Science of the Total Environment 771 (2021) 145427

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Review

Fate and transport of per- and polyfluoroalkyl substances (PFASs) in the vadose zone

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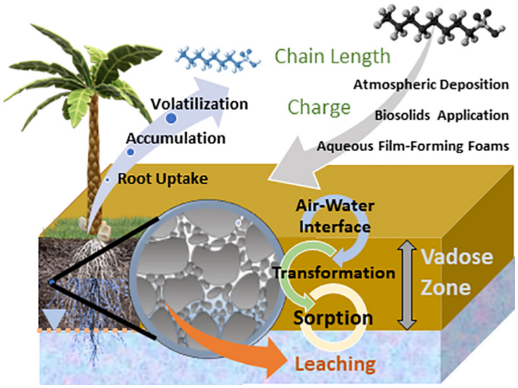
HIGHLIGHTS

- The vadose zone is a critical compartment at many PFAS-contaminated sites.
- PFAS sources, distribution and speciation in the vadose zone are discussed.
- Processes such as sorption, biotransformation, and plant uptake are covered.
- The interrelations of the processes controlling PFAS fate and transport are revealed.
- Current knowledge gaps, key challenges, and research needs are identified.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 20 November 2020
Received in revised form 19 January 2021
Accepted 21 January 2021
Available online 26 January 2021

Editor: Jay Gan

Keywords:
PFAS sources
Sorption
Air-water interface
Biodegradation
Microbial community impact
Plant uptake

ABSTRACT

Per- and polyfluoroalkyl substances (PFASs) are a heterogeneous group of persistent organic pollutants that have been detected in various environmental compartments around the globe. Emerging research has revealed the preferential accumulation of PFASs in shallow soil horizons, particularly at sites impacted by firefighting activities, agricultural applications, and atmospheric deposition. Once in the vadose zone, PFASs can sorb to soil, accumulate at interfaces, become volatilized, be taken up in biota, or leach to the underlying aquifer. At the same time, polyfluorinated precursor species may transform into highly recalcitrant perfluoroalkyl acids, changing their chemical identity and thus transport behavior along the way. In this review, we critically discuss the current state of the knowledge and aim to interconnect the complex processes that control the fate and transport of PFASs in the vadose zone. Furthermore, we identify key challenges and future research needs. Consequently, this review may serve as an interdisciplinary guide for the risk assessment and management of PFAS-contaminated sites.

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https://doi.org/10.1016/j.scitotenv.2021.145427
0048-9697/

Contents

1. Introduction

Per- and polyfluoroalkyl substances (PFASs) are a highly complex group of anthropogenic chemicals comprising thousands of individual species (Barzen-Hanson et al., 2017; Wang et al., 2017). PFASs may vary in functional group substitution, ionization state, chain length, degree of branching and other characteristics, but their perfluoroalkyl moiety provides a common chemical and thermal stability along with both hydrophobic and oleophobic properties (Buck et al., 2011). In addition, polar and ionizable headgroups cause surface-active behavior (Brusseau and Van Glubt, 2019; Psillakis et al., 2009; Schaefer et al., 2019; Silva et al., 2019). These unique features have resulted in a broad use of PFASs in consumer products such as non-stick cookware, food packaging, paints, cosmetics, carpets and textiles, and in applications such as fluoropolymers, aqueous film-forming foams (AFFFs), papermaking, oil production, mining, metal plating and electronics (Tokranov et al., 2018; Wang et al., 2017).

Inadvertent PFAS emissions occur during fluoropolymer manufacturing as well as during use, degradation, and disposal of PFAS-containing products (Wang et al., 2014). While labile non-fluorinated moieties of PFASs are prone to partial abiotic and biotic transformation processes, the chemical and thermal stability of the perfluoroalkyl groups translates into an extraordinary recalcitrance in the environment. PFAS migration in the environment can proceed at a local or regional level via surface water and groundwater (Hu et al., 2016), and at a global level through long-range oceanic and atmospheric transport (Armitage et al., 2009; Young and Mabury, 2010). However, awareness of their global occurrence and environmental persistence only started to emerge in the early 2000s, some five decades after commencing their large-scale commercial production, when perfluorooctane sulfonate (PFOS) was detected in wildlife from remote habitats (Giesy and Kannan, 2001) and when several perfluoroalkyl acids (PFAAs) were widely detected in human blood serum samples (Calafat et al., 2007; Kannan et al., 2004). Concerns about bioaccumulation led to the gradual phase-out of long-chain species in several countries by 2015, and an associated shift in production to short-chain alternatives (Wang et al., 2019; Heydebreck et al., 2015; Munoz et al., 2019; Strynar et al., 2015).

While the distribution of PFASs in the atmosphere and hydrosphere is comparably well investigated (Hu et al., 2016; Rauert et al., 2018; Wang et al., 2015), data on soil contamination is sparse (Table 1). In contrast to other environmental contaminants with subsurface sources such as underground storage tanks or pipelines, PFASs are nearly always released to the environment through above-ground activities (i.e., AFFF application, land application of biosolids, etc.), with a few notable exceptions such as unlined landfills. As a result, when PFASs are released in terrestrial environments, they will almost always interact with soils before impacting groundwater or surface water, suggesting an even greater need to understand PFAS behavior in soils. Studies conducted thus far consistently report the accumulation of PFASs is predominantly in shallow soil horizons (Nickerson et al., 2020; Sepulvado et al., 2011; Hale et al., 2017; Xiao et al., 2015) (Table 1), implying that PFASs in the vadose zone represent a primary reservoir for long-term groundwater contamination (Brusseau and Van Glubt, 2019; Barzen-Hanson et al., 2017). The vadose zone is the unsaturated zone of the subsurface that extends from the terrestrial surface to the groundwater table and includes soil or sediment, pristine and weathered organic material, and a partially saturated capillary fringe. This shallow surface horizon harbors high densities of microbial biomass, with distinct species capable of thriving under relatively low water availability conditions (Holden and Fierer, 2005). The vadose zone is connected intimately to the biosphere. As water and its solutes percolate downward, the vadose zone is a critical space for nutrient cycling as well as water and nutrient uptake by animals and plants in the root zone (Xin et al., 2019). Furthermore, the vadose zone is also protective of the underlying groundwater through adsorption, partitioning, ion exchange, volatilization, and degradation processes affecting the fate and transport of environmental contaminants.

Consequently, appropriate risk assessment and environmental management of PFAS-contaminated sites require an interdisciplinary understanding of the various processes that govern the deposition, accumulation, retardation, transformation, and uptake of PFASs in the vadose zone (Fig. 1). Often, this assessment is exacerbated by the complex nature of PFASs and transient changes in the speciation of innumerable non-quantifiable polyfluorinated precursors to recalcitrant PFAAs (Nickerson et al., 2020). To address these critical challenges, the objectives of this review are threefold: (1) to review existing data on PFAS distribution in the vadose zone, (2) to discuss the current state of the knowledge on the nature and interrelations of the processes controlling PFAS fate and transport in the vadose zone, and (3) to provide recommendations for future research addressing the most pressing knowledge gaps.

2. Sources of PFAS contaminations in the vadose zone

In the context of this review, it is important to delineate the types of PFASs whose fate and transport is of concern in the vadose zone. As introduced by Buck et al. (2011), both perfluorinated and polyfluorinated substances are included under the PFAS umbrella, the latter (e.g., fluorotelomer alcohols, FTOHs) of which can serve as precursors in the environment to PFAAs. In either case, individual chemicals or groups of chemicals are generally discussed herein, but these non-polymeric PFASs are specifically differentiated from the polymeric PFASs (Fig. 2). Most environmental research and concerns have focused on non-polymeric PFASs (both poly and per), but, as will be discussed, there is a small body of literature on polymeric PFASs, particularly side-chain fluorinated polymers which have the potential to break down to non-polymeric poly- and perfluoroalkyl substances (Chu and Letcher, 2017; Letcher et al., 2020; Schellenberger et al., 2019). Though non-polymeric PFASs have been and are still used in the manufacturing of fluoropolymers and perfluoropolyether polymers, these polymer subclasses are not explicitly addressed in this review. For more details on PFAS nomenclature, we refer the reader to Buck et al. (2011) and ITRC (2020).

Various sources may contribute to vadose zone contamination with PFASs. Direct sources include atmospheric deposition, application of AFFFs and accidental releases (Nickerson et al., 2020; Gottschall et al., 2017), and are generally comprised of non-polymeric PFASs. Indirect sources include the land application of biosolids and municipal sludges, irrigation with PFAS-contaminated water including reclaimed wastewater, and possibly stormwater (Ahmed et al., 2020; Ray et al., 2019; Sepulvado et al., 2011; Szabo et al., 2018; Blaine et al., 2014b). Besides non-polymeric species, some indirect sources such as biosolids may contain polymeric PFASs, especially side-chain fluorinated polymers from textiles and household products (Chu and Letcher, 2017; Letcher et al., 2020; Schellenberger et al., 2019). At complex contaminated sites with several PFAS sources, their compositional variability creates a “fingerprint” that may be used for forensic source tracking and allocation, which is the focus of ongoing research efforts (Kibbey et al., 2020; Washington et al., 2020). Landfill leachate and surface water contaminated by wastewater discharges are known sources, but thought to be of minor relevance for vadose zone PFAS contamination as these types of discharges occur directly to the impacted water source.

2.1. Atmospheric deposition

Airborne PFASs originating from major sources such as manufacturing facilities and urban centers mainly comprise neutral volatile polyfluorinated compounds such as FTOHs, but also ionic species, including perfluorooctanoic acid (PFOA) and PFOS (Ahrens et al., 2012; Barton et al., 2006; Piekarz et al., 2007; Yao et al., 2017). At reported

Table 1

Overview of previously reported PFAS soil contaminations (potentially incomplete) including information about location, source, major detected PFAS species and their maximum concentrations and depths relative to the surface and water table (where available). For sites where polyfluorinated species were reported as the major PFAS, additional information about the most prevalent perfluoroalkyl acid (PFAA) is provided in the respective row below.

Sample location	PFAS source	Major PFAS species	Max. concentration of major PFAS species (μg/kg)	Depth of max. concentration (m)	Depth to groundwater (m)	Reference
Fire-training area, Norway	AFFF	PFOS	2400	1–2	>4	Hale et al., 2017
Fire-training area, USA	AFFF	TAmPr-FHxSA[a]	140,000	n.p.	n.p.	Nickerson et al., 2020
Fire-training area, USA	AFFF	PFOS	54,000	n.p.	n.p.	Nickerson et al., 2020
Fire-training area, USA	AFFF	TAmPr-N-MeFBSA[b]	9816	4.0	<3	Nickerson et al., 2020
Fire-training area, USA	AFFF	PFOS	1050	4.6	<3	Nickerson et al., 2020
Fire-training area, USA	AFFF	PFOS	754	1.8	<3	Nickerson et al., 2020
Fire-training area, Sweden	AFFF	PFOS	2510	0.5–1	<2	Rosenqvist et al., 2017
Fire-training area, Sweden	AFFF	PFOS	8520	0–0.5	n.p.	Filipovic et al., 2015
Fire-training area, USA	AFFF	PFOS	20,000	5–6	2–8	Houtz et al., 2013
Fire-training area, France	AFFF	PFOS	55,200	0–0.25	20–40	Dauchy et al., 2019
Military building, USA	AFFF	PFOS	9700	n.p.	n.p.	Anderson et al., 2016
Train accident site, Canada	AFFF	6:2 FTAB	1908	n.p.	n.p.	Mejia-Avendaño et al., 2017
Train accident site, Canada	AFFF	PFPeA	157	n.p.	n.p.	Mejia-Avendaño et al., 2017
Manufacturing facility, USA	Atmospheric	PFOA	66.2	n.p.	n.p.	Galloway et al., 2020
Manufacturing facility, China	Atmospheric	PFOA	120	0–0.05	n.p.	Chen et al., 2018
Agricultural land, Canada	Biosolids	PFOA	0.8	0–0.3	≤2	Gottschall et al., 2017
Agricultural land, USA	Biosolids	PFOS	483	0–0.16	n.p.	Sepulvado et al., 2011

n.p. = information not provided.

[a] *N*-Trimethylammoniopropyl perfluorohexane sulfonamide.

[b] *N*-Trimethylammoniopropyl *N*-methylperfluorobutane sulfonamide.

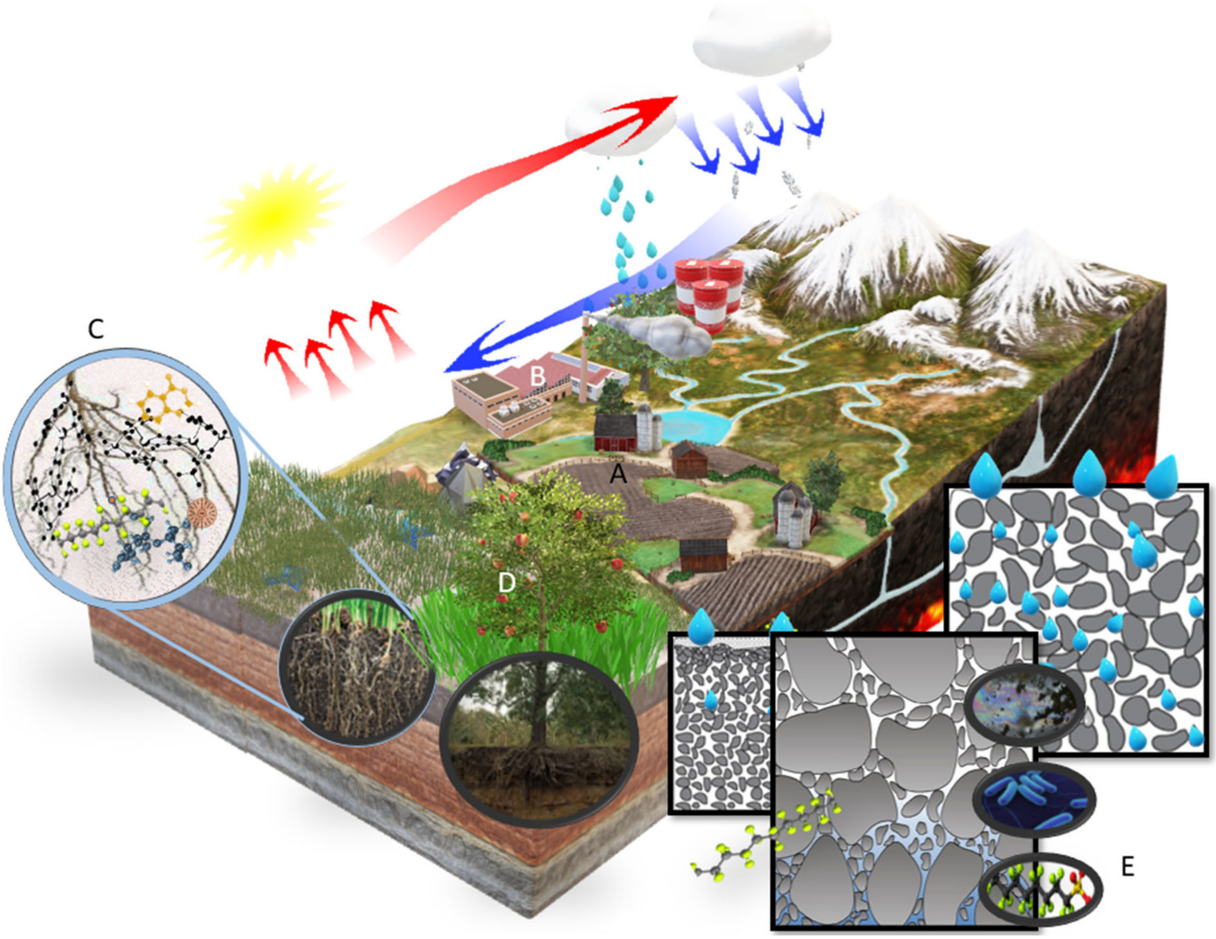

Fig. 1. Major sources of PFASs and their vadose zone fate & transport processes. (A) Agricultural sources such as biosolids application and irrigation with reclaimed wastewater. (B) Emissions from manufacturing and subsequent atmospheric transport. (C) Interactions with plants in soils that lead to accumulation and potentially transformation. (D) Plant uptake and potential phytovolatilization. (E) Interactions between water, soil gas, nonaqueous phase liquids, and soil where microorganisms play a governing role in PFAS transformation.

lifetimes on the order of tens of days, polyfluorinated precursors undergo atmospheric oxidation to form PFAAs (Ellis et al., 2004; D'eon et al., 2006; Piekarz et al., 2007; Ellis et al., 2003). PFASs partition between gas and particle phases in the atmosphere and eventually return to the Earth's surface based on wet or dry deposition processes (Galloway et al., 2020; Fang et al., 2018). Due to the highly dispersed nature of wind direction and speed in combination with the unique stability of PFAAs, atmospheric transport and deposition processes can lead to widespread PFAS contamination and create a regional “background” level in terrestrial ecosystems (Brusseau et al., 2020; Xiao et al., 2015). In a global study, all analyzed soil samples contained at least three perfluoroalkyl carboxylic acids (PFCAs) (Chen et al., 2018; Washington et al., 2020). Total concentrations of PFCAs and perfluoroalkane sulfonic acid (PFSAs) ranged from 29 to 14,300 ng kg^{-1} and from below quantification limit to 3270 ng kg^{-1}, respectively (Rankin et al., 2016). Closer to stationary sources, Xiao et al. (2015) reported PFOS and PFOA concentrations of up to 5500 and 125,700 ng kg^{-1}, respectively, near a former manufacturing facility and historical disposal site in a U.S. metropolitan area. Several studies demonstrated a direct correlation between PFAS concentrations in environmental samples and the major wind direction from the respective sources (Galloway et al., 2020; Chen et al., 2018; Washington et al., 2020; Xiao et al., 2015). While long-range atmospheric transport processes have resulted in PFAS deposition in remote locations of the Earth (Young et al., 2007), maximum PFAS soil contaminations are usually found within tens of km from the source (Galloway et al., 2020).

2.2. Aqueous film-forming foams

Aqueous film-forming foams (AFFFs) are Class B firefighting foams used to extinguish hydrocarbon fuel fires. Besides water, they contain hydrocarbon surfactants, organic solvents, polymers, other additives, and fluorosurfactants (ITRC, 2020). AFFFs have been fabricated through two main processes: electrochemical fluorination (ECF) (Buck et al., 2011), which was discontinued in the U.S. in 2001, and fluorotelomerization. While both types of foams contain polyfluorinated species, ECF foams are dominated by PFOS, other PFSAs, and their precursors (Backe et al., 2013; Place and Field, 2012; Houtz et al., 2013; Anderson et al., 2016; Barzen-Hanson et al., 2017). In contrast, fluorotelomerization leads to the exclusive formation of partially fluorinated homologues differing by C_2F_4 units (Backe et al., 2013; Houtz et al., 2013; Barzen-Hanson et al., 2017). Long-chain species were used in fluorotelomer foams until 2016, when manufacturers began focusing on short-chain “C6 foams” (USEPA, 2018; Kempisty et al., 2018). As a safety measure for fire suppression and firefighting training, military installations, airports, petroleum refineries, chemical manufacturing plants as well as fuel and chemical storage facilities are required to use and store AFFFs (Anderson et al., 2016; Thalheimer et al., 2017). Releases of AFFFs into the environment may occur through controlled activities, such as fire training, and uncontrolled incidents, such as leaks and accidents during transport (Moody et al., 2002; O'Carroll et al., 2020). Thus far, the limited number of studies that have addressed the distribution of AFFF-derived fluorosurfactants at impacted sites have consistently identified PFOS as the major species as

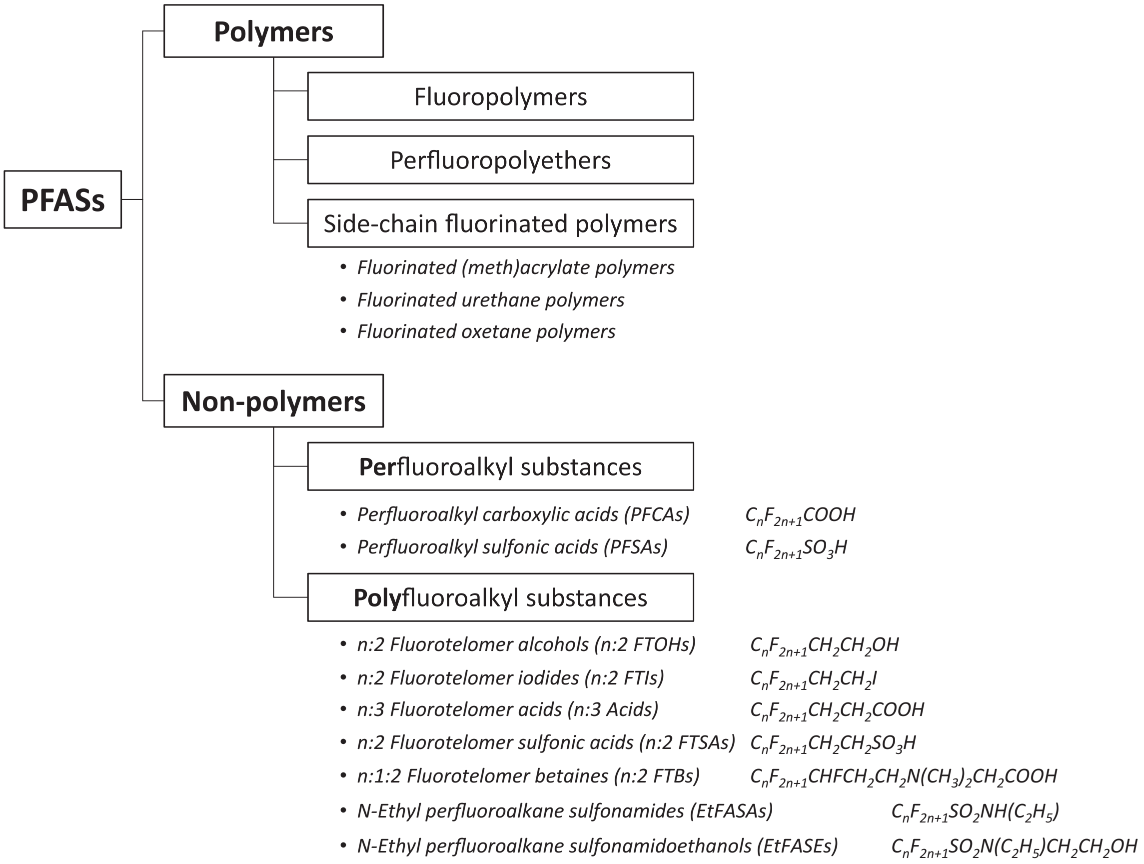

Fig. 2. Classification of PFASs based on Buck et al. (2011) with examples relevant to this review.

well as maximum PFAS concentrations in the top 5 m of the subsurface, often in the top meter (Houtz et al., 2013; Filipovic et al., 2015; Nickerson et al., 2020; Dauchy et al., 2019). However, in contrast to atmospherically deposited PFASs, polyfluorinated precursor compounds typically represent a major fraction of the PFAS pool in AFFF-impacted media. For instance, Nickerson and co-workers reported that cationic and zwitterionic species contributed up to 97% to the total PFAS mass in a soil core collected at an AFFF-impacted fire training area (Nickerson et al., 2020).

2.3. Biosolids

Both municipal and industrial sources contribute to PFAS influent loads to wastewater treatment plants (WWTPs), carrying monomeric species but also fluorinated polymers (Chu and Letcher, 2017; Letcher et al., 2020; Schellenberger et al., 2019). While perfluorinated compounds are generally not removed by wastewater treatment processes, polyfluorinated precursors may be transformed to PFAAs (Loganathan et al., 2007; Schultz et al., 2006). With increasing hydrophobicity, PFASs tend to sorb to solid particles and accumulate in residual sludges (Milinovic et al., 2016). The land application of WWTP sludges and related products such as biosolids, recycling fertilizers, or biocomposts is a common international practice as it recycles nutrients and improves soil properties and fertility (Clarke and Smith, 2011; Clarke and Smith, 2011). The annual biosolids land application was reported to be ~7 million tons (55% of generated biosolids) in the US EPA (2007) and ~4.5 million tons (41% of generated biosolids) in the European Union (Gottschall et al., 2017). However, this practice also transfers PFASs to agricultural soils, resulting in contamination of the shallow vadose zone and ultimately potable water resources, crops, and dairy products (Krepich, 2019; Gribble et al., 2015). In the U.S., an estimated 1375–2070 kg of biosolids is applied to agricultural lands annually, and PFOS is recognized as the most abundant PFAS species (403 ± 127 ng g^{-1}), followed by PFOA (34 ± 22 ng g^{-1}) (Venkatesan and Halden, 2013). A similar finding was reported from Australia (Sleep and Juhasz, 2020), where PFOS was the most abundant PFAS in biosolids at an average level of 25 ng g^{-1} (Gallen et al., 2018). Differences in PFAS concentrations between urban and rural WWTP sludges are considered negligible (Loganathan et al., 2007). However, biosolids may also contain significant levels of polyfluorinated precursor compounds that may transform after land application to more persistent PFAAs (Sepulvado et al., 2011; Lazcano et al., 2020). Due to surface application, maximum PFAS concentrations in biosolids-amended soils are generally found in the most shallow layer of the vadose zone, from which they may be mobilized by leaching, runoff, volatilization, or uptake by plants and soil organisms (Hamid and Li, 2016; Sepulvado et al., 2011; Gottschall et al., 2017; Venkatesan and Halden, 2013).

3. Transport processes of PFASs in the vadose zone

Upon surface deposition and subsequent infiltration into the vadose zone, several transport processes exist that govern the fate of PFASs. Neutral species such as FTOHs, either present in the source material or generated during degradation of precursor compounds (see Section 4 below), may become volatilized (Stoiber et al., 2020; Navarro et al., 2017). PFAS dissolution in infiltrating water from precipitation, irrigation, runoff, or stormwater leads to their leaching and downward migration, where they may be taken up by plant or soil organisms, until they eventually reach the aquifer and form groundwater plumes. Along the way, PFASs may sorb to soil or accumulate at air-water interfaces, two key transport processes that are discussed in detail below. Other transport mechanisms exist depending on the nature of the release, such as co-contaminant interactions including competitive sorption/ion exchange to soil or partitioning into hydrocarbon fuel non-aqueous phase liquids (NAPLs), which often co-occur at AFFF-impacted firefighting or training sites (Guelfo and Higgins, 2013). The extent of PFAS retention in the vadose zone is also dependent on the soil matrix and its moisture content. For example, precipitation leads to higher soil moisture, which may decrease PFAS retention due to less available air-water interfacial area (Silva et al., 2020b; Lyu et al., 2018). The adsorption and retention behavior of PFASs in the vadose zone changes throughout natural cycles of drainage, infiltration, and evapotranspiration. Also, the governing roles of soil texture (i.e., percentages of organic matter, silt, clay and sands) and moisture content are critical, impacting soil hydraulic properties. Overall, heterogeneous textures, moisture content, pressure, slope and temperature complicate PFAS transport behavior in soils (Costanza et al., 2019; Silva et al., 2020a). Additionally, kinetic limitations, varying physiochemical properties and non-ideal competitive adsorption add to the complexity of their transport behavior in the vadose zone (Zhang et al., 2014; Sharifan, 2020).

3.1. Background on PFAS sorption at fluid-fluid interfaces

The PFAS surfactant nature facilitates their sorption to fluid-fluid interfaces. Air-water interfaces that are present in the vadose zone, therefore, have the potential to significantly contribute to the overall PFAS mass balance, and ultimately impact PFAS migration. Previous studies using non-fluorinated surfactants have shown the relative importance of air-water interfacial sorption in unsaturated sands or soils is strongly dependent on: (1) the grain size, where smaller diameter sand/soils have a greater specific air-water interfacial area (a_{aw}), which is typically defined in units of reciprocal length (Peng and Brusseau, 2005; Brusseau et al., 2009); (2) the water content, where a_{aw} generally increases with decreasing moisture content (Schaefer et al., 2000b; Sung and Chen, 2011); and (3) the relative affinity of the surfactant to the air-water interface relative to the solid phase (Kim et al., 1997). These factors are expected to be equally as relevant for PFASs.

Several recent studies have been performed to examine the role of PFAS sorption at the air-water interface. These studies consist of three general approaches: interfacial tension (IFT)-based approaches, unsaturated column retardation approaches, and batch system mass balance approaches. IFT-based approaches have been the most common (Brusseau and Van Glubt, 2019; Costanza et al., 2019; Silva et al., 2019; Vecitis et al., 2008), where various IFT measurement techniques have been employed to determine the air-water interfacial tension as a function of surfactant concentration. This approach relies on the Gibbs Adsorption Equation to relate the IFT to PFAS mass at the air-water interface as follows (Adamson and Gast, 1997; Gurkov et al., 2005):

$$\Gamma = \frac{-1}{RT}\frac{\partial \sigma}{\partial\ \ln\left[C_T\right]} \tag{1}$$

$$C_T = C\ (C + C_s) \tag{2}$$

where σ is the measured air-water interfacial tension, Γ is the surfactant mass sorbed per unit area of interface, C_T is the square of the mean ionic activity, C is the surfactant concentration, C_s is the concentration of background electrolyte (scaled to the valence of the ionic surfactant), R is the gas constant, and T is the temperature. IFT measurements can be performed relatively quickly, thus allowing estimates of PFAS air-water interfacial sorption without the need for PFAS analysis. However, measurable decreases in IFT are typically limited to PFAS concentrations greater than approximately 0.1 mg/L, requiring selection of an appropriate interfacial sorption model to extrapolate Γ to lower concentrations that might be more relevant for historic PFAS-impacted field sites.

Several studies have employed unsaturated column experiments under steady flow conditions to determine PFAS adsorption at air-water interfaces in unsaturated sands and soils (Brusseau et al., 2020; Brusseau and Van Glubt, 2019; Lyu et al., 2018). In these experiments, PFAS retardation factors and ultimately values for Γ are determined by comparing PFAS elution to a conservative tracer that is not surface-active. While these experiments require significantly more effort than IFT measurements, they have the advantage of providing a direct measure of the impact of air-water interfacial uptake on PFAS elution during steady flow in unsaturated sands and soils, and experiments can be performed over a large range of concentrations (including concentrations in the ng/L range). However, the actual air-water interfacial area that PFASs are exposed to during column migration is often uncertain (Culligan et al., 2004; Schaefer et al., 2000a). Thus, attaining accurate estimates of Γ using this technique can be challenging.

Finally, various studies have employed the use of batch experiments where decreases in bulk water PFAS concentrations due to accumulation at the air-water interface are measured over time (Schaefer et al., 2019; Reth et al., 2011). In these experiments, the ratio of air-water surface area to water volume is known in the batch vessel. The decrease in bulk aqueous PFAS concentration due to PFAS uptake at the air-water interface is measured, allowing (via mass balance) for an estimate of Γ at a given PFAS concentration. This method has the advantage of being relatively simple compared to the column method and also consists of a well-defined air-water interfacial area (a_{aw}) for the experimental system. However, practical geometric constraints typically limit the surface area-to-water ratio, thereby limiting the applicability of this method to the more surface-active PFASs, as the mass fraction of less surface-active PFASs that adsorbed to the air-water interface is too small to reliably measure (Costanza et al., 2019).

3.2. Factors controlling PFAS sorption at air-water interfaces

The vast majority of published data on PFAS accumulation at air-water interfaces have focused on PFAAs, and even more specifically on PFOA and PFOS (Schaefer et al., 2019; Lyu et al., 2018). Through the use of all the approaches described above, studies have shown that PFAA sorption at air-water interfaces increases with perfluorinated chain length, and that PFSAs and PFCAs with the same perfluorinated chain length exhibit similar interfacial sorption (Schaefer et al., 2019; Silva et al., 2019). It has also been observed that the counteraction associated with PFOA (e.g., H^+, Na^+, K^+) can have a considerable impact on interfacial sorption (Brusseau and Van Glubt, 2019). Background electrolyte also can have a substantial impact on PFAS interfacial sorption (with respect to overall ionic strength as well as the valence of the background cations), as well as solution pH, as indicated in several IFT studies (Brusseau and Van Glubt, 2019; Costanza et al., 2019; Schaefer et al., 2019; Silva et al., 2019). Lyu and Brusseau (2020) further demonstrated pH and ionic strength impacts on PFOA elution in a series of column studies, confirming their impacts on PFOA migration through unsaturated media. These observations highlight the need to perform interfacial sorption experiments with attention given to geochemical conditions, and to PFAS counterions.

To quantify PFAS sorption at the air-water interface relative to the bulk PFAS aqueous concentration, an interfacial partition coefficient is typically defined as follows:

$$K_{aw} = \frac{\Gamma}{C} \tag{3}$$

where K_{aw} is the air-water interfacial sorption coefficient defined in units of length (Costanza et al., 2019; Lyu et al., 2018). Fig. 3 summarizes values of K_{aw} for PFOS and PFOA in 0.01 M NaCl or synthetic groundwater

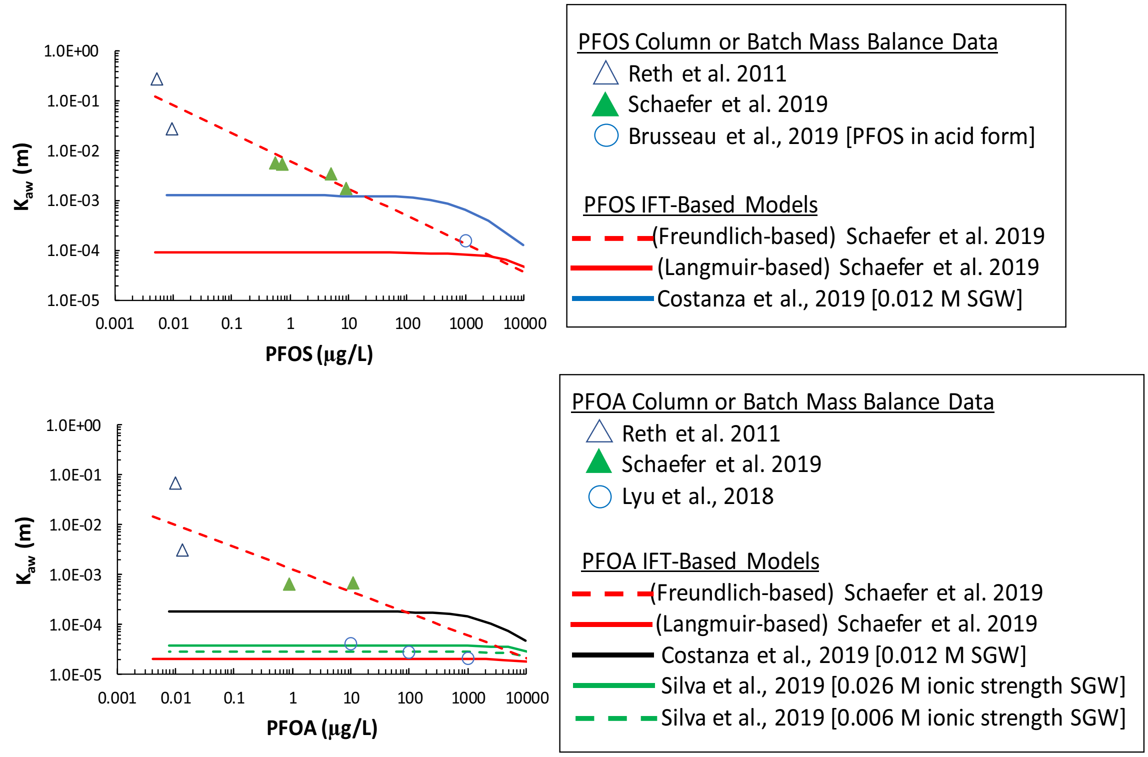

Fig. 3. K_{aw} as a function of PFOS and PFOA concentration. The potassium form of PFOS and acid form of PFOA are used, except where noted. Results are for 0.01 M NaCl solutions, except where noted. Data points from Reth et al. (2011) were based on calculations described in Schaefer et al. (2020). SGW = synthetic groundwater. SGWs contained a mixture of monovalent and divalent cations.

(containing monovalent and divalent cations) from several studies, except where noted. The discreet data points were obtained from either column experiments or the previously described batch mass balance approach. The model lines represent IFT-based experiments where extrapolation below approximately 100 µg/L was based on the selection of either a Langmuir-based isotherm (Costanza et al., 2019; Silva et al., 2019), or a Freundlich-based isotherm (Schaefer et al., 2019).

While both the Langmuir- and Freundlich-based approaches for relating IFT data to PFOS and PFOA surface concentration yield similar results at concentrations >1000 µg/L (Arshadi et al., 2020; Schaefer et al., 2019), their extrapolations to low concentrations differ substantially. It is worth mentioning that at high PFAS concentrations, hemimicelles and micelles may form at the air-water interface and/or the water-soil interface (Chen et al., 2017; Yu et al., 2009). For PFOA, the formation of hemimicelles on adsorbent surfaces were reported in the range of 0.01–0.001 times the critical micelle concentration of 15,700 mg/L (Kissa, 2001).

Fig. 3 highlights the need for selecting an appropriate sorption model when assessing PFAS uptake at low concentrations. The appropriateness of a Langmuir vs. a Freundlich isotherm for accurately describing PFAS accumulation at the air-water interface remains an important area of debate, as concerns with a Freundlich-based model have been raised (Arshadi et al., 2020; Schaefer et al., 2020). Finally, the extrapolated IFT-based models highlight the importance of geochemical conditions on PFOS and PFOA interfacial accumulation at low concentrations, as Langmuir-based model predictions for PFOS and PFOA K_{aw} values differ by approximately an order of magnitude among the studies, likely due in large part to difference in the salt composition.

Relatively few studies have been performed examining PFAS mixtures that include polyfluorinted species that. Brusseau and Van Glubt (2019) performed IFT experiments with perfluorotridecanoic acid (PFTrDA) and PFOA, and showed that IFT was controlled by the more hydrophobic PFTrDA. Schaefer et al. (2019) evaluated individual PFAAs and corresponding equimolar PFAA mixtures using IFT measurements, and showed that the mixture data could be predicted from the single solute data assuming ideal dilute behavior at the interface and in bulk solution. These results were confirmed at low (0.5 µg/L) PFAA concentrations using the batch mass balance approach. Similar results using single component solutions and an equimolar mixture of PFOS and 6:2 fluorotelomer thioether amido sulfonate (FtTAoS), a polyfluorinated anionic compound found in some AFFFs, also were obtained, thereby demonstrating the appropriateness of ideal dilute behavior of a PFAA and polyfluorinated compound mixture (Schaefer et al., 2019). Hill et al. (2018) performed IFT measurements on three different non-ionic or zwitterionic PFASs used in AFFF formulations, and showed that these PFASs were substantially more surface-active than PFOS; K_{aw} values were orders of magnitude greater than those typically measured for PFOS. However, additional studies evaluating a broad range of cationic, zwitterionic, and anionic PFAS mixtures, particularly at concentrations in the ng/L to µg/L range, are to our knowledge not available in the literature. Recent work by Silva et al. (2020a) showed that, for PFAS mixtures at elevated concentrations approaching monolayer coverage of the air-water interface, non-ideal PFAS interfacial adsorption occurs.

3.3. Models to describe PFAS migration in the presence of air-water interfaces

Unsaturated steady flow of PFAS-impacted water through sands and soil have been successfully modeled using a retardation factor that accounts for PFAS accumulation at both the air-water interface and sorption to the sand/soil (Lyu and Brusseau, 2020; Lyu et al., 2018; Brusseau and Van Glubt, 2019). These models rely on estimates of air-water interfacial areas based on grain size and water saturation, and on PFAS uptake at the air-water interface based on the techniques described in the previous section. Simulation results for unsteady unsaturated flow indicated also have been able to describe PFOS retardation due to uptake at the air-water interface (Guo et al., 2020), as PFOS migration was simulated over a period of decades to describe migration through an initially clean vadose zone. One key challenge for these unsteady flow models is estimating the air-water interfacial area under the drainage-imbibition cycles that occur under natural vadose zone conditions, as such processes can substantially impact PFAS partitioning in unsaturated systems (Lyu et al., 2018; Schaefer et al., 2000b; Reeves and Celia, 1996).

3.4. Interactions between PFASs and soil particles

Interactions between PFASs and whole soil or specific soil components have largely been evaluated using saturated systems, excluding the influence of interfacial phenomena. Li et al. (2018) critically analyzed most of the published data before the year 2018 for major anionic PFAAs such as PFOS and PFOA and found that no single soil or sediment bulk property can adequately explain the solid-water distribution coefficient (K_d). The finding is not unexpected given the surface-active properties of PFASs, simultaneous oleophobic and hydrophobic nature, and the low propensity of a perfluoroalkyl chain to engage in van der Waals interactions (Kissa, 2001). The paradigm of soil organic carbon (OC) as the only important predictor of K_d values, does not hold for PFASs. Nevertheless, OC remains a crucial soil property to be considered, particularly for long-chain PFAAs. The extent of correlation between K_d and OC is highly variable; strong correlations were reported only in some studies (Guelfo and Higgins, 2013; Oliver et al., 2020). NMR spectroscopy revealed that PFOA exhibits almost exclusive preference for the proteinaceous domain of humic substances, either dissolved or solid-phase (Longstaffe et al., 2012), which is consistent with some observations that K_d is positively correlated to soil protein content for PFOA (Li et al., 2019a). In contrast, PFOS interacts with dissolved humic acids primarily due to the desolvation effect or hydrophobic interactions, not the protein domains (Oliver et al., 2020).

The anionic nature of PFAAs predicts that K_d could have an inverse relationship with the cation exchange capacity (CEC) of soil and a positive relationship with the anion exchange capacity (AEC). However, CEC and AEC values are infrequently reported in the literature, and high-quality data are far and few among the high number of publications, insufficient to allow confirming the postulations. Oliver et al. (2020) examined the impact of oxalate-extractable Al (responsible for AEC) of 28 tropical soils, and found that the parameter can only explain some data variation for PFOS or PFOA sorption without exhibiting a significant correlation.

In the absence of OC, the sorption of PFAAs onto individual soil components strongly depends on the surface characteristics, as interfacial adsorption tends to dominate. When the solution phase chemistry (e.g., pH, cations, anions) is appropriately factored in, sorption to negatively charged sand, high iron sand, and kaolinite is generally weak (Johnson et al., 2007). Sorption to positively charged metal oxides and oxyhydroxides (e.g. alumina, boehmite, goethite and hematite) can be significant due to ionic attraction (Johnson et al., 2007; Gao and Chorover, 2012; Wang et al., 2012a; Wang and Shih, 2011; Zhang et al., 2018), as well as complexation between the anionic head group and surface hydroxyl groups on Al and Fe oxides (Gao and Chorover, 2012). Sorption by the positively charged montmorillonite clay was stronger than negatively charged kaolinite, with some evidence that PFOS can also partition into the interlayer space of montmorillonite (Zhang et al., 2014). Though empirical correlations between K_d with a combination of multiple soil properties can be applied to improve over using a single property (Li et al., 2018), fundamental understanding of PFAA sorption is lacking for many types of soils and soil components. In particular, molecular-level elucidations of the interactions between PFAS and different soil components or specific domains are yet to be developed.

For cationic and zwitterionic PFASs that are identified in AFFFs and AFFF-impacted soil and groundwater, their interactions with soils are even more complex (Nguyen et al., 2020). Xiao et al. (2019) reported that sorption of cationic PFASs correlated strongly with the soil organic matter (SOM) content, while Mejia-Avendaño et al. (2020) found that sorption of cationic PFAS only weakly correlated with soil CEC. Nguyen et al., 2020 suggested that using multiple soil properties (e.g., soil texture, OC, pH, CEC) can better describe soil sorption of PFAS than any single property. In addition, as PFAS speciation and soil chemistry change with solution pH and these newly emerged PFASs can have pK_a values in environmentally relevant pH range, strongly site-specific sorption behaviors highly subject to changes to environmental conditions may occur.

3.5. Key challenges and specific research needs

Further evaluation of PFAS interfacial sorption behavior at low concentrations (where IFT measurements cannot be made) is needed to confirm behavior at concentrations that may be relevant for many sites with aged sources within the vadose zone. Only a relatively limited number of studies have evaluated PFAS mixtures. Since many sites (e.g., AFFF-impacted source areas) likely consist of a mixture of both fluorinated and non-fluorinated surfactants, an improved understanding of interfacial behavior is needed for these mixed systems. Also, interfacial sorption studies utilizing natural waters impacted with PFASs are lacking and are needed to provide further insight, as well as field-scale studies to confirm the role of air-water interfacial sorption on PFAS migration in situ.

Nearly all of the PFAS interfacial sorption efforts have focused on PFASs associated with AFFF. Several other classes of PFASs (e.g., perfluoroalkyl ethers) remain insufficiently studied with respect to uptake at fluid-fluid interfaces. In addition, the fate and transport of volatile or semi-volatile PFASs, including their uptake at air-fluid interfaces, has to our knowledge not been investigated.

Although the understanding of interfacial and phase behavior for anionic PFAAs is starting to take shape, Nickerson et al. (2020) recently reported that in two soil cores from former fire-training areas, cationic and zwitterionic PFASs contributed up to 97% of the total PFAS mass, especially at shallow depths. This phenomenon may be only specific to such AFFF source zones, but there is a general lack of high-resolution analysis of soils from other areas. Furthermore, several laboratory sorption studies revealed that sorption mechanisms for the cations and zwitterions are even more complex and cannot be predicted by any bulk soil properties (Barzen-Hanson et al., 2017; Mejia-Avendaño et al., 2020). These newly emerged PFASs can have multiple pK_a values with some in environmentally relevant pH range, implying strongly site-specific sorption behaviors and highly subject to changes to environmental conditions. Future work is needed to expand the development of interfacial behavior modeling into more chemically diverse PFASs of environmental significance and integrate with models for chemical, physical, and biological processes as recently reviewed by Sima and Jaffé (2021).

4. Biotransformation of PFASs

As chemical structures determine (bio)degradability, distinctions are necessary between the *perfluoroalkyl* (e.g., PFOS and PFOA) and *polyfluoroalkyl* chemicals, and among PFAS manufactured by different processes, when deciphering (bio)degradability of PFASs comprising of many classes (Liu and Mejia-Avendaño, 2013). Biogeochemical processes heavily influenced by redox potential primarily control the fate of organic pollutants in vadose zones (Holden and Fierer, 2005), and PFASs are of no exception.

4.1. Biodegradability of perfluoroalkyl chemicals

As of 2020, the predominant belief is that PFAAs are biologically inert, but some studies have claimed the bacterial degradation of PFAAs is possible. Thermodynamics predicts that reductive defluorination of PFAAs is feasible, despite less energy yield compared with dechlorination (Dolfing, 2003). However, most studies have not provided crucial experimental evidence (e.g., defluorination, realistic metabolite identification) that definitively proved PFAA biodegradability, let alone mineralization (Mejia-Avendaño et al., 2015; Presentato et al., 2020; Butzen et al., 2020). PFOS is particularly persistent; many strong chemical oxidants (e.g., persulfate) and reductants (e.g., zero-valent iron and zinc) do not show reactivity toward PFOS for C—S bond cleavage or defluorination (Blotevogel et al., 2018; Bruton and Sedlak, 2017; Zhang et al., 2018), demanding that biological degradation studies on PFAAs be critically evaluated. Huang and Jaffé (2019) reported that defluorination of perfluoroalkyl acids may occur in the Feammox process - anaerobic oxidation of ammonium coupled to ferric iron reduction. The Feammox process, recently discovered as part of the natural nitrogen cycle, is active in tropical rainforest soils and wetland sediments (Li et al., 2019c). These naturally reduced zones have not been closely examined for the fate of PFASs.

4.2. Biotransformation of fluorotelomers

Among several thousands of PFASs inventoried by OECD (Ritscher et al., 2018), only a meager fraction has subjected to laboratory biodegradability assessment (Liu and Mejia-Avendaño, 2013; Butt et al., 2014). Nevertheless, dozens of studies conducted using soils, sediments, activated sludge, and microbial cultures suggest that many *polyfluoroalkyl* chemicals (or precursors to PFAAs) can (bio)transform under the conditions relevant to vadose zone processes.

Central to the understanding of the ultimate fate of fluorotelomer compounds are n:2 fluorotelomer alcohols (FTOHs) and iodides (Liu et al., 2010b; Wang et al., 2009; Ruan et al., 2013). Various polymeric materials, surfactants, and other synthesis intermediates that are made from n:2 FTOHs may eventually breakdown to n:2 FTOHs (Fig. 4), which undergo defluorination in aerobic conditions to form PFCAs. Polyfluoroalkyl acids, ketones, and secondary alcohols are also important intermediates or final products, making up a significant fraction of "missing mass" (Liu et al., 2010b; Wang et al., 2009; Liu et al., 2010a; Shaw et al., 2019). The key biotransformation steps follow "α-oxidation like" pathways, or "one-carbon removal" pathways in microbial systems. The n:3 fluorotelomer acids are major biotransformation products of fluorotelomers and can potentially be used as marker

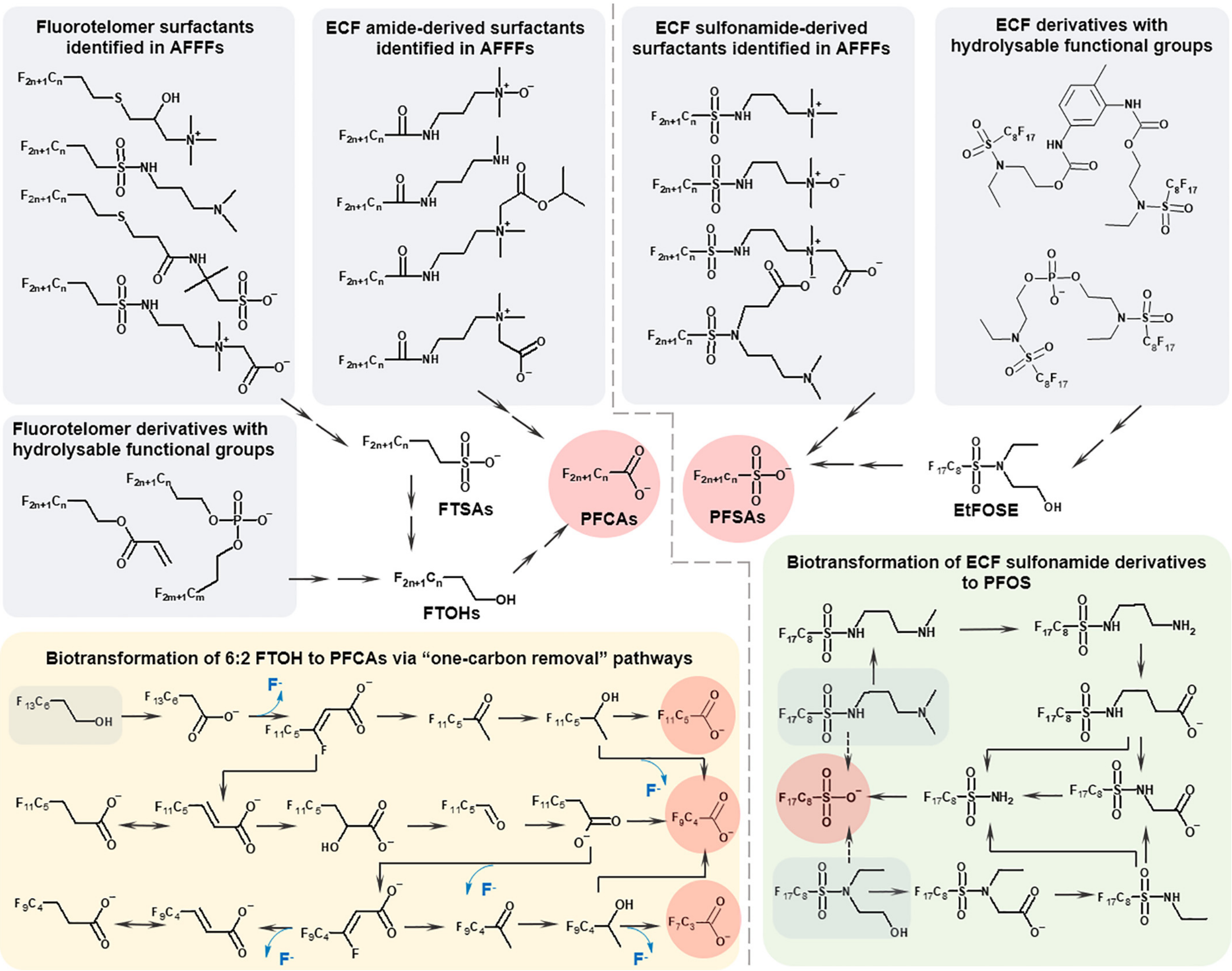

Fig. 4. Illustration of possible aerobic biotransformation of four classes of polyfluoroalkyl substances (precursors) to PFCAs or PFSAs in vadose zones. Two representative transformation pathways that are common to many precursors are shown on the bottom: "one-carbon removal" pathways where 6:2 FTOH degrades to three PFCAs, and the pathways for ECF-sulfonamide derivatives to degrade to PFOS.

compounds for source tracking purposes, but have been infrequently monitored in the field (Wang et al., 2012a, b). FTOHs and some of their transformation products may form significant soil-bound residues, the long-term fate of which is completely unexplored. Biotransformation of FTOHs of high volatility can also form semi-volatile fluoroalkyl ketones and secondary alcohols (Liu et al., 2010a). Whether these semi-volatiles pose a significant vapor intrusion issue in vadose zones is an open question.

Many fluorotelomers undergo microbially mediated hydrolysis to release FTOHs, as documented for fluorotelomer monoacrylates, urethanes, esters, phosphate esters and polymeric oligomers (Liu and Mejia-Avendaño, 2013; Dasu and Lee, 2016; Dasu et al., 2013; Dasu et al., 2012; Liu and Liu, 2016; Russell et al., 2010; Russell et al., 2008). Whether redox conditions affect such microbially-mediated hydrolysis is unresolved, as studies have only focused on aerobic conditions. Side-chain polymeric materials, making up a large volume of fluorotelomer products, can be released during washing from textiles in the form of microplastic fibers (Schellenberger et al., 2019). For polymeric oligomers (Russell et al., 2008; Russell et al., 2010), the fluorinated sidechains could be cleaved off from the hydrocarbon backbones, but it is uncertain if similar hydrolysis reaction can occur for high molecular weight polymers (Washington et al., 2009). Impurities and experimental artifacts intrinsic to long-term laboratory studies render experimental data highly unreliable; alternatively, simulation can provide a broad prediction of PFAA burdens arising from side-chain polymers (Schellenberger et al., 2019; Prevedouros et al., 2006; Paul et al., 2009).

The fluorotelomers formulated into AFFFs are anionic, cationic or zwitterionic surfactants, many of which contain an organosulfur or sulfonamide linker to connect the perfluoroalkyl chain to the hydrophilic non-fluorinated head groups (Korzeniowski et al., 2019; D'Agostino and Mabury, 2014; Place and Field, 2012). A few compounds have been evaluated for biotransformation potential, including FtTAoS, 6:2 sulfonamidoalkyl betaine (6:2 FTAB), and 6:2 sulfonamidoalkyl amine (6:2 FTAA) (Gonzalez et al., 2021; Yi et al., 2018; Harding-Marjanovic et al., 2015; Li et al., 2019b; D'Agostino and Mabury, 2017; Shaw et al., 2019). These studies confirmed that aerobic transformation starts from the non-fluorinated groups to form common transformation intermediates of n:2 fluorotelomer sulfonates (n:2 FTSA). Further breakdown of n:2 FTSAs requires C—S cleavage, which is linked to sulfur-regulated metabolism in bacteria (Shaw et al., 2019; Van Hamme et al., 2013). The half-lives of 6:2 FTSA range from 4 to 5 days (e.g., in aerobic sediment or a *Gordonia* pure culture) to months or years as in aerobic sludges or soils (Wang et al., 2011; Zhang et al., 2016; Shaw et al., 2019; Van Hamme et al., 2013). This may explain the persistent and high levels of n:2 FTSAs observed at many AFFF sites – the environment being such that desulfonation of such fluorotelomers is energetically unfavorable for microorganisms (Backe et al., 2013; Mejia-Avendaño et al., 2017).

An emerging class of fluorotelomers, though not necessarily new chemistry or products, are comprised of linear n:3 perfluoroalkyl structures and n:1:2 type of structures. At several AFFF sites, they have been found to be more abundant than PFAAs in soils and earthworm tissues (Mejia-Avendaño et al., 2017; Munoz et al., 2020). Biotransformation potential of these newly emerged fluorotelomers is completely unknown.

4.3. Biotransformation of ECF-based PFASs

ECF-derived PFASs are characterized by a sulfonamide group adjacent to the perfluoroalkyl chain ($F(CF_2)_n{-}S(O)_2NH^-$). In contrast, amide-containing equivalents ($F(CF_2)n{-}C(O)NH^-$) were also used and sometimes could be present as impurities (Zabaleta et al., 2018; Mejia-Avendaño et al., 2016; Korzeniowski et al., 2019). Limited laboratory studies have shown the microbial transformation of ECF-derived PFASs, if occurring, produce perfluoroalkyl sulfonates from the sulfonamides, or carboxylates from the amides; no further defluorination or mineralization of perfluoroalkyl chains have been observed (Mejia-Avendaño et al., 2016).

ECF-derived PFASs that contain hydrolyzable functional groups, such as perfluorooctane sulfonamido ethanol-based phosphate esters (mono-, di- and tri-), can similarly undergo initial microbially-mediated hydrolysis as the fluorotelomers to produce fluorinated alcohols, e.g., perfluorooctane sulfonamido ethanol (e.g., EtFOSE) (Benskin et al., 2012). Then aerobic biotransformation of EtFOSE involves the breakdown of its non-fluorinated segment to produce acid, aldehyde or amine intermediates, with PFOS being the end product (Mejia-Avendaño and Liu, 2015; Liu et al., 2019; Zabaleta et al., 2018). The ECF-derived PFASs identified in AFFFs are also diverse types of surfactants with different polarities (Barzen-Hanson et al., 2017), but their biotransformation potential has only been sparsely evaluated. The high number of chemical structures makes prioritizing current and future work challenging (Barzen-Hanson et al., 2017; D'Agostino and Mabury, 2014). Mejia-Avendaño et al. (2016) first demonstrated that ECF-derived PFASs with a quaternary ammonium group, despite strong sorption to soil and biocidal nature, can undergo aerobic transformation to produce PFOA or PFOS, with the PFOS precursor exhibiting very long half-life (≫180 d) even in laboratory microcosms. The ongoing studies in aerobic soils of six more structures further confirm that many of the fluorosurfactants in AFFFs may eventually break down; kinetics or DT_{50} (time for reach 50% decline of initial mass) vary vastly depending on environmental conditions and chemical structures of both the non-fluorinated head groups and the perfluoroalkyl chains (Liu et al., 2020; Chen et al., 2020).

Isomer-specific microbial transformation of ECF-derived PFASs has been examined as a possible tool for source tracking (Liu et al., 2019; Benskin et al., 2010). Each precursor or each transformation step in the entire pathways may have isomer-specific biotransformation kinetics, so the ultimate PFOS isomer ratio strongly depends on the relative abundance of multiple precursors at a specific site (Liu et al., 2019). Given the lack of isomer analytical standards and an understanding of the impact of biogeochemical processes on isomeric ratios, the use of isomer ratios for source tracking or PFAS forensics remains quite challenging.

4.4. Anaerobic and abiotic transformation

An anaerobic environment or niche within a dominantly aerobic zone is an integral part of the vadose zone that influences the environmental fate of organic pollutants. Anaerobic transformation potential for most PFASs is unexplored, except for a few fluorotelomers showing minimal transformation or no change. 6:2 FtTAoS undergoes minor changes under various reducing conditions with perfluoroalkyl chain remaining intact and no production of n:2 FTSAs, n:2 FTOHs or PFCAs (Yi et al., 2018). Anaerobic biotransformation of FTOHs under methanogenic conditions produced only polyfluoroalkyl acids with n:2 or n:3 designations, but not PFCAs (Zhang et al., 2013). In addition, 6:2 FTSA did not undergo any detectable transformation in anaerobic sediment after 100-d incubation (Zhang et al., 2016). To date, no studies have looked into ECF-derived PFASs, but we suspect they are highly persistent under anaerobic conditions.

Polyfluoroalkyl substances may also transform abiotically. A few fluorotelomer esters experience solvent-induced hydrolysis during soil extraction to release FTOHs (Dasu et al., 2010; Liu and Liu, 2016), whereas some fluorotelomer surfactants can experience hydrolysis or sulfur oxidation at the organosulfur linkage in the presence of a strong acid or base during soil extraction (Munoz et al., 2018; Nickerson et al., 2020). Breakdown of polyfluoroalkyl substances in sterilized soils or activated sludge were also reported for both fluorotelomers and ECF-based PFASs (Chen et al., 2020; D'Agostino and Mabury, 2017). Though these phenomena were mainly reported as experimental trivia, it implies the instability of some PFASs and their tendency to undergo natural abiotic or chemical transformations; little is known about these processes. Geochemical factors, as well as the interplay between microbial and geochemical processes, can play an important role.

4.5. Field investigations

Field observations are often confounded by the occurrence of numerous PFAS species and sample heterogeneity. Nevertheless, deciphering the PFAS composition in AFFF formulations revealed that a lower percentage of PFAAs in AFFFs than those detected in AFFF-impacted groundwater or soil samples (Backe et al., 2013), suggesting *in-situ* transformations of precursors in the natural environment. In the aftermath of a massive AFFF release, Mejia-Avendaño et al. (2017) tracked the changing PFAS profiles in soil samples collected two years apart. Increasing proportions of PFAAs and n:2 FTSAs over time, despite the decline of total PFASs, was consistent with the trends observed with laboratory precursor transformation. McGuire et al. (2014) attributed the unexpected ratio of PFHxS to PFOS in groundwater in a former firefighter training area to the biosparging-enhanced microbial activities during remedial activities of hydrocarbons, resulting in unintended PFAS transformation. Barzen-Hanson et al. (2017) observed in groundwater the same transformation product of FtTAoS as laboratory aerobic microcosms, but absent in AFFF formulations. Vadose zones could be the primary locations where precursor degradation occurs to create generally more mobile transformation products such as PFAAs.

The ubiquitous presence of PFCAs in surface soils is well documented (Rankin et al., 2016), but few investigations focused on FTOHs, the occurrence of which in surface soil or vadose zones could be the evidence that FTOHs or derivatives continuously contribute to the PFCA loads (Yoo et al., 2011; Yoo et al., 2010). Agricultural fields with a history of biosolids land application contained FTOHs, though at levels lower than PFAAs. Field-derived half-life values of FTOHs in agricultural lands ranged from 0.85 to 1.8 years, orders of magnitude longer than 2 d to 30 days determined from laboratory soil microcosms (Yoo et al., 2010). The discrepancy implies that the half-lives of other precursors in vadose zones probably considerably longer than those observed in laboratory studies conducted under optimized conditions.

4.6. Microorganisms

Biotransformation of polyfluoroalkyl substances appears widespread in aerobic environments such as aerobic soils, activated sludge, and enriched cultures (Liu and Mejia-Avendaño, 2013). However, no functional genes have been identified that are responsible for catalyzing extensive defluorination observed in fluorotelomers; little is known about the correspondence between microbial community structures and dominant degradation pathways. Multiple pure bacterial and fungal cultures capable of transforming FTOHs, 6:2 FTSA or 6:2 FTAB have been discovered (Kim et al., 2014; Kim et al., 2012; Shaw et al., 2019; Van Hamme et al., 2013; Merino et al., 2018; Tseng et al., 2014), but their abundance and role in carrying out PFAS transformation in vadose zone environments have not been investigated. The influence of vegetation on PFAS biotransformation kinetics and pathways could be of great interest. In particular, root exudates are known to cause significant changes to microbial communities in the rhizosphere and enhance the transformation of organic pollutants. Zabaleta et al. (2018) reported considerably higher yields of PFOS from *N*-ethyl perfluorooctane sulfonamide (EtFOSA) than any previous studies, pointing to the likely strong influence of vegetation (carrots in this case).

4.7. Earthworms

Earthworms in the vadose zone may participate in PFAS biotransformation, degradation, and accumulation. A variety of earthworm species such as *Eisenia fetida* and *Lumbricus terrestris* have shown a potential for degradation of cationic and zwitterionic PFASs (Jin et al., 2020). However, the metabolic response of earthworms depends on the physiochemical properties of the PFASs. Their accumulation in *E. fetida* showed higher uptake of PFSAs and lower absorption of PFCAs and zwitterionic PFASs, respectively (Munoz et al., 2020). Rich et al. (2015) observed increases in bioaccumulation factors with increasing PFCA but decreasing PFSA chain lengths. Cationic PFASs appear to be significantly less metabolized than zwitterionic PFASs in terms of yields and number of metabolites (Jin et al., 2020). Zhao et al. (2016) reported that N-EtFOSE was transformed by *E. fetida* to N-EtFOSAA, *N*-ethyl perfluorooctane sulfonamidoacetic acid (FOSAA), perfluorooctane sulfonamide (FOSA), and eventually to the terminal product PFOS. In contrast, Munoz et al. (2020) did not find *Eisenia fetida* to metabolize fluorotelomer precursors (e.g., 6:2 FTAB), which other studies found susceptible to microbial transformation or metabolism by higher-trophic level organisms (e.g., rats, fish). The transformation of PFASs by earthworms was found to be driven by enzymatic activities including glutathione *S*-transferase and cytochrome P450 rather than by gut microbes (Zhang et al., 2020a, b).

4.8. Key challenges and specific research needs

Molecular structure and environmental conditions will affect the magnitude of the precursor contributions to PFAA burdens, with aerobic environments being most conducive to the significant transformation of precursors. Sorption to porous media, partitioning into NAPLs and sorption at the air-water and NAPL-water interfaces are expected to moderate PFAS bioavailability and, thus transformation rates. The transformations from precursor to PFAAs are a multi-step processes in which the transformations of intermediates can also be the rate-limiting step (Zhang et al., 2017a), thus knowing only the half-lives of the initial precursor limits predicting PFAA future trends. The complex dynamics involved in biotransformation, particularly at the field-scale, make it difficult to accurately predict the importance of a precursor source zone of varying age to downstream concentrations of the more commonly monitored and more mobile PFASs. Future studies should be focused on the characterization of transformation pathways in relevant media and for both legacy and newly emerged precursors, and elucidation of biochemical processes and functional genes involved in defluorination reactions. Overarching success will be limited by the availability of adequate analytical tools and chemical standards to support PFAS biotransformation research.

5. PFAS impacts on the soil microbiome

At the bottom of any ecosystems, microorganisms play important roles in biogeochemical cycling, chemical transformation, contaminant degradation, maintaining the health of the ecosystems at the foundational level and supporting activities of those in the upper food chain (Londono et al., 2017, 2019; Kennedy and Stubbs, 2006). Specific to emerging contaminants, especially PFASs, investigations on understanding how these compounds affect microbial communities at different levels are very limited.

Depending on concentrations, chain lengths and functional groups, PFASs are known to be toxic to specific microorganisms (Weathers et al., 2016). The identified modes of toxicity include oxidative damage, DNA damage, general cell lesions and membrane damage (Nobels et al., 2010). On the other hand, microorganisms in the lineages of *Pseudomonas* (Yi et al., 2016; Yi et al., 2019; Chetverikov et al., 2017; Kwon et al., 2014), *Gordonia* and the others (Dasu et al., 2013; Dasu et al., 2012; Shaw et al., 2019; Wang et al., 2011) have demonstrated capabilities in transforming PFASs or utilizing these chemicals partially as a source of nutrients. Thus, it is reasonable to expect that PFASs would impact the microbial communities to different extents.

Among all reported studies, some of them studied the interactions between PFASs and microorganisms by dosing these chemicals to either soil or sediment. Others evaluated the impact of PFASs on microorganisms at field sites (Bao et al., 2018; O'Carroll et al., 2020; Chen et al., 2019). The following section discusses the impact on microbial community composition and function brought by the exposure to PFASs.

5.1. Impact to microbial community structure

Adopting next-generation DNA sequencing techniques, the structure of microbial communities can be elucidated by analyzing the 16S rDNA amplicons. The common procedure involves extracting DNA from target samples, amplifying the 16S rDNA using different pairs of primers and polymerase chain reaction (PCR), sequencing the amplicons using different sequencing platforms, and performing bioinformatic analysis of the resulting sequences in millions or billions of base pairs using well established or newly developed data analysis pipelines and software. At the end, the community's composition, diversity, evenness, richness, and structure can be obtained. Oftentimes, these results are compared with those not exposed to PFASs or at different locations to infer impacts resulting from PFASs only.

Using these approaches, the effect of PFASs, either single or mixed, on different samples, has been reported. These samples include groundwater samples collected from two aquifers in a fire training area in Canada (O'Carroll et al., 2020), surface sediment samples collected from Pearl River Delta (Chen et al., 2019), sediment samples along the Xiaoqing River in China (Sun et al., 2016), soil samples contaminated by PFASs (Bao et al., 2018), soil samples spiked with PFASs (Qiao et al., 2018), grassland soil dosed with an emerging PFAS (Ke et al., 2020), soil samples collected from a plant uptake of PFAS study (Zhang et al., 2019b) and freshwater pond samples exposed to PFASs (Zhang et al., 2019a).

Although the samples had different characteristics and different PFASs were studied at different concentrations, some observations are common to all studies. First, PFASs do significantly affect community composition. The only exception is the study that profiled microbial communities at 18 stations around the Pearl River Delta. At these locations, PFAS concentrations ranged between 24.2 and 181.4 pg g^{-1} sediment (dry weight). These much lower PFAS concentrations than those reported elsewhere were assumed to be the reason for lack of negative impact from PFASs (Chen et al., 2019). For groundwater samples exposed to AFFF for several decades, compared to oxidation-reduction potential (ORP) and pH, PFASs were not found to be the driving force for changing the overall microbial community structure. At localized scales, however, individual PFASs were observed to exert significant influence on community composition (O'Carroll et al., 2020). Second, different PFASs, even studied at the same concentration, had a different effect on microbial community richness and diversity, likely due to their different physicochemical properties. These differences are reflected by different carbon chain lengths and functional groups. Generally speaking, greater disruptive effects on soil bacterial communities were observed from PFASs with longer carbon chains vs. those with shorter chains (Qiao et al., 2018). Third, different microorganisms responded to PFASs differently. Some microorganisms had increased abundance, while others demonstrated decreased abundance as a result of PFAS exposure. For instance, the *Desulfococcus* genus had positive correlations with PFASs while the family of *Oxalobacteraceae* had lower abundance with increasing PFAS concentrations (O'Carroll et al., 2020). For soil samples maintained in a greenhouse, PFASs stimulated the growth of Firmicutes, Acidobacteria and Actinobacteria, but inhibited those in the phyla of Latescibacteria and Chloroflexi (Qiao et al., 2018). Regarding sediment samples spiked with 6:2 FTOH, microbial transformation of this compound, and the resulting intermediates led to certain microorganisms, such as those in the phylum of Proteobacteria, Chloroflexi and Verrucomicrobia to become dominant over time (Zhang et al., 2017b).

Besides legacy PFASs targeted in the aforementioned studies, an emerging PFAS has also been studied with regard to its impact to microbiota. In one study, sodium *p*-perfluorous nonenoxybenzene sulfonate (OBS), a perfluoroether sulfonic acid, was amended to grassland soil at different dosages (0, 1, 10 and 100 mg/kg). It was reported that both archaeal and bacterial community structures were changed significantly as a result of this OBS exposure (Ke et al., 2020).

5.2. Impact to microbial community functions

Shifts in microbial community composition naturally lead to changes in functions of a given community. In one study (Qiao et al., 2018), sucrase and urease activities were measured for soil samples exposed to each of six PFASs. While short-chain PFASs, such as PFBS and PFHxS, increased activities of sucrase and urease in the soil, long-chain PFASs, for example, PFOS and 6:2 FTSA, played opposite roles. In particular, as the concentration of PFOS and the exposure time increased, greater inhibition of these enzymes' activities was observed. However, as an indication of the microbial community's resilience, activities of these two enzymes were dynamic, and trends of stimulation, inhibition, and recovery were observed with time.

Weathers et al. (2016) observed significant inhibition of a chlorinated ethene-degrading methanogenic culture at mg/L-level PFAA concentrations representative of source zones. Phylogenetic analysis showed adverse impacts on the relative abundance of trichloroethene (TCE)-dechlorinating *Dehalococcoides*, potentially due to a stress response or inhibition of vitamin B_{12} uptake. Varied effects on the community composition were noted, with enhancement of methanogenic Archaea, which actively compete with *Dehalococcoides* for the electron donor hydrogen.

Besides measuring enzymatic activities directly, ammonia oxidation by bacteria and archaea was also measured by quantifying the gene copies using quantitative PCR (Ke et al., 2020). It was observed that the potential nitrifying activity (PNR) of the soil microbial community was negatively affected by OBS depending on the dosage. Between ammonia-oxidizing bacteria and ammonia-oxidizing archaea, the abundance of the former had a positive correlation with the PNR.

5.3. Key challenges and specific research needs

Understanding the interactions between microbial communities and PFASs serves at least three purposes. First, it assists in the targeted isolation of PFAS-transforming organisms. In this case, microorganisms that show increased abundance responding to PFAS exposure should be aimed for enrichment studies with the ultimate goal of obtaining pure PFAS transformers or degraders and for ascertaining the feasibility of bioremediation. Second, it helps to elucidate the overall impact of PFASs to communities of microorganisms in a given environment. In this scenario, the potential toxicity of all PFASs to all bacteria and archaea in that environment can be understood. Third, it helps to understand whether soil health or functions are changed as a result of PFAS exposure.

At present, how a microbial community's functions are affected by PFASs is largely an unaddressed question. Future research aiming to understand, for example, how nitrification, denitrification, and other key element cycling in subsurface are impacted is thus warranted. In addition, most of the studies listed above spiked PFASs to uncontaminated samples and the effects were observed after certain experimental duration. This approach certainly is valuable in elucidating the short-term response of microbes to PFASs. It is unclear, however, whether this spiking can genuinely represent what takes place in the real subsurface environment. At these locations, PFASs interact with microorganisms, soil organic matter, particles, metals, and other organic compounds for a much longer time. Furthermore, as PFASs generally present themselves in the environment as mixtures at different concentrations, research on the collective effect from these mixtures at environmentally relevant concentrations needs to be further explored.

6. Plant interactions and uptake

Plants can dominate the biogeochemical processes of the vadose zone, and thereby greatly impact the fate of compounds throughout the unsaturated zone where PFASs may be present (Bagheri et al., 2020). Dominant processes include evapotranspiration of subsurface moisture, exudation and sloughing of reduced organic carbon, and impacting subsurface redox potential (Bagheri et al., 2019). Through these processes, plants impose the largest energy transfer into (photosynthesis, organic carbon) and out of (evapotranspiration) the vadose zone. Via this energy transfer, organic compounds such as PFASs can be transported to root surfaces with the evapotranspirate (Blaine et al., 2014b; Navarro et al., 2017). At the root membranes, organic molecules can accumulate at or cross the root membranes and enter the plant tissue (Sharifan et al., 2020a). If not transferring across the root membrane, organic molecules can undergo enhanced transformation and also be held in place, and thus be limited from leaching with water to the saturated zone. The increased organic carbon deposited through plant roots also retard organic pollutant movement by increasing vadose zone sorption capacity, a process described as phytostabilization.

Many studies addressed the plant uptake of PFASs by exposing crops to certain doses under controlled greenhouse conditions (Ghisi et al., 2019; Zhang et al., 2019; Zhao et al., 2018), while PFAS-affected sites (i.e. fire training areas) are not designed for crop cultivations. However, planting trees may be a long-term solution that drives the biogeochemical cycle of the vadose zone, reduces the mobility of PFASs, and provides time for microbial transformation. Only one study has thus far investigated the accumulation of PFASs in different trees (Gobelius et al., 2017), but PFAS accumulation in deep roots and corresponding PFAS concentrations in the surrounding groundwater was not determined. Bioaccumulation and translocation of PFASs can be evaluated by compartmental bioconcentration, root concentration, shoot concentration, and shoot-root transfer factors (Felizeter et al., 2012; Sharifan et al., 2019). Transpiration stream concentration factor is another index that can explain the translocation of chemicals from roots to shoots through xylem (Trapp, 2000; Sharifan et al., 2020b).

6.1. Plant-root system

Plants are highly exposed to released PFASs in the environment in the top two meters of the subsurface (i.e. perennial plants) or more (i.e. mature trees) through the extensive radial development of root systems in the vadose zone. Depending on the type of plant, roots can provide a safety zone for further distribution of PFASs in the soil profile. For example, mature trees have a predominant aromatic domain of suberin polymer in their root structure compared to primary roots (Schreiber, 2010), which may impact the uptake and storage of the PFASs. Also, as part of the root development, the role of proteins and lipids in the accumulation and distribution of PFASs in plants may be significant (Wen et al., 2016). Wen et al. found a significant positive correlation between the root protein contents and the accumulation of both PFOS and PFOA in roots, while their correlation with root lipid contents was negative (Wen et al., 2016).

Despite few PFAS plant uptake studies, none have considered the ionic properties of the PFASs that had been subjected to varying redox conditions in the vadose zone. Many previous studies have addressed the interaction of plants with organic and inorganic contaminants (Sharifan et al., 2019; Sharifan et al., 2020b). Still, plant response in the presence of PFASs in the vadose zone has not been adequately addressed.

6.2. Plant species

Studies on plant uptake of PFASs are limited to the biochemistry of subsurface soil where the cultivation of crops or plants with short-length roots takes place (Ghisi et al., 2019; Zhang et al., 2019). However, trees with long root systems in the vadose zone play the primary role in driving the soil organic matter pool. Besides root exudates and dissolved organic matter (OC), the root litter and turnover are significant sources of OC in the vadose zone (Spielvogel et al., 2014; Sharifan et al., 2020a). The distribution of OC in soils differs among tree species (Spielvogel et al., 2014); this was reflected in the root/soil concentration factor of PFASs reported by Gobelius et al., (2017). For example, at the same sampling site, the accumulation of PFASs in a birch tree (*Betula pendula*) was comparably high at 97 ng/L, while the PFAS concentration in bird cherry (*Prunus padus*) and mountain ash (*Sorbus aucuparia*) was 4.3 and 2.1 ng/L, respectively (Gobelius et al., 2017).

Trees with long root lengths could significantly change the biogeochemical processes in the vadose zone compared to crops and perennials, which mostly affect the subsurface soils. For example, a birch tree with an average root length of five meters may absorb PFASs from the groundwater directly or by capillary forces. In contrast, perennial plants experience shorter exposure times and limited surface absorption of PFASs.

6.3. Uptake mechanism

Recent studies have suggested that the uptake of PFASs from soil into the plant is primarily a passive mechanism (Zhang et al., 2020b; Zhao et al., 2017), meaning that a high PFAS concentration around the root zone can drive their diffusion into the root system (Scher et al., 2018). For example, in birch, a significant portion of the water-soluble PFCAs (48%) was detected in its leafy tissues (Gobelius et al., 2017). Similarly, in yam, maize and sugarcane with shallow root extension, the uptake of two PFCAs (perfluoroheptanoic acid, PFHpA and perfluorononanoic acid, PFNA) were observed as high as 140 pg g^{-1} dw for PFHpA (45% of ΣPFASs) and 72 pg g^{-1} dw for PFNA (36% of ΣPFASs), while certain PFASs were not detected in plant tissues (Dalahmeh et al., 2018). A comparison between the translocation factors (TF) of seven commonly used crops found a similar TF of PFOA/PFOS for the crops with similar root length as shown in Table 2. In maize, the presence of PFASs was shown to be 125-fold higher in leaves than in the grains, suggesting a critical role of evapotranspiration in PFASs localization and uptake in plants (Muschket et al., 2020). Meanwhile, the question of active versus passive uptake has not been sufficiently answered yet. Two previous studies have demonstrated that the uptake of PFAAs into various plants is passive as revealed by linear concentration-accumulation relationships (Blaine et al., 2014b; Stahl et al., 2009). In contrast, Wen et al. (2013) suggested that PFOA and PFOS may have different uptake mechanisms in maize, with potential active uptake by anion channels for PFOA and entry by aquaporins or different anion channels for PFOS. Wang et al. (2020) provided evidence for active transport of PFOA and PFOS through aquaporin and anion channels in the wetland plant *Alisma orientale*. However, the latter findings may have been biased by phytotoxicity effects that can alter the uptake pattern of plants (Sharifan, 2017).

6.4. PFAS chain length effects in plant uptake

Along with the plant type, soil organic matter, and hydrophilicity of PFASs, their molecular length seems to govern their dynamics in the root zone area and retardation in the vadose zone. PFASs with longer CF_2 chains have stronger hydrophobicity and more readily adsorb onto the hydrophobic portion of the soil substrate through non-specific interactions (Zhang et al., 2020a, b). Therefore, short-chain PFASs are generally more mobile and thus have a higher availability for plant uptake. Several studies have reported the accumulation of long-chain PFASs in the roots and transfer of short-chain PFASs into the aerial parts of the plant (Stahl et al., 2013; Blaine et al., 2014a; Felizeter et al., 2014). Our current understanding is that the available fraction of PFASs in interstitial water will adsorb onto the root epidermis, diffuse through the epidermis,

Table 2
The ratio of translocation factor (TF) of PFOA to PFOS for a variety of plants with similar root length.

Plants	Scientific name	TF (PFOA/PFOS)	PFOA soil conc. (ng g^{-1})	PFOS soil conc. (ng g^{-1})	References
Soybean	*Glycine* max L. Merrill	0.59	416	155	Wen et al., 2016
Lettuce	*Lactuca sativa* L	0.52	416	155	Wen et al., 2016
Maize	*Zea mays* L. cv. Nongda 108	0.51	416	155	Wen et al., 2016
Alfalfa	*Medicago sativa* L. cv. Chaoren	0.43	416	155	Wen et al., 2016
Narrowleaf cattail	*T. angustifolia*	0.42	405	4220	Zhang et al. 2020
Wheat	*Triticum aestivum* L	0.37	500	200	Zhao et al., 2017
Mung bean	*Vigna radiata* L. Wilczek	0.15	416	155	Wen et al., 2016
Ryegrass	*Lolium multiflorum* Lam	0.23	416	155	Wen et al., 2016
Radish	*Raphnus sativus* L. cv. Dahongpao	0.10	416	155	Wen et al., 2016

and is finally transported to the leaves through the xylem driven by the transpiration effect. However, further studies are needed to elucidate the localization of the long-chain PFASs and their transformation in root cells. There is a possibility that metabolic enzymes will transform long-chain polyfluorinated substances into smaller, water-soluble compounds.

6.5. Surface charge and soil pH effects

Besides the higher potential for short-chain PFAS uptake, cationic PFASs may show higher affinity for plant uptake due to the negatively charged root surface. Soil irrigation or flooding events may lead to higher uptake of PFASs with negative or neutral surface charge by reducing soil redox potential (E_h) (Pezeshki and DeLaune, 2012) and less chance of PFAS oxidation. Additionally, the presence of divalent cations in the rhizosphere may bridge between negatively charged sorbent surfaces and PFASs with anionic functional groups (Li et al., 2018). Therefore, the carryover of PFASs from soil to plants depends not only on the initial PFAS concentrations in the solution but also on PFAS speciation and water quality. Ma et al. (2020) have shown that in the rhizosphere soil, the pH tends to be more acidic compared to bulk soil due to the release of root exudates, which may affect the PFAS bioavailability. Therefore, it is expected to detect more of anionic PFASs toward the groundwater level in the soil profile.

6.6. In-planta transformation and metabolism

Only recently, insights into the biotransformation of a limited number of PFASs in plants has emerged. Once translocated in vascular plants, PFASs may be subject to plant metabolism, often referred to as green-liver metabolism (Sandermann Jr, 1994). Plant metabolism is a defense mechanism, not catabolic or anabolic. Green-liver metabolism has been related to detoxification of polluted sites for a wide variety of anthropogenic organics that reside in the vadose zone and termed ‘phytodegradation’ (Burken, 2003). Green-liver metabolism can proceed through many metabolic pathways for different molecules, but is typically noted for three primary steps, Activation, Conjugation, and Sequestration, resulting in transformed parent molecules sequestered in plant cell walls or vacuoles (Jiao et al., 2020). The first step of activation is predominantly an oxidation/hydroxylation step, most commonly carried out by cytochrome P450. Recent findings indicate this process is active for a wide range of PFASs, as oxidized metabolites were identified in maize, wheat, Jerusalem artichoke, and ryegrass (Muschket et al., 2020). Intermediate metabolites identified were 16 FTOH or perfluoroalkane sulfonamidoethanol (FASE) transformation products. Parent compounds detected were PFAAs, therefore the FTOH and FASE metabolites are fully consistent with the P450 attack and hydroxylation (Muschket et al., 2020). Additionally, 36 suspected intermediate PFAS transformation products were qualitatively analyzed, below quantification limits (Muschket et al., 2020). The metabolite structures are also consistent with P450 metabolic attack. Analysis of plant tissues detected FTOH- and/or FASE-based intermediate transformation products in all plant tissues that also contained EtFOSAA and FOSA. The identification of metabolites was also accompanied by high concentrations of parent PFASs, introduced to the identified field site as contaminated sludge obtained from surface-treated paper manufacture. The identification of metabolites is encouraging for potential phytoremediation of PFAS-contaminated sites, primarily for short-chain PFASs that are subject to high transport in the vadose zone and translocation in vascular plants. However, a collection of PFCAs including PFOA were also found in carrots and lettuce (Muschket et al., 2020). In a soil/plant environment, PFOS seems to be the final stable biodegradation metabolite of EtFOSE (Bizkarguenaga et al., 2016).

6.7. Key challenges and specific research needs

The interactions between PFASs and plants in the vadose zone are very complex and mainly depend on the environmental conditions, plant species, and type of PFASs (i.e., surface charge and chain length). Plants are mainly exposed to PFASs through atmospheric deposition, application of biosolids on agricultural soil, and irrigation with reclaimed wastewater. Phytoremediation of PFASs may offer a potentially safe and feasible approach to remove PFASs from the soil, bearing the incineration costs. However, there is not enough information about hyperaccumulating species and the required time from cultivation to harvest to remediate PFASs from the subsurface. Expanding our knowledge about the toxic impact of PFASs on different plant species is another factor, which is of paramount importance in the phytoremediation. Besides the positive role of phytoremediation in the removal of PFASs, it should be noted that the use of plant residues (such as maize stover) in animal feeds can contaminate the food chain (Ghisi et al., 2019). Identification of the intermediate transformation products of PFASs in plant tissues is challenging due to highly variable physicochemical properties. Therefore, the extraction and clean-up procedures require extensive analytical development.

7. Conclusions and general research needs

Due to their widespread use, dispersion, diverse physicochemical properties and extraordinary recalcitrance, PFASs have migrated into all environmental compartments. Of particular importance for sites impacted by agricultural and firefighting activities is the vadose zone, where complex processes govern the uptake of PFASs into plants and soil organisms as well as the leaching of PFASs into groundwater. As more data on the individual processes discussed in this review are being collected, critical research needs still exist that should address their interconnectedness to enable a better mechanistic and predictive understanding of PFAS fate and transport in the vadose zone:

- More high-resolution soil core analyses are urgently needed. Besides depth-resolved quantification and speciation of PFASs, these investigations should include correlated plant and groundwater analysis. In addition to microbial community analyses as described above, soil composition and properties should be characterized in great detail to start unraveling the relative contributions of sorption to organic and inorganic phases, ion exchange etc., ideally supported by mechanistic laboratory-scale studies (Duchesne et al., 2020).

- In the U.S. (and other countries), nationally approved standard analytical methods for PFASs in soils and sediments are still lacking (Cui et al., 2020; Naidu et al., 2020). Method ASTM D7968-17a provided by the American Society for Testing and Materials and Clean Water Act Method 1600 (currently anticipated for 2021) can be used for the quantification of a limited number of PFASs in soil by liquid chromatography coupled with tandem mass spectrometry (LC/MS-MS). However, nontargeted analytical methods based on high-resolution accurate mass spectrometry are central to understanding PFAS speciation and precursor transformation. As the quantification of the great number of PFASs is notoriously limited by the lack of commercial reference standards, semiquantitative approaches in combination with fluorine-specific bulk measurements (total oxidizable precursor (TOP) assay, total organofluorine via combustion ion chromatography, total fluorine via particle-induced gamma-ray emission (PIGE) spectroscopy) are currently the most comprehensive approach.
- Further evaluation of low-concentration interfacial sorption behavior for a broader and more chemically diverse set of PFASs is critically needed to unravel their fate and transport within aged vadose zone sources. Especially field-scale studies are needed to confirm the role of air-water interfacial sorption on PFAS migration in situ.
- As PFASs tend to accumulate at air-water interfaces, the careful selection and implementation of soil coring methods is critical. Standard coring methods such as direct push, hollow-stem auger, and rotosonic drilling are well-known to suffer from incomplete sample recovery as well as perturbation and redistribution of pore fluids. In contrast, cryogenic core collection freezes the subsurface using liquid nitrogen and has been shown to improve core recovery while keeping pore fluids in place (Kiaalhosseini et al., 2016). However, the impacts of freezing on the integrity of mineral phases and fluid-fluid interfaces have not yet been sufficiently investigated.
- As mentioned above, redox conditions govern the fate of organic chemicals and likely play a key role in precursor transformation. While the shallowest soil layer is usually oxic and promotes aerobic biodegradation processes, redox potentials typically decrease with increasing depth due to the oxidation of organic matter, especially at sites with additional organic carbon loading by biosolids, sludges or hydrocarbon fuels. As precursor transformation may still be significant under suboxic or anoxic conditions, possibly at different rates and through distinct metabolic pathways, future field investigations should include high-resolution characterization of ORPs in the unsaturated zone, for instance using real-time ORP sensors that work in low-soil moisture environments (McGregor, 2018; Sale et al., 2021).
- Understanding the mechanisms and rates of PFAS leaching from sources in the vadose zone is critical to assessing long-term groundwater contamination impacts (Høisæter et al., 2019). Laboratory-scale single-species sorption experiments are important to determine short-term mechanistic aspects, and much remains to be understood about the particular sorption behavior of this diverse chemical class (e.g., Guelfo and Higgins, 2013; Mejia-Avendaño et al., 2020). In addition, given that many AFFF-impacted sites are years or decades old, leaching experiments on aged real-world samples would be helpful for investigating weathering impacts on hysteretic or possibly irreversible PFAS sorption behavior. Collectively, these findings will need to be included in subsurface PFAS transport models.
- While it has been established that PFAS transport into plant tissues is governed by molecular properties such as chain length and molecular weight, information regarding plant species variability, root architecture, soil property impacts and plant species-specific interactions on uptake and fate are lacking.
- Further research is necessary on *in planta* transformation of PFASs, for instance, via cytochrome P450 metabolism or laccases, which have been shown to transform even perfluorinated species such as PFOA and PFOS (Luo et al., 2015, 2018).
- With few exceptions, climatic impacts on the fate and transport of PFASs at the terrestrial surface and in the vadose zone have not yet been addressed. These factors include, but are not limited to, temperature impacts on sorption and transformation, the impact of freeze-thaw cycles on PFAS mobilization, precipitation impacts on leaching, plant uptake, as well as the effect of these processes on microbial abundance and activity.

CRediT authorship contribution statement

Hamidreza Sharifan: Writing – original draft, Conceptualization, Writing – review & editing. **Majid Bagheri:** Writing – original draft, Writing – review & editing. **Dan Wang:** Writing – original draft, Writing – review & editing. **Joel G. Burken:** Writing – original draft, Writing – review & editing. **Christopher P. Higgins:** Writing – original draft, Writing – review & editing. **Yanna Liang:** Writing – original draft, Writing – review & editing. **Jinxia Liu:** Writing – original draft, Writing – review & editing. **Charles E. Schaefer:** Writing – original draft, Writing – review & editing. **Jens Blotevogel:** Writing – original draft, Project administration, Writing – review & editing.

Declaration of competing interest

The authors declare no competing financial interests.

Acknowledgements

Support for this review was provided by SERDP grants ER-2718 and ER20-1265 to J.B.; by the National Science Foundation under Award Number 1606036 to J.G.B.; by SERDP grants ER-2720, ER-1259, and ER-1204 to C.P.H.; by the University at Albany, SUNY to Y.L.; by SERDP grant ER20-1023 and NSERC Discovery Grant Accelerator (RGPIN-2018-05667) to J. L.; and by SERDP grant ER18-1204 to C.E.S. The authors thank Anastasia Nickerson at the Colorado School of Mines for assistance in compiling PFAS soil concentration data.

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