and variable physical and chemical properties of the adsorbent and adsorbate. AFFF formulations

have been found to consist of over 50 unique PFAS compounds ranging from 2 to 12 C atoms [18,33,35,36]. Within the literature, investigations of PFAS fate and transport typically do not account for the presence of numerous PFAS compounds or co-contaminants [37–39]. PFAS-based AFFF formulations encompass far more than just PFAS with other constituents, including hydrocarbon surfactants, organic solvents, polymers, and other additives in addition to PFAS surfactants [40]. Additionally, co-contaminants will likely include non-aqueous-phase liquids (NAPL), such as hydrocarbon-based fuels [41–43]. The presence of non-PFAS co-contaminants is not well-studied, although it has been shown that co-contaminants can affect PFAS fate and transport [41,43,44]. Precursor compounds (i.e., fluorotelomers) also add to the complexity of PFAS fate and transport as they can function as a lingering source of PFAAs in the subsurface long after the final application of AFFF through transformation and degradation [29,45].

In this review, we seek to examine a variety of factors that influence PFAS fate and transport, including PFAS sorption, transformation, and plant interactions, with a focus on literature pertaining to AFFF discharge sites where possible (Figure 1). We also present several case studies at AFFF discharge sites to examine the factors impacting fate and transport processes at real-world sites, which is the unique characteristic of this review. The remainder of this review is structured as follows: Section 2 describes PFAS sorption; Section 3 focuses on transformation and degradation; Section 4 highlights plant interactions; Section 5 presents case studies and implications for AFFF sites; and Section 6 highlights some conclusions and discusses several critical future research directions. Note that Section 2 on PFAS sorption is the most expansive, covering sorption mechanisms, sorption isotherms, impacts of characteristics of the adsorbent, adsorbate, and solution chemistry on sorption, and behavior in the variably saturated vadose zone.
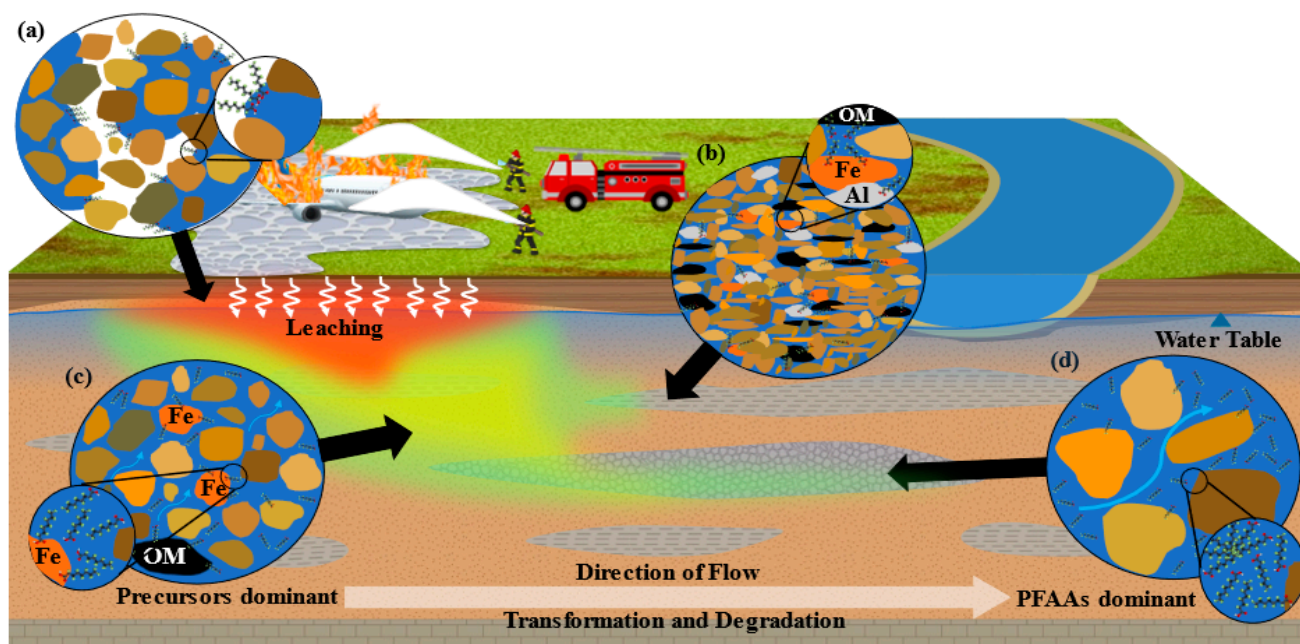

Figure 1. Conceptual model of PFAS fate and transport in a fire training area (FTA). Depicted are the impacts of physical and chemical heterogeneity in the subsurface, air–water interface (AWI), and transformation and degradation. A PFOS molecule is used to represent PFAS throughout the model. Black arrows indicate where popouts (**a**–**d**) are representative of. (**a**) PFAS sorption to AWI due to hydrophobic interactions in the unsaturated zone. (**b**) PFAS sorption in silts and clays. (**c**) PFAS sorption in higher-permeability materials, such as sand. (**d**) PFAS sorption in gravel-dominated sediments. Depicted as well is the formation of a hemi-micelle.

2. PFAS Sorption

2.1. PFAS Adsorption Mechanisms

The primary adsorption mechanisms identified in the literature are electrostatic interactions and hydrophobic interactions. Hydrogen bonding has been discussed in previous reviews; however, this mode of adsorption was found to be insignificant in typical environmental conditions [46,47]. In the following subsections, we examine both electrostatic and hydrophobic interactions. We should note that sorption and adsorption are technically different, with sorption being used when the mechanism for sorptive behavior is not specified and adsorption used when the mechanism is adhesion to a surface.

2.1.1. Electrostatic Interaction

PFAS exist in numerous ionic states (i.e., anionic, cationic, or zwitterionic). Thus, electrostatic interactions play a significant role in PFAS sorption [28,48,49]. In typical environmental conditions, many PFAS are found to be anionic (negatively charged), resulting in attraction to positively charged soil and sediment surfaces [42,50] (Figure 1b,c). With many sediment surfaces being negatively charged, cation bridging could also be an important mechanism [51]. Electrostatic interactions can be affected by a variety of factors, including pH, ionic concentrations, presence of metals such as iron and aluminum, organic carbon (OC), and PFAS chain length, all discussed further in Section 2.3.

Cationic (positively charged) and zwitterionic (variably charged) PFAS have not received as much attention as their anionic counterparts. Barzen-Hansen et al. found that cationic PFAA precursor compounds, such as 6:2 fluorotelomer sulfonamidoamine (6:2 FtSaAm), and zwitterionic PFAA precursor compounds, such as fluorotelomer sulfonamido betaines (FtSaB), sorb more via electrostatic interactions when compared to anionic fluorotelomer sulfonates (FtS) [28]. Xiao et al. generated similar findings using cationic perfluorooctaneamido ammonium salt (PFOAAmS) and zwitterionic perfluorooctaneamido betaine (PFOAB) when compared to PFOA. Zhi and Liu performed unique batch sorption experiments as they included a variety of pyrogenic carbonaceous materials (i.e., biochar and chimney soot) to simulate potential soil constituents after a fire [49]. They also found that cationic PFOAAmS and zwitterionic PFOAB and 6:2 fluorotelomer sulfonamido betaine (6:2 FTAB) sorbed more readily than their anionic counterparts PFOA and PFOS due to electrostatic interactions. Although not discussed in this work, these differences may also be influenced by differences in dissociation constants (p*K*a) of the select PFAS compounds. They concluded that the presence of pyrogenic carbonaceous material enhanced sorption of cationic and zwitterionic compounds, which likely has implications for AFFF discharge sites.

2.1.2. Hydrophobic Interaction

Hydrophobic interactions are commonly identified as a primary contributor of PFAS sorption in subsurface sediments and soils [21,27,28,52–55]. Hydrophobic interactions are driven by the hydrophobic PFAS C–F tail and its attraction to hydrophobic surfaces in the subsurface environment [11,42]. This process is seemingly counterintuitive as many of the attractions would seem to conflict with anticipated electrostatic repulsion. For example, anionic PFAS can sorb to negatively charged OC surfaces exhibiting electrostatic repulsion. However, the hydrophobicity of both the C–F tail and the hydrophobic portions of the OC surface will overcome the electrostatic interactions, resulting in hydrophobic-induced sorption (Figure 1b,c) [24–26]. Long-chained PFAS will exhibit increased potential for hydrophobic interaction when compared to shorter-chained PFAS [52,56–58]. A linear PFAS will exhibit higher hydrophobicity than a branched PFAS of the same chemical formula [59]. In the unsaturated zone, PFAS's amphiphilic properties result in adsorption of PFAS at air–water interfaces (AWI) (Figure 1a) [37,38,41,60] and NAPL–water interfaces [42,43,50]. Additionally, the hydrophobic C–F tails have been shown to coalesce, resulting in the creation of micelles and hemi-micelles at relatively high concentration (Figure 1d) [61–63].

Hydrophobic interaction is not the primary sorption mechanism for cationic and zwitterionic PFAS [28,48]. Barzen-Hansen et al. found that hydrophobic interactions of cationic FtSaAm and zwitterionic FtSaB were negligible due to the electrostatic interaction between positively charged PFAS and negatively charged surfaces [28]. They note that hydrophobic interactions play some role in zwitterionic sorption as C–F chain length in zwitterionic PFAS was found to affect sorption. Similar results were observed in batch experiments using cationic PFOAAmS, the zwitterionic PFOAB, and 6:2 FTAB, where hydrophobic interaction was negligible [48,49].

2.2. PFAS Sorption Isotherms and Kinetics

Sorption isotherms are used to quantify PFAS sorption by determining a sorption distribution (or partition) coefficient, K_d. Sorption isotherms can be calculated with laboratory data; however, field data typically show higher retardation than can be attributed to laboratory-derived K_d values [51]. This is a common issue for solutes undergoing sorption. Studies on other compounds (e.g., volatile organic compounds and trace metals) have attributed this discrepancy to scale effects [64–66]. The most frequently used isotherms to describe PFAS sorption are the linear, Freundlich, and Langmuir isotherms (Figure S2). Other isotherms found in the literature include the Virial isotherm [21] and the Donnan model [53]. Commonly used models of PFAS sorption kinetics include the first-order, pseudo-first-order, pseudo-second-order, and intraparticle diffusion models [21,47,48,54].

2.2.1. Linear Isotherm

The linear isotherm has been used to describe PFAS sorption either exclusively or in conjunction with a non-linear model, such as Freundlich or Langmuir (Figure S2) [54,55,58,67,68]. It has been shown that the linear sorption isotherm is acceptable when low PFAS concentrations (environmentally relevant) are considered [69,70]. The linear isotherm is written as:

$$C_s = K_d C_w$$

where C_s is the solid phase concentration at equilibrium, K_d is the distribution coefficient, and C_w is the aqueous concentration at equilibrium.

2.2.2. Freundlich Isotherm

The Freundlich isotherm is one of the most commonly used non-linear isotherms (Figure S2) [39,48,60,71,72]. The Freundlich isotherm is written as:

$$C_s = K_F C_w^n$$

where K_F is the Freundlich distribution coefficient and n is the Freundlich exponent used to adjust linearity. When examining PFAS sorption in sediment and soil, n is typically near 1, indicating a near-linear sorption isotherm [27,55,72]. The non-linearity of the isotherm indicates that the distribution coefficient is dependent on solute concentration.

2.2.3. Langmuir Isotherm

The Langmuir isotherm is another common choice when calculating a non-linear PFAS sorption isotherm (Figure S2). Langmuir includes a term to quantify the maximum sorption capacity, S_m, which is affected by properties of both porous media and the PFAS compound. Additionally, the Langmuir isotherm could be attractive for examining sorption behavior when competitive PFAS sorption occurs [2]. The Langmuir isotherm is written as:

$$C_s = \frac{K_L C_w S_m}{1 + K_L C_w}$$

where K_L is the Langmuir distribution coefficient [73,74].

2.2.4. Sorption Kinetics

Because PFAS sorption can be rate-limited, kinetic models are used to better understand transport beyond just equilibrium isotherms. Commonly used models of PFAS sorption kinetics include the first-order, pseudo-first-order, pseudo-second-order, and intraparticle diffusion models [2,21,47]. The first-order model is used to describe sorption when multiple kinds of sorption sites are present (can be modified to include more or fewer sorption sites) and is written as:

$$F_w = F_0 + F_1 e^{-k_1 t} + F_2 e^{-k_2 t}$$

where F_w is the fraction of PFAS in aqueous solution at time t (h), F_0 is the fraction of PFAS in aqueous solution at equilibrium, F_1 and F_2 are the fraction of PFAS sorbed to two kinds of sorption sites, k_1 and k_2 are rate coefficients for those sorption sites, and e is Euler's number [21].

Pseudo-first-order and pseudo-second-order models are written as follows:

$$S_t = S_e \left(1 - e^{-\mu_1 t}\right)$$

$$\frac{t}{S_t} = \frac{1}{\mu_2 S_e^2} + \frac{t}{S_e}$$

where S_t is PFAS sorbed at time t (µg/g), S_e is PFAS sorbed at equilibrium, and μ_1 (1/h) and μ_2 (g/µg h) are sorption rate coefficients for pseudo-first-order and pseudo-second-order models, respectively [2].

The intraparticle diffusion model is written as:

$$S_t = \mu_i t^{0.5} + B_i \tag{1}$$

where μ_i (µg/g/h$^{0.5}$) is the sorption rate coefficient and B_i is a constant representing the boundary layer effect on sediment surfaces (µg/g) [2].

2.3. Factors Impacting PFAS Fate and Transport in Both Saturated and Unsaturated Media

There are numerous factors that affect the fate and transport of PFAS in subsurface environments (Figure 1). We split these into three categories: characteristics of the adsorbent (e.g., soil and sediments), characteristics of the adsorbate (e.g., PFAS), and solution characteristics. Additionally, we explore phenomena unique to the unsaturated zone as it has important implications for the AFFF discharge sites. Li et al. and Anderson et al. both performed meta-analysis and found that it is impossible to reliably attribute sorption of PFAS to an individual factor but instead must be attributed to a combination of factors (e.g., OC, clay content, and pH) [51,75]. It should be noted that these characteristics along with the sorption mechanism and time can also affect the ability of PFAS to desorb from sediment, potentially resulting in irreversible sorption in environmental conditions [21,48,54,55,76].

2.3.1. Characteristics of the Adsorbent

Field- and laboratory-scale studies have analyzed properties of sediments to better understand PFAS fate and transport. Key factors include OC content, mineralogy, clay content, and ion exchange capacities. The most frequently examined characteristic is OC content [21,51,68,75]. A higher OC content will typically result in increased sorption. Prior work has shown that OC is the primary driver of PFAS sorption [21,68,77,78]. Wang et al. (2021) showed that 19–42% of PFOS sorption is controlled by OC in sand-dominated media with varying geochemical properties (except in pure sand, where 100% of sorption was attributed to OC). However, Li et al. (2018) found that OC alone is not statistically significant when attempting to correlate with changes in K_d values. A significant statistical relationship was observed when OC was combined with clay content and pH in multiple linear regression analysis [51].

Mineralogy, clay content, and cation and anion exchange capacities are not well-studied. Mineralogy and elemental composition are important to the sorption of anionic PFAS, especially in sediments and soils with limited OC [67,73,79,80]. Lyu et al. performed

column experiments with different soils and showed an interesting trend in soils with negligible OC fractions [79]. Differential retention of PFOA was explained by differing elemental compositions, where the soil with higher retention had twice the aluminum and iron contents. Lyu et al. found that aluminum oxides had a greater impact than iron oxides on PFOA sorption [80]. Hellsing et al. similarly found that PFOA, PFOS, PFHxA, and PFNA display an affinity for aluminum oxides due to electrostatic interactions with shorter-chained PFAS shown to sorb at higher concentrations [73]. Additionally, Hellsing et al. showed that electrostatic attraction to aluminum was quite weak as PFAS desorbed with a water rinse [73]. This behavior indicates that a rainfall event could remobilize anionic PFAS sorbed to aluminum. Adamson et al. (2020) and Nickerson et al. (2021) both studied an AFFF discharge site and attributed higher concentrations of zwitterionic and cationic PFAS to silt- and clay-rich areas of high cation exchange capacity [52,59]. Similarly, other studies concluded that anion exchange can augment sorption of anionic PFAS, whereas cation exchange can promote anionic PFAS transport [75,81]. Li et al. determined clay content to be one of the significant characteristics dictating PFAS sorption alongside OC content and pH [51].

2.3.2. Characteristics of the Adsorbate

One of the difficulties in understanding PFAS fate and transport is the simple fact that there are thousands of unique PFAS compounds differing in the C–F chain length, functional group, and electrical charge, with each affecting transport behavior. The C–F chain length drives hydrophobic interactions, with longer chains displaying higher degrees of hydrophobicity. This trend has been shown in both field- and laboratory-scale studies [35,42,56,58]. Higgins and Luthy found that, for each additional CF_2 in the C–F chain, the log K_d will increase by 0.5 to 0.6 [27]. Anderson et al. used regression analysis to estimate the K_{oc} of 15 unique PFAS compounds. They found that the log K_{oc} of short-chained PFAS falls between 2.5 and 3, whereas long-chained PFAS have estimated log K_{oc} values of 3.5 to 4.25 [75]. While not directly discussed in the PFAS literature, it is also possible that longer chain lengths can render the sorption process more irreversible. This is because one stage of the sorption process is driven by diffusion (mass transfer from dissolved phase to solid phase), which can decrease for larger chain length or particle/molecule size according to Stokes–Einstein equation [82,83]. The second stage of the sorption process is the physio-chemical binding of the sorbate molecules to the sorbent. This binding can be stronger for longer chain lengths [84]. Additionally, PFAS functional groups have also been shown to impact sorption [27,58,85,86]. Sörengård et al. performed batch sorption experiments with 17 PFAS compounds and 44 unique sorbents and found that sorption of PFAS with identical chain length increased from FTSA, PFCA, PFSA to perflouuooctanesulfonamide (FOSA) [58]. Higgins and Luthy reported similar findings, with PFSAs sorbing more than PFCAs [27].

2.3.3. Characteristics of the Solution

The characteristics of the solution (beyond PFAS) have also been shown to impact fate and transport of PFAS in the subsurface environment. Two solution characteristics typically investigated are pH and inorganic ion concentration. It has also been found that sorption to particulate in the solution (e.g., particulate OC) can have a significant effect on PFAS transport; however, this effect is less studied [57]. The influence of pH is reported as an inverse relationship with sorption. A decrease in pH will typically result in an increase in sorption of anionic PFAS and vice versa due to alterations in charge at potential sorption sites in soils with variably charged clays [27,56,66,72,85]. However, the majority of prior studies hold pH constant. Studies have also found that pH will control how PFAS compounds interact with sediment and soil (i.e., hydrophobic vs. electrostatic). At lower pH, electrostatic interactions are expected to dominate. At environmentally relevant pH conditions, hydrophobic interactions are favorable [27,76]. Additionally, Campos-Pereira et al. (2018) found that changes in pH affected longer-chained PFAS more than short-chain

PFAS. Functional groups also seem to have an effect on how PFAS react to changes in pH, with PFOA found to be less impacted by alterations to pH than PFOS [87]. Although not discussed in this work, these differences may also be influenced by differences in dissociation constants (pKa) of the select PFAS compounds. Two meta-analyses identified pH as one of three important controls on PFAS sorption, which also included OC and clay content of soils and sediments [51,75].

Ionic strength of solution has also been identified as a solution characteristic that affects PFAS sorption. The cations Ca^{2+} (calcium), Na^+ (sodium), Mg^{2+} (magnesium), and K^+ (potassium) are the most commonly investigated. Typically, an increase in ionic strength correlates to an increase in sorption [27,38,72,88]. Higgins and Luthy (2006) investigated the impact of altering Ca^{2+} and Na^+ ionic strength on sorption of a variety of anionic PFAS. They found that log K_d increased by 0.36 ± 0.04 with each log unit increase of Ca^{2+}, but there were no significant changes correlated to changes in Na^+. Chen et al. (2012) performed similar experiments to investigate the impact of altering the concentration of Ca^{2+}, Na^+, Mg^{2+}, and K^+ on the sorption of PFOS in a saltwater environment. For PFOS at a concentration of 10 μg/L, they found the log K_d increased 0.48 ± 0.03 per log unit of salinity. For the monovalent cations, they found that an increase in K^+ resulted in no changes, whereas an increase in Na^+ doubled the sorbed PFOS. For divalent cations, it was found that, per log unit increase of Ca^{2+} and Mg^{2+}, the log K_d increased by 0.50 and 0.52, respectively. Meta-analysis by Li et al. (2018) found no significant relationships between the change in Ca^{2+} and Na^+ and the sorption of PFOS and PFOA. However, they did find that Ca^{2+} displayed significant relations with EtFOSAA and PFDS. It has been noted that it is difficult to isolate the impact of changes in ionic strength as these changes are likely to alter pH [27,51].

2.3.4. Transport in Unsaturated Zone

In the unsaturated zone, surfactant behavior of PFAS (e.g., hydrophobicity of the C–F tail) results in adsorption (or accumulation) to AWIs [37,38,41,60] and fluid–fluid interfaces (FFI), such as NAPL–water [42,43,50]. Due to surficial discharge (e.g., AFFF discharge), PFAS behavior in the unsaturated zone is of critical importance. As such, investigation of interfacial sorption has increased in recent years [89,90]. Both AWI and FFI enhance retardation, with air–water interface adsorption (AWIA) found to be more significant. AWIA can account for over 70% of PFAS mass [60,91]. Both forms of interfacial sorption have been fitted with a variety of sorption isotherms, including the linear [92], Freundlich [74], and Langmuir isotherms [43,91]. Prior studies found that the linear isotherm is sufficient to describe low environmentally relevant PFAS concentrations [92]. Others have concluded that the Langmuir isotherm can only be reliably used at higher concentrations as it significantly underestimates interfacial sorption at low concentrations [74]. This underestimation is because the surface activity of PFAS increases with lower concentrations, resulting in elevated interfacial sorption [74].

AWIA is influenced by characteristics of the solution and adsorbate. Silva et al. (2019) found that AWIA of PFCAs is influenced by chain length, with longer chains (higher hydrophobicity) resulting in increased AWIA. Additionally, pH and ionic strength of solution have also been found to affect AWIA, with increases in both resulting in enhanced sorption [38,41,43]. Lyu and Brusseau (2020) found that ionic strength was more important than pH [38]. Li et al. (2019) found that increases in both Ca^{2+} and Na^+ result in enhanced AWIA, with Ca^{2+} having a larger impact [21]. Saturation is also a critical factor determining the amount of PFAS sorbed (Figure S3). Guo et al. (2020) modeled the fate and transport of PFOS in the unsaturated zone [60]. They found that sediments of higher permeability (e.g., sand) had higher retardation factors due to enhanced AWIA when compared to materials of lower permeability (e.g., clay). They attributed this to increased AWI area at lower saturations (fine-grained media retains more water compared to larger-grained media). Similar findings of both the influence of saturation and grain size on AWIA have been generated in several recent studies [41,93]. Some studies have proposed estimating

AWI area by using soil water content and the van Genuchten model equations [93–96]. Additionally, AWIA can account for PFAS residence times on decadal time scales and has been observed in field studies, which has implications for AFFF discharge sites [52,59,78].

3. Transformation and Degradation

Polyfluorinated PFAS have been shown to transform and degrade (e.g., defluorination) in both field- and laboratory-scale studies. However, all facets of the transformation and degradation process are not well understood [1,2,97,98]. What is known is that PFAAs are quite stable under environmental conditions and typically represent the end product of a degradation pathway [99–101]. Conversely, precursor compounds, such as FTSAs, FTCAs, and FTOHs, have shown the capability to be degraded and transformed through a variety of abiotic and biotic processes [97,102–106]. When degradation occurs, the resulting PFAS compound will typically exhibit a reduction in C–F chain length and/or a change in functional group [107,108]. Complete degradation to inorganic constituents is not expected under typical environmental conditions [109].

The n:2 FTOHs and ECF-derived perfluoroalkane sulfonamido derivates, such as N-ethyl perfluorooctane sulfonamidoethanol (EtFOSE), have been identified as critical to greater understanding of PFAS degradation and transformation [98,100]. These compounds are of particular interest because they are intermediate products in the degradation of many larger, more complex precursor compounds that eventually result in degradation to PFAAs [97,110–113]. For example, a proposed degradation pathway for EtFOSE to PFOS is as follows: EtFOSE to N-ethyl perfluorooctanesulfonamido acetic acid (EtFOSAA) to N- ethylperfluorooctane sulfonamide (EtFOSA) to perfluorooctane sulfonamide (FOSA) to perfluorooctane sulfinate (FOSI) to PFOS [114]. This transformation pathway (or portions of it) has been observed in numerous studies of biotransformation, including bacteria, plants, and earthworms [100,115–118]. Biotransformation of polyfluoroalkyl substances has also been observed under typical environmental conditions (e.g., aerobic soils) (Figure 2) [100,119]. Additionally, biotransformation and degradation pathways of anionic, zwitterionic, and cationic fluorotelomers, such as FTOHs, 6:2 fluorotelomer thioether amido sulfonate (FtTAoS), 6:2 sulfonamidoalkyl betaine (6:2 FTAB), 6:2 sulfonamidoalkyl amine (6:2 FTAA), 6:2 fluorotelomer sulfonates (6:2 FTSA), and 6:2 sulfonamidoalkyl betaines (6:2 FTAB), have been observed [120–122]. The n:2 FTSA has been identified in lab studies as a product of aerobic transformation that is difficult to further degrade in environmental conditions [123]. Field observations at AFFF discharge sites have supported this degradation pathway, with relatively high levels of FTSA [124]. Additionally, availability of oxygen has been found to influence biotransformation of precursors, with aerobic conditions being the most favorable, followed by anoxic and anaerobic conditions [100,108,125]. Ultimately, biotransformation can be a slow process dependent upon the characteristics of the PFAS compound and soil and sediments it inhabits [1,100]. Lithology has a strong influence on redox condition and the distribution of aerobic and anaerobic zones within the subsurface environment [126,127].

Observations at AFFF discharge sites support PFAS degradation, where measured PFAS in the subsurface does not align with AFFF formulations that are known to have been used [27,34]. Barzen-Hanson et al. found that FtTAoS was present in AFFF- contaminated groundwater and was not within the AFFF formulation used at the site [28]. Nickerson et al. determined two forms of potential PFAS degradation: fluorotelomer degradation to PFCAs and a variety of ECF-derived sulfonamides to perflourohexane sulfonamide (FHxSA) [59]. Degradation of fluorotelomers to PFCAs was presented as an explanation to increasing concentrations of PFCAs and decreasing concentrations of fluorotelomers regarding downgradient movement. McGuire et al. discovered an unusual PFHxS to PFOS ratio, which was attributed to enhanced microbial activity resulting from hydrocarbon remediation at Ellsworth Air Force Base [78]. Mejia-Avendaño et al. observed increasing levels of PFAAs and n:2 FTSA, coinciding with an overall decrease in PFAS over two years at an AFFF discharge site [124].
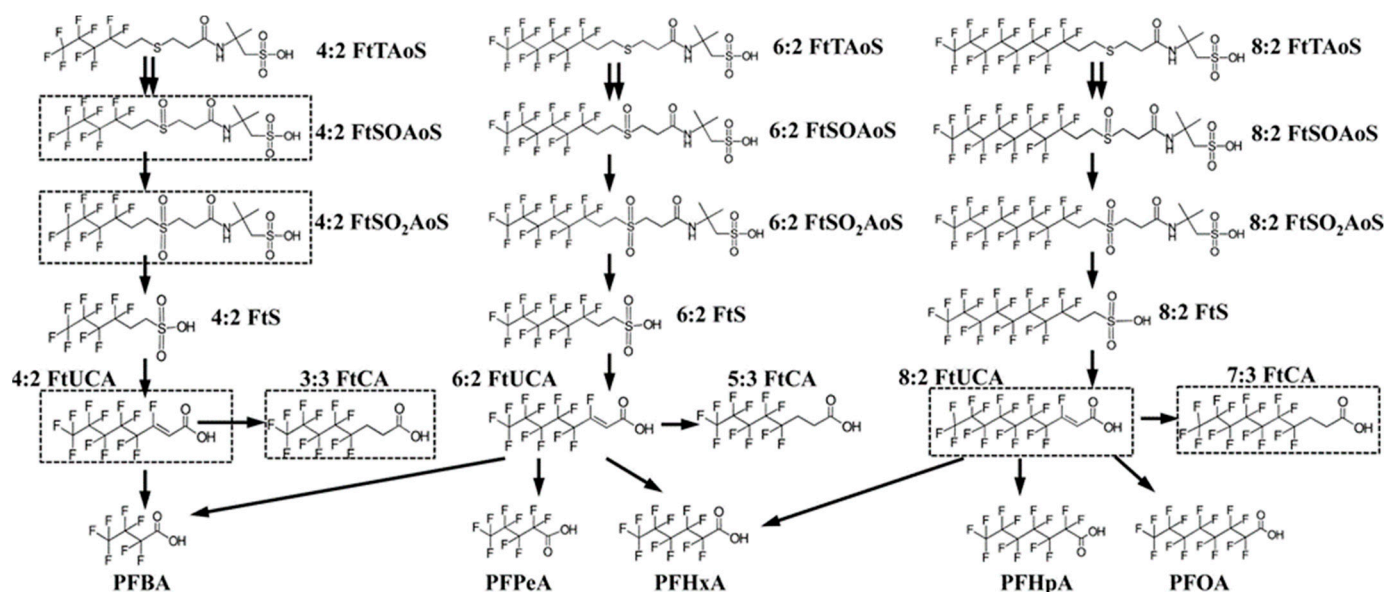
Figure 2. Biotransformation pathways of n:2 FtTAoS in aerobic soil as proposed by Harding-Marjanovic et al. [119]. Boxed compounds are inferred degradation products and were not observed in experimentation. Single arrows indicate biologic degradation. Double arrows indicate both biologic and abiotic degradation. From Harding-Marjanovic et al. [119]. Reprinted with permission of American Chemical Society.

4. Plant Interactions

Within AFFF-impacted sites, we acknowledge that plant interactions may not be as prevalent as in other PFAS-contaminated sites. At a fire training area (FTA), it is inherently unsafe to have plants and vegetation beyond grass species due to an increased flame risk. Thus, interactions with plants with expansive root systems (e.g., trees) are less likely. However, plants present a major biogeochemical feature within the unsaturated zone, which in turn impacts PFAS fate and transport [98].

Plant uptake is typically described using a bioconcentration factor (also known as bioaccumulation factor) or transpiration stream concentration factor [128]. To date, plant interactions with PFAS are typically investigated in controlled conditions of a greenhouse using primarily food crops and some native plants [128–131]. Gobelius et al. investigated trees surrounding a AFFF discharge site at a Swedish airport in order to determine phytoremedial potential of various species (Figure 3) [132]. They proposed a series of potential phytoremediation strategies, including birch and spruce timber stands removing 1.4 g PFAS per hectare/year and a mix of bushes and ground cover removing 0.55 g PFAS per hectare/year. A similar greenhouse study concluded that the combination of herbaceous plants (i.e., grasses) and woody plants (i.e., trees) would maximize phytoremediation [129].

PFAS characteristics have been found to influence plant interactions. Short-chained PFAS are more likely to be absorbed by plants, which has been attributed to sorption of long-chained PFAS to sediment and soil (and thus higher concentrations/bioavailability of short-chained PFAS in solution) [131]. Additionally, it has been found that shorter-chained PFAS are more likely to migrate upward through the plant (i.e., stem, leaves, etc.), whereas longer-chained PFAS are more likely to be found in the roots [133–136]. Charge of the PFAS compound can also affect plant interactions, with cationic PFAS potentially being more likely to interact with plants due to negatively charged root surfaces [98].
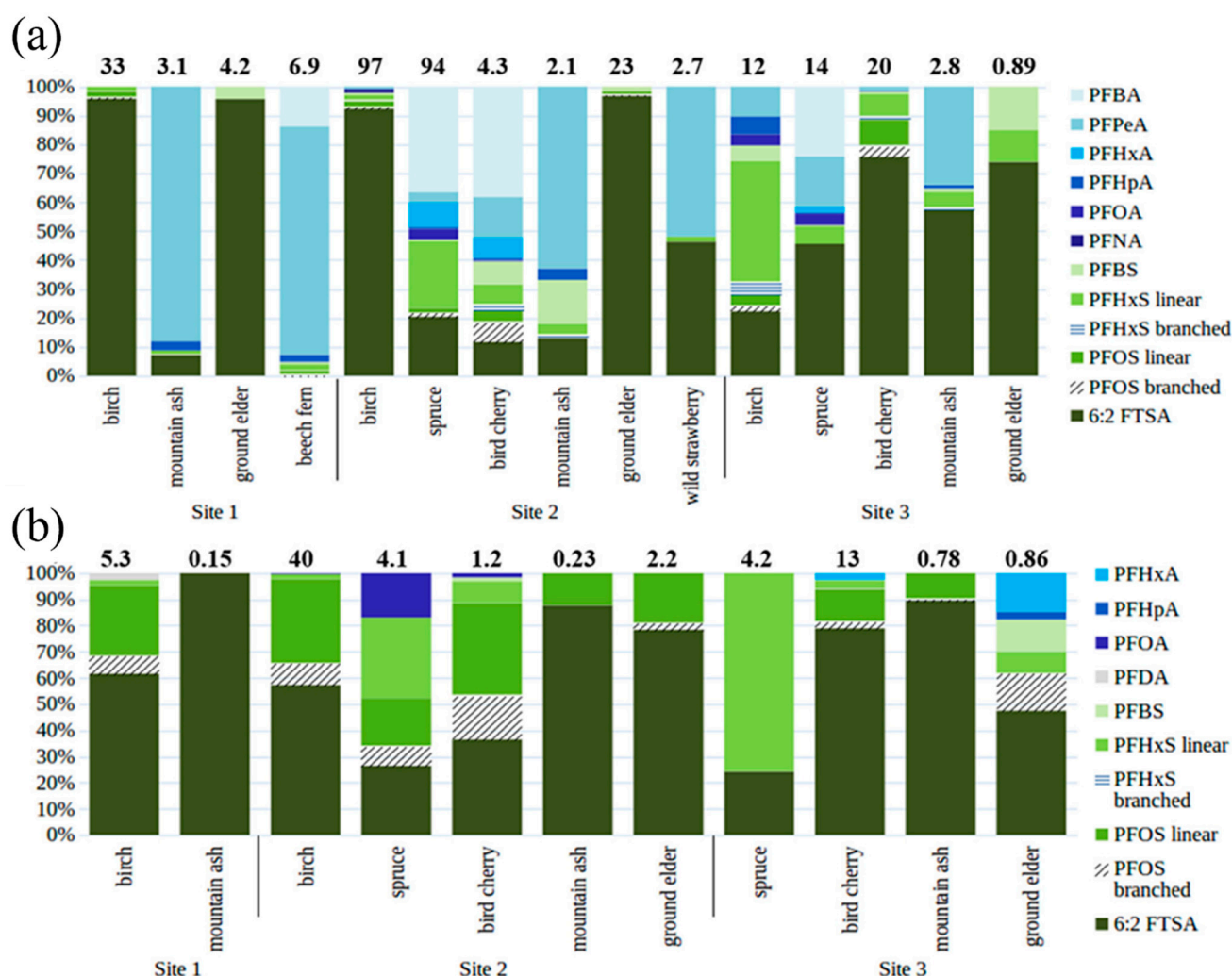
Figure 3. PFAS concentrations in a variety of plant species ((**a**) foliage; (**b**) twigs and stems) collected around a fire training site at the Stockholm Aranda airport in Stockholm, Sweden. Both plots' species are separated as trees, bushes, and ground cover. Total PFAS mass (ng/g) is presented at the top of each bar. From Gobelius et al. (2017) [132]. Reprinted with permission of American Chemical Society.

5. Case Studies and Implications for AFFF-Impacted Sites

5.1. Unspecified US Military Firefighter Training Area

Adamson et al. and Nickerson et al. both examined PFAS distribution related to an FTA active from 1968 to 1991 at an unnamed military base in the United States [52,59]. The FTA was a 36 m unlined shallow pit in which firefighters used AFFF for training using a variety of vehicles and equipment coupled with hydrocarbon fuels. The underlying geology of the site consists of heterogeneous layers of sand, silt, and clay. The uppermost 1–2 m of material at this site was remediated for hydrocarbon contamination in 1994. Samples used to characterize PFAS distribution at the site were collected in 2017, 26 years after the final AFFF release.

Nickerson et al. examined the PFAS concentrations in both soil and groundwater samples [59]. The highest concentration of PFAS was found in the FTA and slightly down-gradient of the FTA, which was attributed to overspray at the site. A surface sample located downgradient of the FTA had a higher PFAS concentration than the FTA itself, which was attributed to the 1994 remediation effort. Increasing PFAS concentration with depth was attributed to downward vertical flow and retention in lower-permeability layers of silt and clay due to low flow and higher sorption. Specifically, PFOA and PFOS concentrations both increased with depth. However, PFOA showed a more consistent downward increasing

trend. This was attributed to higher retention of PFOS in surficial soils or potentially differences in AFFF formulation throughout the site's usage. Cationic and zwitterionic compounds experienced limited lateral and vertical downward transport, with zwitterionic compounds being more readily transported than cationic compounds. This is important because source areas can be a sink for cationic and zwitterionic PFAS precursors. The source area can later act as a source of more mobile anionic PFAAs via degradation. Two forms of potential PFAS degradation products were reported: fluorotelomer degradation to PFCAs and degradation of a variety of ECF-derived sulfonamides to perflourohexane sulfonamide (FHxSA). Degradation of fluorotelomers to PFCAs was presented as an explanation of increasing concentrations of PFCAs and decreasing concentrations of fluorotelomers when moving downgradient. Furthermore, fluorotelomers were found to be more common in groundwater samples than in unsaturated soil samples, which promote fluorotelomer's bioavailability and transformation to PFCAs. A similar trend was observed between ECF-derived sulfonamide zwitterions and FHxSA. ECF-derived sulfonamides were observed in higher concentrations upgradient of the discharge site, whereas FHxSA was observed in higher concentrations downgradient of the discharge site.

Adamson et al. used measurements by Nickerson et al. and calculated the total mass and the mass distribution throughout the site [52,59]. They found that the total mass was split 48:52 between PFAAs and polyfluorinated precursors, respectively. Of the precursor compounds, 83% of those were either cationic or zwitterionic. As for spatial distribution, 47% of the total PFAS mass was located at or close to the FTA, and 53% was located downgradient of the discharge site (Figure 4). Partitioning between precursor compounds and PFAAs was apparent, with 69% of precursors located within or near the FTA and 77% of PFAAs found downgradient of the discharge site. Zwitterionic and cationic precursor compounds were the primary precursors retained in and near the FTA. This retention was attributed to electrostatic interactions with the sediment. Anionic precursors were found downgradient along with the anionic PFAAs (Figure 4). Chain-length-based partitioning of PFAAs was also observed. This partitioning was attributed to differences in sorption due to hydrophobic interactions, where long-chain PFAS underwent more sorption and short-chain PFAS were more mobile. Additionally, PFAS were found to concentrate in sediments of lower permeability. Specifically, 82% of PFAS total mass and 91% of precursors were found within low-permeability sediments (e.g., silt and clay). Retention in low-permeability sediments was even higher in the source area, with 93% and 99% of total PFAS mass and precursor compounds retained, respectively. Ultimately, PFAS retardation in and near the FTA could be due to a combination of sorption due to hydrophobic and electrostatic interactions and diffusion into low-permeability silts and clays.
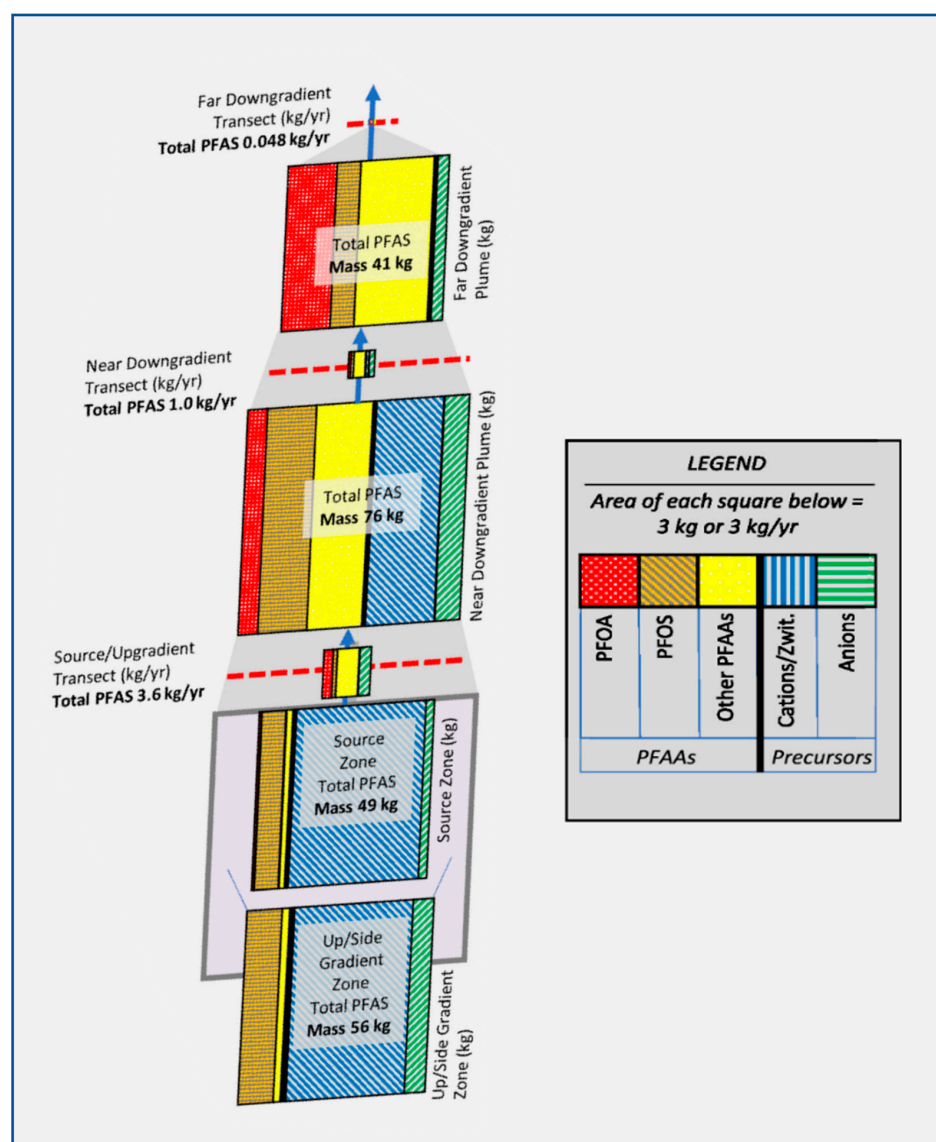
Figure 4. PFAS mass distribution and discharge rates at a fire training site on an undisclosed US military base. Modified from Adamson et al. (2020) [52]. Reprinted with permission of American Chemical Society.

5.2. Ellsworth Air Force Base Firefighter Training Area

McGuire et al. (2014) examined PFAS distribution related to an FTA active from 1942 to 1990 at Ellsworth Air Force Base in South Dakota [78]. A variety of groundwater remediation techniques were used at the site from 1996 to 2011. The FTA was a 36.5 m diameter unlined pit used to extinguish fires set on a variety of oils, solvents, and fuels. The underlying geology of the site consists of clay loam and gravely sandy loam soil ranging in thicknesses of 3 to 9 m with interbedded lenses of sand and clay. The unconsolidated sediments are underlain by shale bedrock. Samples used to characterize PFAS distribution were collected in 2011 and 2012, 21 years after the final AFFF release.

Efforts to characterize PFAS distribution were achieved by sampling surface soils 0.6 m below the ground surface, sediment samples immediately above the water table, and groundwater samples. Analysis revealed that the highest PFAS concentrations were located in and around the FTA. Surface samples had the highest concentrations and were similar to results in other field studies [137] in which AWIA was found to have a strong influence [37,38,41,60]. The PFAS distribution in the sediments from immediately above the water table mostly followed the distribution of a known volatile organic compounds

(VOC) plume, with the highest PFAS concentrations being downgradient of the FTA (Figure 5a–c). PFOS was an exception, with a plume that had dispersed perpendicular to expected groundwater flow. A similar trend was observed within groundwater samples (Figure 5d–f). Chain-length-based partitioning of the PFAS plume was not observed (e.g., long- and short-chain PFAS seemingly travelling at the same rate). Elevated concentrations of polyfluorinated PFAA compounds were found in the same area with elevated PFOS concentrations. Variable PFAS plume distribution is potential evidence of alterations to the plume during remediation of other contaminants. During remedial processes, biogeochemical transformations were likely enhanced by oxygen injection, stimulating microbial processes. The authors propose that transformation of precursors to PFAAs was accelerated during remedial efforts, explaining the relatively low concentrations within the area of the VOC plume. They also proposed that transformation of precursors to PFAAs would explain the lack of expected chain-length-based partitioning of PFAAs. The authors state that the observed mass of PFAAs were not released during AFFF-related training exercises but were attributed to degradation of precursors.
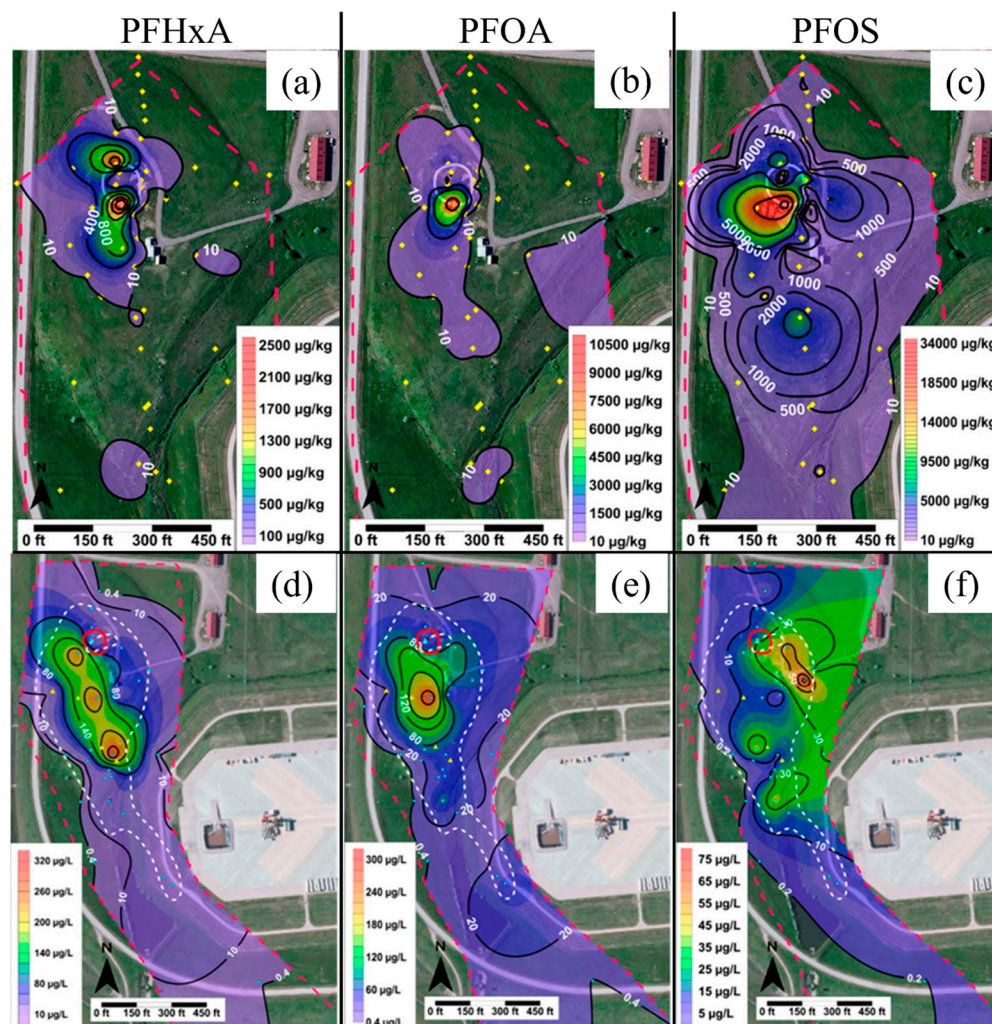

Figure 5. PFAS plume concentrations in soil (**a–c**) and groundwater (**d–f**) at the FTA in the Ellsworth Air Force Base. In all plots, the red dashed line represents the extent of the point-sampled data. In plots (**a–c**), yellow diamonds represent soil sampling locations. In plots (**d–f**), the white dashed line indicates the extent of a benzene plume in 2002, yellow triangles represent oxygen infusion wells, and blue circles are groundwater sample locations. From McGuire et al. (2014) [78]. Reprinted with permission of American Chemical Society.

5.3. Non-Fire-Training-Area AFFF Release Sites on a Variety of US Air Force Installations

Anderson et al. examined PFAS distribution related to non-FTA AFFF discharges at ten active US Air Force bases with reported discharges between 1970 and 1990 [35]. This study is unique in that it excludes FTAs in order to examine sites with less AFFF discharge. The selected sites did not undergo significant remedial actions to minimize human impacts on PFAS. Survey sites were subdivided into low-, medium-, and high-volume AFFF discharge sites representing emergency response locations, hangars, buildings, and testing and maintenance sites, respectively.

Common trends were observed across each of the sample location types. PFOS was the most commonly detected PFAS and also found in the highest concentrations. PFHxS was the second most common. However, the detection frequencies of the 16 PFAS compounds examined varied depending on the historic discharge frequency, with high- and medium-volume discharge sites sharing similar detection frequencies and low-volume discharge sites having significantly lower detection frequencies. Beyond examining non-FTAs, this study is also unique regarding its use of linear discriminant analysis. Using this method, the authors were able to investigate numerous PFAS transport relationships, including solid- vs. aqueous-phase concentrations and the influence of chain length on transport. It was determined that PFAS compounds have an affinity for solid-phase sorption processes. Differences in sorption between PFAS compounds were determined to be dependent on chain length and functional group, with chain length being the dominant factor. The impact of chain length on sorption was found to be non-linear, with longer-chain PFAS being more likely to sorb, especially those with >C8 chains. The impact of functional group was found to be important for PFAS compounds with <C8 chains, with PFSAs having a higher affinity for the solid phase in relation to PFCAs. Additionally, the influence of precursor transformation was proposed as the cause of relatively high concentrations of PFOS and PFHxS, with 40% and 36% of each compound formed via precursor transformation, respectively.

6. Conclusions and Future Research Directions

PFAS are a diverse group of chemicals consisting of over 5000 species. The fate and transport of these chemicals in subsurface environments are quite complex and difficult to fully understand and quantify. The behavior of PFAS is affected by a number of properties of the adsorbent, adsorbate, and aqueous solution. Within the literature, primary controls on PFAS sorption have been identified as the C–F chain length and functional group of the PFAS compound, OC and clay content of soil and sediments, and pH and ionic strength of the aqueous solution, with other properties having less and variable impacts. Further complicating fate and transport are plant interactions, transformation, and degradation. Longer-chained PFAS compounds have an affinity for plant roots, while shorter-chained PFAS will be removed from the subsurface system and transmitted to above ground portions of the plant. Polyfluorinated precursors have been found to transform and degrade on timescales ranging from days to years, which presents a long-term indirect source of PFAS in the subsurface. Furthermore, in the case of transport in the unsaturated zone, such as an AFFF discharge site, PFAS have displayed enhanced retardation due to an affinity to different interfaces (e.g., AWI and fluid–fluid interfaces). AWI in particular has been shown to have the ability to increase residence times in the unsaturated zone by decades. With these factors in mind, we suggest a more comprehensive approach to PFAS research endeavors that accounts for the wide variety of environmental variables that have been shown to impact PFAS fate and transport. Several critical areas of required future research have been identified:

- The impact of subsurface heterogeneity on PFAS fate and transport at the field scale is not well understood. Prior work on fate and transport of non-reactive and reactive solutes, including sorptive solutes such as perchloroethylene (PCE), have concluded that subsurface transport in soil and sedimentary aquifers cannot be understood without understanding, characterizing, and modeling physical and chemical heterogene-

ity [138–140]. Specifically, hydrogeologic and sedimentologic field studies have created a body of literature studying the link between geologic structure and heterogeneity in permeability and/or K_d values [141,142]. Soltanian et al. have shown that reactive transport models accounting for proper representation of geologic structure and resulting variability in permeability and/or K_d can effectively capture the non-ideal behavior of sorptive contaminant plume (e.g., plume retardation and macrodispersion) without curve fitting [143,144]. These studies relied on highly resolved datasets in order to quantify the spatial co-variability between permeability and/or K_d within and across geologic units to explain a PCE plume behavior. There are currently no data available quantifying such spatial co-variability for PFAS compounds. As reactive transport models require a representation of how permeability and/or K_d vary in space [64,145–148], basic research on quantifying the spatial variability in PFAS reactive attributes and the co-variability between permeability and the reactive attributes needs to be investigated.

- Tracers in field-scale studies that have been found to exhibit transport behavior similar to PFAS without the negative effects need to be utilized in future research. Sörengård et al. (2020) performed batch sorption experiments with a variety of PFAS compounds and dyes and found that some dyes and PFAS shared similar sorption characteristics. Thus, such dyes could be used in field experiments to examine the impacts of heterogeneity on fate and transport in a well understood field site, similar to that of work at the Canadian Forces Base Borden site [149].

- A better understanding of PFAS in the unsaturated zone is critical. AFFF is applied to the ground surface and transported in runoff. These chemicals have been shown to be retarded in the unsaturated zone and thus more investigations into transport in the unsaturated environment are warranted. More expansive column experiments and modeling using a variety of sediments and PFAS compounds similar to prior work using sands are needed [60,71].

- Adsorptive behaviors of contaminants in the subsurface could enhance our understanding of existing and emerging remedial techniques. For example, if it is determined what retards transport of a particular PFAS in the subsurface, then those principles could be applied to remedial technologies. Thus, more research on individual factors influencing PFAS sorption is needed.

- A combination of factors (e.g., OC, clay content, and pH) is required to describe PFAS sorption onto sediments [51,75]. To further this understanding, the development of a more mechanistic understanding is needed in order to account for more complex process-based models, such as surface complexation, which has previously been used to better understand contaminants [150,151].

- Borthakur et al. demonstrated that flow interruptions can significantly increase PFAS concentrations in the pore water of saturated soil due to the release of soil colloids carrying PFAS [152]. This phenomenon was found to be dependent on chain length, with higher increases observed for PFOA compared to perfluorobutanoic acid (PFBA), potentially due to the greater affinity of PFOA for soil colloids. This study underscores the potential of colloids in facilitating the transport of PFAS, which may contribute to exceedances in PFAS concentrations beyond the health advisory limit set by the USEPA. Importantly, this research highlights that neglecting the role of colloids could lead to an underestimation of PFAS concentration in water samples, suggesting the need to desorb PFAS from colloids prior to analysis for estimating the true PFAS concentration. However, this area remains underexplored, and additional research is required to further elucidate the role of colloid-facilitated transport in the fate and transport of PFAS in natural subsurface media. Future studies could focus on investigating the influence of various soil types and flow conditions on colloid–PFAS interactions and the resulting effect on PFAS transport. Moreover, developing analytical techniques to accurately measure PFAS concentration in the presence of colloids would also be a valuable contribution to the field.

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