

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/348724699>

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

Article in *Science of The Total Environment* · January 2021

CITATIONS

0

READS

4

1 author:



Hamidreza Sharifan

University of California, Davis

21 PUBLICATIONS 150 CITATIONS

SEE PROFILE

Some of the authors of this publication are also working on these related projects:



Interaction of plants with nanoparticles [View project](#)

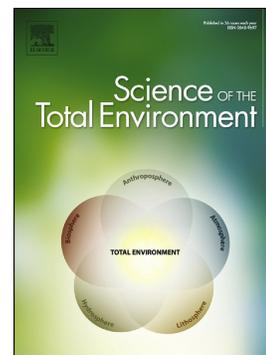


Source Tracking and Environmental Fate of PFAS [View project](#)

Journal Pre-proof

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

Hamidreza Sharifan, Majid Bagheri, Dan Wang, Joel G. Burken, Christopher P. Higgins, Yanna Liang, Jinxia Liu, Charles E. Schaefer, Jens Blotvogel



PII: S0048-9697(21)00495-2

DOI: <https://doi.org/10.1016/j.scitotenv.2021.145427>

Reference: STOTEN 145427

To appear in: *Science of the Total Environment*

Received date: 20 November 2020

Revised date: 19 January 2021

Accepted date: 21 January 2021

Please cite this article as: H. Sharifan, M. Bagheri, D. Wang, et al., Fate and transport of per- and polyfluoroalkyl substances (PFASs) in the vadose zone, *Science of the Total Environment* (2021), <https://doi.org/10.1016/j.scitotenv.2021.145427>

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2021 Published by Elsevier.

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

Hamidreza Sharifan^a, Majid Bagheri^b, Dan Wang^c, Joel G. Burken^b, Christopher P. Higgins^d, Yanna Liang^e, Jinxia Liu^c, Charles E. Schaefer^f, Jens Blotvogel^{a}*

^a Department of Civil and Environmental Engineering, Colorado State University, Fort Collins, CO 80523, USA

^b Civil, Architectural and Environmental Engineering Department, Missouri University of Science and Technology, Rolla, MO, USA

^c Department of Civil Engineering, McGill University, Montreal, Quebec, H3A 0C3, Canada

^d Department of Civil and Environmental Engineering, Colorado School of Mines, Golden, CO 80401, USA

^e Department of Environmental and Sustainable Engineering, University at Albany, SUNY, Albany, NY 12222, USA

^f CDM Smith, 110 Fieldcrest Avenue, #8, 6th Floor, Edison, NJ 08837, USA

* Corresponding author at:

Colorado State University, Department of Civil and Environmental Engineering, Fort Collins, CO 80523, USA. E-mail address: jens.blotvogel@colostate.edu (J. Blotvogel)

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.

Keywords

PFAS sources, sorption, air-water interface, biodegradation, microbial community impact, plant uptake

1 Introduction

Per- and polyfluoroalkyl substances (PFASs) are a highly complex group of anthropogenic chemicals comprising thousands of individual species (Barzen-Hanson et al. 2017b; 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, MacLeod, and Cousins 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 (Brusseu and Van Glubt 2019; Barzen-Hanson et al. 2017b). 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.

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	Maximum concentration of major PFAS species ($\mu\text{g}/\text{kg}$)	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)}	140000	<i>n.p.</i>	<i>n.p.</i>	Nickerson et al. 2020
Fire-training area, USA	AFFF	PFOS	54000	<i>n.p.</i>	<i>n.p.</i>	Nickerson et al. 2020
Fire-training area, USA	AFFF	TAmPr-FHxSA ^{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	<i>n.p.</i>	Filipovic et al. 2015
Fire-training area, USA	AFFF	PFOS	20000	5-6	2-8	Houtz et al. 2013
Fire-training area, France	AFFF	PFOS	55200	0-0.25	20-40	Dauchy et al. 2019
Military building, USA	AFFF	PFOS	9700	<i>n.p.</i>	<i>n.p.</i>	Anderson et al. 2016
Train accident site, Canada	AFFF	6:2 FTAB	1908	<i>n.p.</i>	<i>n.p.</i>	Mejia-Avendaño et al. 2017
Train accident site, Canada	AFFF	PFPeA	157	<i>n.p.</i>	<i>n.p.</i>	Mejia-Avendaño et al. 2017
Manufacturing facility, USA	Atmospheric	PFOA	66.2	<i>n.p.</i>	<i>n.p.</i>	Galloway et al. 2020
Manufacturing facility, China	Atmospheric	PFOA	120	0-0.05	<i>n.p.</i>	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	<i>n.p.</i>	Sepulvado et al. 2011

n.p. = information not provided

^{a)} *N*-Trimethylammoniopropyl perfluorohexane sulfonamide

^{b)} *N*-Trimethylammoniopropyl *N*-methylperfluorobutanesulfonamide

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 (Figure 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 (Figure 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, Chu, and Smyth 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).

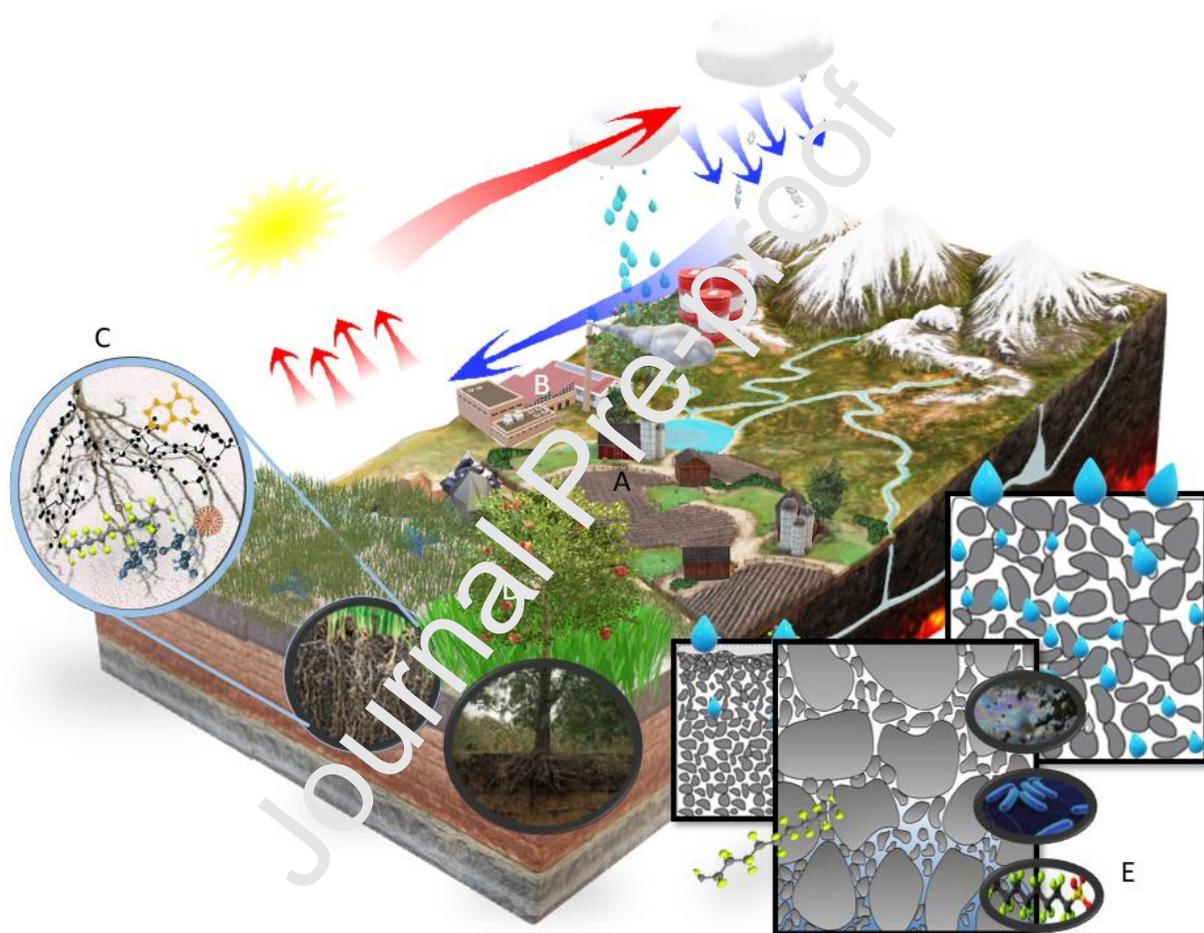


Fig. 1. Major sources of PFASs and their vadose zone fate & transport processes. (A) Agricultural sources such as biosolids application and irrigation with reclaimed wastewater. (B) Emissions from manufacturing and subsequent atmospheric transport. (C) Interactions with plants in soils that lead to accumulation 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. *(no color in print)*

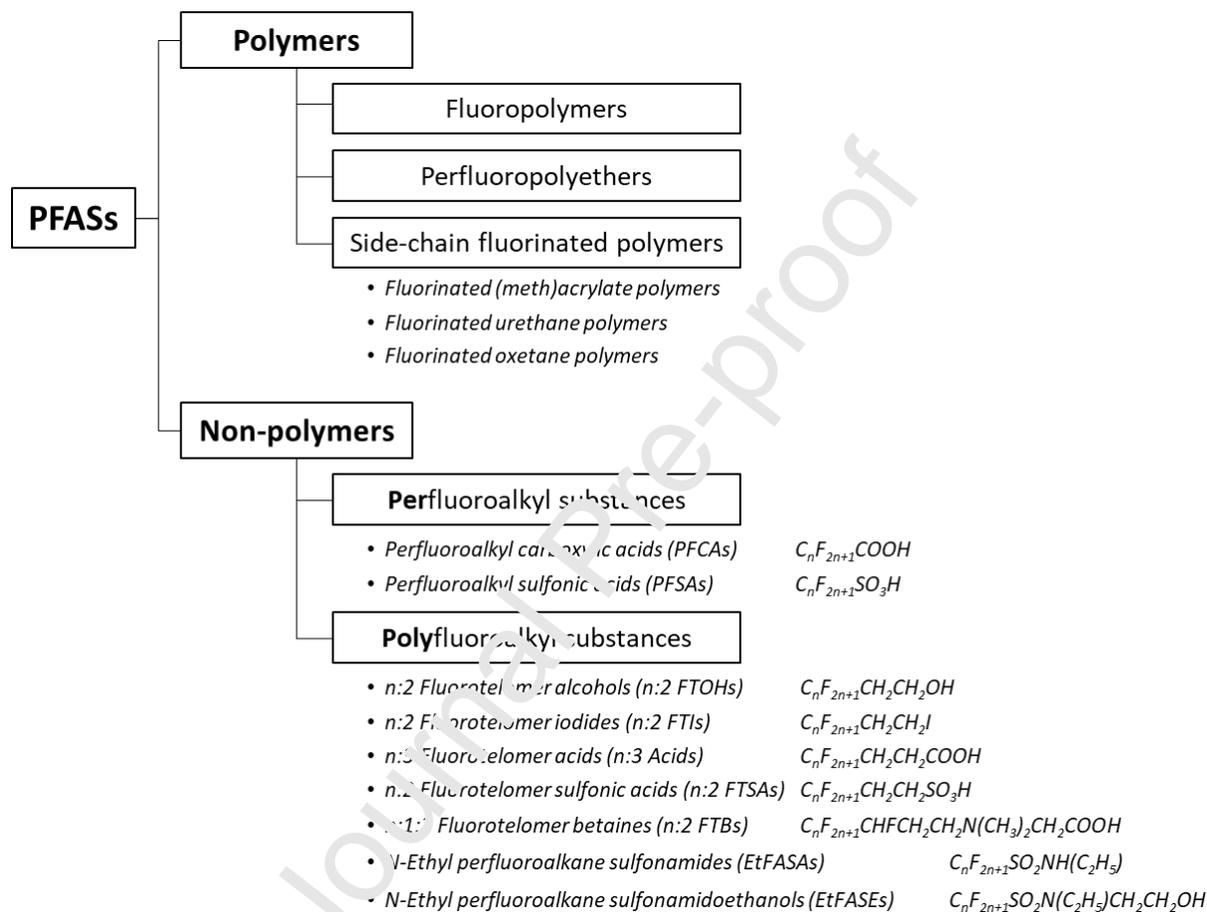


Fig. 2. Classification of PFASs based on Buck et al. (2011) with examples relevant to this review. *(no color in print)*

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, Rich, Sedlacko, Hyland, 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, Chu, and Smyth 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 discharge 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 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, Anderson, and Guo 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 less than 2% fluorosurfactants (ITRC 2020). AFFFs have been fabricated through two main processes: electrochemical fluorination (ECF) (Buck et al. 2011; Mejia-Avendaño et al. 2016), 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, Day, and Field 2013; Place and

Field 2012; Houtz et al. 2013; Anderson et al. 2016; Barzen-Hanson et al. 2017b). In contrast, fluorotelomerization leads to the exclusive formation of partially fluorinated homologues differing by C_2F_4 units (Backe, Day, and Field 2013; Houtz et al. 2013; Barzen-Hanson et al. 2017b). Long-chain species were used in fluorotelomer foams until 2016, when manufacturers began focusing on short-chain “C6 foams” (USEPA 2018; Kempisty, Xing, and Racz 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 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, Chu, and Smyth 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 U.S. (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 ($403 \pm 127 \text{ ng g}^{-1}$), followed by PFOA ($34 \pm 22 \text{ ng g}^{-1}$) (Venkatesan and Halden 2015). 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; Kim 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, Evans, and Naidenko 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 nonaqueous 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 2020c).

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 improve 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, DiCarlo, and Blunt 2000b; Sung and Chen 2011); and (3) the relative affinity of the surfactant to the air-water interface relative to the solid phase (Kim, Rao, and Annable 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):

$$\Gamma = \frac{-1}{RT} \frac{\partial \sigma}{\partial \ln[C_T]} \quad \text{Eq. 1}$$

$$C_T = C (C + C_s) \quad \text{Eq. 2}$$

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 (Brusseu, Anderson, and Guo 2020; Brusseu 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, DiCarlo, and Blunt 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:

$$K_{aw} = \frac{r}{c} \quad \text{Eq. 3}$$

where K_{aw} is the air-water interfacial sorption coefficient defined in units of length (Costanza et al. 2019; Lyu et al. 2018). Figure 3 summarizes values of K_{aw} for PFOS and PFOA in 0.01 M NaCl or synthetic groundwater (containing monovalent and divalent cations) from several studies, except where noted. The discrete 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 $\mu\text{g/L}$ 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).

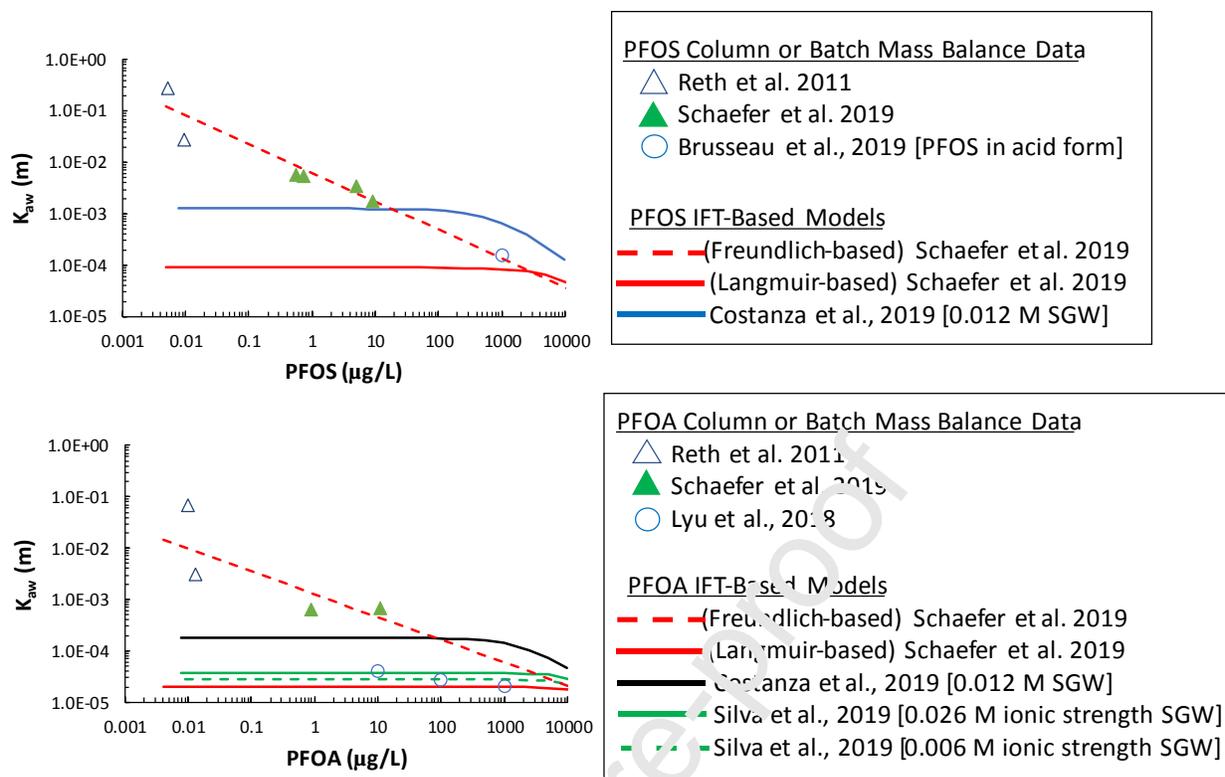


Figure 3. K_{aw} as a function of PFOS and PFOA concentration. The potassium form of PFOS and acid form of PFOA are used, except where noted. Results are for 0.01 M NaCl solutions, except where noted. Data points from Reth et al. (2011) were based on calculations described in Schaefer et al. (2020). SGW = synthetic groundwater. SGWs contained a mixture of monovalent and divalent cations. (no color in print)

While both the Langmuir- and Freundlich-based approaches for relating IFT data to PFOS and PFOA surface concentration yield similar results at concentrations $>1,000 \mu\text{g/L}$ (Arshadi et al., 2020; Schaefer et al., 2019), their extrapolations to low concentrations differ substantially. It is worth mentioning that at high PFAS concentrations, hemi-micelles 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 hemi-micelles on adsorbent surfaces were reported in the range of 0.01–0.001 times the critical micelle concentration of 15,700 mg L⁻¹ (Kissa 2001).

Figure 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_{ow} 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, or PFASs other than PFAAs. 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 $\mu\text{g/L}$ 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, Zeng, and Brusseau 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, DiCarlo, and Blunt 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, Fang, et al. 2019). 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 amongst 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, Liu, and Shih 2012; 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, Yan, and Jing 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, Oliver, and Kookana 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-Avendanos 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, these newly emerged PFASs can have variable pK_a values in environmentally relevant pH range, implying strongly site-specific sorption behaviors and highly subject to changes to environmental conditions.

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. 2017a; 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, Zhong, and Liu 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, Su, et al. 2019). 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, Muir, and Mabury 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, Wang, Szostek, et al. 2010; 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 (Figure 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, Wang, Szostek, et al. 2010; Wang et al. 2009; Liu, Wang, Buck, et al. 2010; 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 compounds for source tracking purposes, but have been infrequently monitored in the field (Wang et al. 2012). 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, Wang, Buck, et al. 2010). 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-Avenidaño 2013; Dasu and Lee 2016; Dasu et al. 2013; Dasu, Liu, and Lee 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, Jones, and Sweetman 2009).

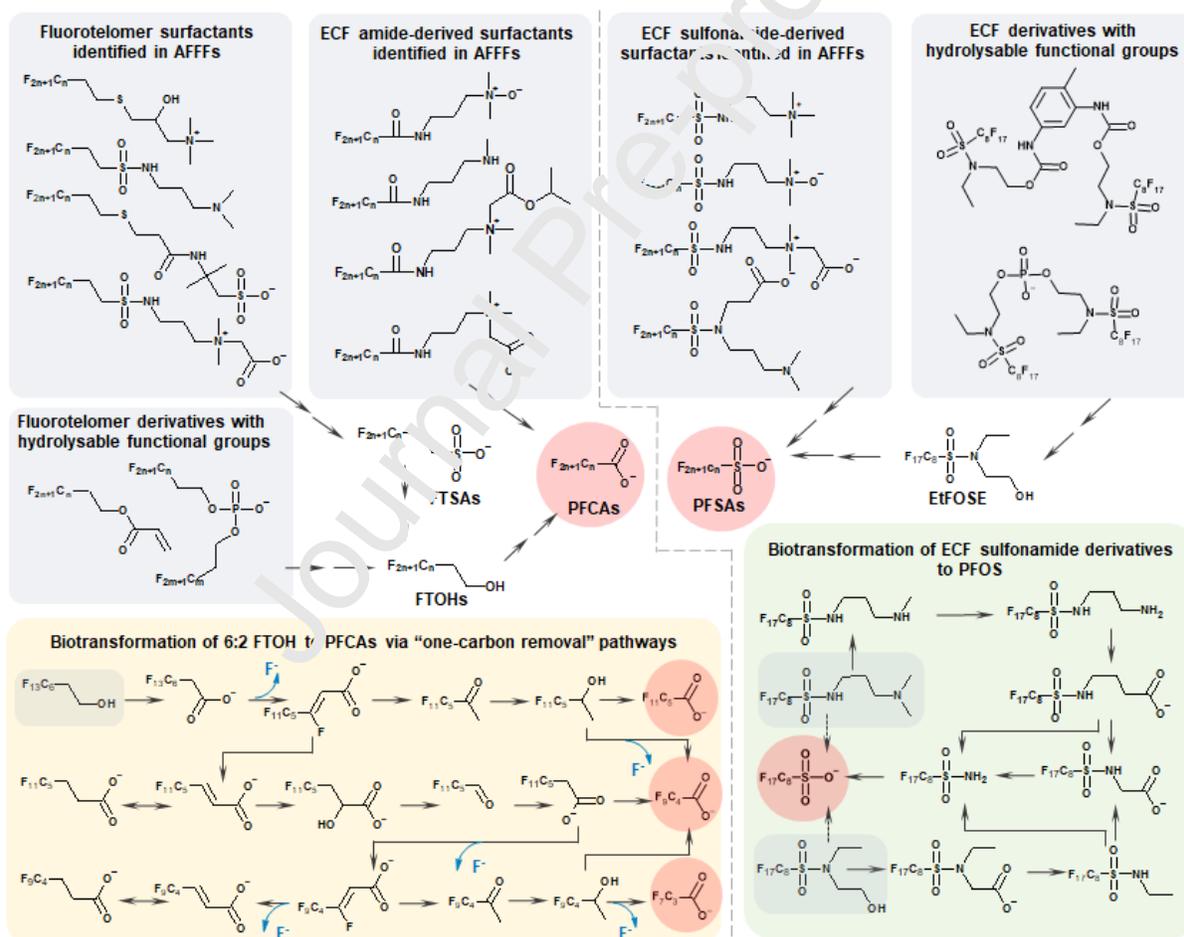


Fig. 4. Illustration of possible aerobic biotransformation of four classes of polyfluoroalkyl substances (precursors) to PFCAs or PFASs in vadose zones. Two representative transformation

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. (*no color in print*)

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, Munoz, et al. 2019; 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 FTSA 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 4-5 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 FTSA observed at many AFFF sites – the environment being such that desulfonation of such fluorotelomers is energetically unfavorable for microorganisms (Backe, Day, and Field 2013; Mejia-Avenidaño, Munoz, Duy, et al. 2017). An emerging class of fluorotelomers, though not necessarily new chemistry or products, are comprised of linear n:3 structures and n:1:2 type of structures. In several AFFF sites, they have been found to be more abundant than PFAAs in soils and earthworm tissues (Mejia-Avenidaño,

Munoz, Duy, 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 ($\text{F}(\text{CF}_2)_n\text{—S}(\text{O})_2\text{NH—}$). In contrast, amide-containing equivalents ($\text{F}(\text{CF}_2)_n\text{—C}(\text{O})\text{NH—}$) were also used and sometimes could be present as impurities (Zabaleta et al. 2018; Mejia-Avenidaño 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-Avenidaño et al. 2016).

ECF-derived PFASs that contain hydrolysable functional groups, such as perfluorooctane sulfonamido ethanol-based phosphate esters (mono-, di- and tri-), can similarly undergo initial microbially-mediated hydrolysis of 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-Avenidaño 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. 2017a), 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. 2017a; D'Agostino and Mabury 2014). Mejia-Avenidaño 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 ($\gg 180$ d) even in laboratory microcosms. Our 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, De Silva, and Martin 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 a 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 FTSA, 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, Day, and Field 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 FTSA 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 0.65 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-Avenidaño 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, Wang, and Chu 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 PFSA and lower absorption of PFCA 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 (rat, 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. 2020).

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, Lee, et al. 2017), 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 lethosis 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, Liu, and Lee 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, Zhang, and Liang 2019b) and freshwater pond samples exposed to PFASs (Zhang, Zhang, and Liang 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 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, Merino, et al. 2017).

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*-perfluorooctanesulfonate (OPS), 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), sucrose 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 sucrose 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 B₁₂ 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, Wang, and Ma 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, Lewis, and Ahrens 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, McLachlan, and De Voogt 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, Moore, and Ma 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 2016), 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 electrostatic 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, Moore, and Ma 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, Vamerali, and Manzetti 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, Moore, and Ma 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. 2020 and Gobelius, Lewis, and Ahrens 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, Lewis, and Ahrens 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. 2020; Zhao, Fan, 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, Lewis, and Ahrens 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 $140 \text{ pg g}^{-1} \text{ dw}$ for PFHpA (45% of ΣPFASs) and $72 \text{ pg g}^{-1} \text{ dw}$ 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 ratio of TF 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).

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	<i>Glycine max L. Merrill</i>	0.59	416	155	Wen et al. 2016
Lettuce	<i>Lactuca sativa L</i>	0.52	416	155	Wen et al. 2016
Maize	<i>Zea mays L. cv. Nongda 108</i>	0.51	416	155	Wen et al. 2016
Alfalfa	<i>Medicago sativa L. cv. Chaoren</i>	0.43	416	155	Wen et al. 2016
Narrowleaf cattail	<i>T. angustifolia</i>	0.42	405	220	Zhang et al. 2020
Wheat	<i>Triticum aestivum L</i>	0.37	500	200	Zhao et al. 2017
Mung bean	<i>Vigna radiata L. Wilczek</i>	0.15	416	155	Wen et al. 2016
Ryegrass	<i>Lolium multiflorum Lam</i>	0.23	416	155	Wen et al. 2016
Radish	<i>Raphanus sativus L. cv. Dahongpao</i>	0.10	416	155	Wen et al. 2016

6.4 PFAS chain length effects in plant uptake

Along with the plant type, soil organic matters, 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 CF₂ chains have stronger hydrophobicity and more readily adsorb onto the hydrophobic portion of the soil substrate through non-specific interactions (Zhang et al. 2020). 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, Rich, Sedlacko, Hundal, et al. 2014a; Felizeter, McLachlan, and De Voogt 2014). Our current understanding is that the available fraction of PFASs in interstitial water will adsorb onto the root epidermis, diffuse through the epidermis, 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, Oliver, and Kookana 2018). Therefore, the carryover of PFASs from soil to plants depends on not only the initial PFAS concentrations in the solution but also on PFAS speciation and water quality. Ma et al. (2020) have shown 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 towards 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 P-450. 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 16¹⁹ fluorotelomer alcohol (FTOH) or perfluoroalkane sulfonamidoethanol (FASE) transformation products. Parent compounds detected were PFAAs, therefore the FTOH and FASE metabolites are fully consistent with the P-450 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 P-450 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 is very complex and mainly depends 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, Vamerali, and Marzetti 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 need to 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 (Nickerson et al. 2020).

- 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, Pfaff, and Breedveld 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 & 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.

Journal Pre-proof

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.

Declaration of Competing Interest

The authors declare no competing financial interests.

Author Statement

Hamidreza Sharifan: Original draft chapters 2, 6 and conceptualization. Majid Bagheri: Original draft chapter 6. Dan Wang: Original draft chapters 3, 4. Joel G. Burken: Original draft chapter 6. Christopher P. Higgins: Original draft chapters 1, 2. Yanna Liang: Original draft chapter 5. Jinxia Liu: Original draft chapters 3, 4. Charles E. Schaefer: Original draft chapter 3. Jens Blotevogel: Original draft chapters 1, 2, 7 and project administration. All authors reviewed and edited all chapters.

References

- Adamson, AW, and AP Gast. 1997. 'Wiley Interscience Publication', *Physical Chemistry of Surfaces, John Wiley & Sons, Inc., New York.*
- Ahmed, M. B., Jahir, M. A. H., McLaughlan, R., Nguyen, L. N., Xu, B., & Nghiem, L. D. 2020. Per- and polyfluoroalkyl substances in soil and sediments: Occurrence, fate, remediation and future outlook. *Science of The Total Environment*, 748: 141251
- Ahrens, Lutz, Tom Harner, Mahiba Shoeib, Douglas A Lane, and Jennifer G Murphy. 2012. 'Improved characterization of gas-particle partitioning for per-and polyfluoroalkyl substances in the atmosphere using annular diffusion denuder samplers', *Environmental science & technology*, 46: 7199-206.
- Anderson, R. Hunter, G. Cornell Long, Ronald C. Porter, and Janet K. Anderson. 2016. 'Occurrence of select perfluoroalkyl substances at U.S. Air Force aqueous film-forming foam release sites other than fire-training areas: Field-validation of critical fate and transport properties', *Chemosphere*, 150: 678-85.
- Armitage, James M, Matthew MacLeod, and Ian T Cousins. 2009. 'Comparative assessment of the global fate and transport pathways of long-chain perfluorocarboxylic acids (PFCAs) and perfluorocarboxylates (PFCs) emitted from direct sources', *Environmental Science & Technology*, 43: 5830-36.
- Arshadi, Masoud, Costanza, Jed, Abriola, Linda M., Pennell, Kurt D. 2020. 'Comment on "Uptake of Poly- and Perfluoroalkyl Substances at the Air-Water Interface"', *Environ. Sci. Technol.*, 54, 7019-7020.
- Backe, Will J., Thomas C. Day, and Jennifer A. Field. 2013. 'Zwitterionic, Cationic, and Anionic Fluorinated Chemicals in Aqueous Film Forming Foam Formulations and Groundwater

- from U.S. Military Bases by Nonaqueous Large-Volume Injection HPLC-MS/MS', *Environ. Sci. Technol.*, 47: 5226-34.
- Bagheri, Majid, Khalid Al-Jabery, Donald Wunsch, and Joel G Burken. 2020. 'Examining plant uptake and translocation of emerging contaminants using machine learning: Implications to food security', *Science of the total environment*, 698: 133999.
- Bagheri, Majid, Khalid Al-jabery, Donald C Wunsch, and Joel G Burken. 2019. 'A deeper look at plant uptake of environmental contaminants using intelligent approaches', *Science of the total environment*, 651: 561-69.
- Bao, Yixiang, Bingxin Li, Shuguang Xie, and Jun Huang. 2018. 'Vertical profiles of microbial communities in perfluoroalkyl substance-contaminated soils', *Annals of Microbiology*, 68: 399-408.
- Barton, Catherine A, Larry E Butler, Charles J Zarzecki, John Flaherty, and Mary Kaiser. 2006. 'Characterizing perfluorooctanoate in ambient air near the fence line of a manufacturing facility: comparing modeled and monitored values', *Journal of the Air & Waste Management Association*, 56: 48-55.
- Barzen-Hanson, K. A., S. C. Roberts, S. Choyke, K. Oetjen, A. McAlees, N. Riddell, R. McCrindle, P. L. Ferguson, C. P. Higgins, and J. A. Field. 2017a. 'Discovery of 40 Classes of Per- and Polyfluoroalkyl Substances in Historical Aqueous Film-Forming Foams (AFFFs) and AFFF-Impacted Groundwater', *Environ Sci Technol*, 51: 2047-57.
- Benskin, Jonathan P, Amila O De Silva, and Jonathan W Martin. 2010. 'Isomer profiling of perfluorinated substances as a tool for source tracking: a review of early findings and future applications.' in, *Reviews of Environmental Contamination and Toxicology Volume 208* (Springer).

- Benskin, Jonathan P., Michael G. Ikonou, Frank A. P. C. Gobas, Million B. Woudneh, and John R. Cosgrove. 2012. 'Observation of a novel PFOS-precursor, the perfluorooctane sulfonamido ethanol-based phosphate (SAmPAP) diester, in marine sediments', *Environ Sci Technol*, 46: 6505-14.
- Bizkarguenaga, E, I Zabaleta, L Mijangos, A Iparraguirre, LA Fernández, A Prieto, and O Zuloaga. 2016. 'Uptake of perfluorooctanoic acid, perfluorooctane sulfonate and perfluorooctane sulfonamide by carrot and lettuce from compost amended soil', *Science of the Total Environment*, 571: 444-51.
- Blaine, Andrea C, Courtney D Rich, Erin M Sedlacko, Lakhwinder S Hundal, Kuldip Kumar, Christopher Lau, Marc A Mills, Kimberly M Harris, and Christopher P Higgins. 2014a. 'Perfluoroalkyl acid distribution in various plant compartments of edible crops grown in biosolids-amended soils', *Environmental science & technology*, 48: 7858-65.
- Blaine, Andrea C, Courtney D Rich, Erin M Sedlacko, Katherine C Hyland, Cecil Stushnoff, Eric RV Dickenson, and Christopher P Higgins. 2014b. 'Perfluoroalkyl acid uptake in lettuce (*Lactuca sativa*) and strawberry (*Fragaria ananassa*) irrigated with reclaimed water', *Environmental science & technology*, 48: 14361-68.
- Blotevogel, Jens, Robert J Giraud, and Thomas Borch. 2018. 'Reductive Defluorination of Perfluorooctanoic Acid by Zero-Valent Iron and Zinc: A DFT-Based Kinetic Model', *Chemical Engineering Journal*, 335: 248-254.
- Brusseau, Mark L, R Hunter Anderson, and Bo Guo. 2020. 'PFAS concentrations in soils: Background levels versus contaminated sites', *Science of The Total Environment*: 140017.

- Brusseau, Mark L, M Narter, G Schnaar, and J Marble. 2009. 'Measurement and estimation of organic-liquid/water interfacial areas for several natural porous media', *Environmental science & technology*, 43: 3619-25.
- Brusseau, Mark L, and Sarah Van Glubt. 2019. 'The influence of surfactant and solution composition on PFAS adsorption at fluid-fluid interfaces', *Water research*, 161: 17-26.
- Bruton, Thomas A., and David L. Sedlak. 2017. 'Treatment of Aqueous Film-Forming Foam by Heat-Activated Persulfate Under Conditions Representative of In Situ Chemical Oxidation', *Environmental Science & Technology*, 51: 13879-85.
- Buck, Robert C, James Franklin, Urs Berger, Jason M Corder, Ian T Cousins, Pim De Voogt, Allan Astrup Jensen, Kurunthachalam Kannan, Scott A Mabury, and Stefan PJ van Leeuwen. 2011. 'Perfluoroalkyl and polyfluoroalkyl substances in the environment: terminology, classification, and origins', *Integrated environmental assessment and management*, 7: 513-41.
- Burken, JG. 2003. 'Uptake and metabolism of organic compounds: green-liver model', *Phytoremediation: transformation and control of contaminants*, 59: 59-84.
- Butt, Craig M., Derek C. G. Muir, and Scott A. Mabury. 2014. 'Biotransformation pathways of fluorotelomer-based polyfluoroalkyl substances: A review', *Environmental Toxicology and Chemistry*, 33: 243-67.
- Butzen, Margaret L, John T Wilkinson, Sean R McGuinness, Samantha Amezcua, Graham F Peaslee, and Jeremy B Fein. 2020. 'Sorption and desorption behavior of PFOS and PFOA onto a Gram-positive and a Gram-negative bacterial species measured using particle-induced gamma-ray emission (PIGE) spectroscopy', *Chemical Geology*: 119778.

- Calafat, Antonia M, Lee-Yang Wong, Zsuzsanna Kuklennyik, John A Reidy, and Larry L Needham. 2007. 'Polyfluoroalkyl chemicals in the US population: data from the National Health and Nutrition Examination Survey (NHANES) 2003–2004 and comparisons with NHANES 1999–2000', *Environmental health perspectives*, 115: 1596-602.
- Chen, Hao, Min Liu, Gabriel Munoz, Sung Vo Duy, Sebastien Sauve, Yiming Yao, Hongwen Sun, and Jinxia Liu. 2020. 'Fast Generation of Perfluoroalkyl Acids from Polyfluoroalkyl Amine Oxides in Aerobic Soils', *Environmental Science & Technology Letters*, in review.
- Chen, Hao, Yiming Yao, Zhen Zhao, Yu Wang, Qi Wang, Chen Ren, Bin Wang, Hongwen Sun, Alfredo C Alder, and Kurunthachalam Kannan. 2018. 'Multimedia distribution and transfer of per-and polyfluoroalkyl substances (PFASs) surrounding two fluorochemical manufacturing facilities in Fuxin, China' *Environmental science & technology*, 52: 8263-71.
- Chen, Lianguo, Mirabelle M. P. Tsui, James C. W. Lam, Qi Wang, Chenyan Hu, Onyx W. H. Wai, Bingsheng Zhou, and Paul K. S. Lam. 2019. 'Contamination by perfluoroalkyl substances and microbial community structure in Pearl River Delta sediments', *Environmental pollution*, 245: 218-25.
- Chen W, Zhang X, Manolodiev M & Wang Z. 2017. Sorption of Perfluorooctane Sulfonate and Perfluorooctanoate on Polyacrylonitrile Fiber-Derived Activated Carbon Fibers: In Comparison with Activated Carbon. *RSC Advances*, 7:2:927
- Chetverikov, S. P., D. A. Sharipov, T. Yu Korshunova, and O. N. Loginov. 2017. 'Degradation of perfluorooctanyl sulfonate by strain *Pseudomonas plecoglossicida* 2.4-D', *Applied Biochemistry and Microbiology*, 53: 533-38.

- Chu, Shaogang, and Robert J Letcher. 2017. 'Side-chain fluorinated polymer surfactants in aquatic sediment and biosolid-augmented agricultural soil from the Great Lakes basin of North America', *Science of the Total Environment*, 607: 262-70.
- Clarke, Bradley O, and Stephen R Smith. 2011. 'Review of 'emerging' organic contaminants in biosolids and assessment of international research priorities for the agricultural use of biosolids', *Environment international*, 37: 226-47.
- Costanza, Jed, Masoud Arshadi, Linda M Abriola, and Kurt D Pennell. 2019. 'Accumulation of PFOA and PFOS at the Air-Water Interface', *Environmental Science & Technology Letters*, 6: 487-91.
- Cui, D., Li, X., & Quinete, N. 2020. Occurrence, fate, sources and toxicity of PFAS: What we know so far in Florida and major gaps. *Trends in Analytical Chemistry*, 130: 115976.
- Culligan, Katherine A, Dorthe Wildenschild, Britt SB Christensen, William G Gray, Mark L Rivers, and Andrew FB Tompson. 2004. 'Interfacial area measurements for unsaturated flow through a porous medium', *Water Resources Research*, 40.
- D'Agostino, Lisa A., and Scott A. Mabury. 2014. 'Identification of Novel Fluorinated Surfactants in Aqueous Film Forming Foams and Commercial Surfactant Concentrates', *Environ. Sci. Technol.*, 48: 121-29.
- D'Agostino, Lisa A., and Scott A. Mabury. 2017. 'Aerobic biodegradation of two fluorotelomer sulfonamide-based aqueous film forming foam components produces perfluoroalkyl carboxylates', *Environmental Toxicology and Chemistry*, 36: 2012-21.
- D'eon, Jessica C, Michael D Hurley, Timothy J Wallington, and Scott A Mabury. 2006. 'Atmospheric chemistry of N-methyl perfluorobutane sulfonamidoethanol, C₄F₉SO₂N

- (CH₃) CH₂CH₂OH: kinetics and mechanism of reaction with OH', *Environmental science & technology*, 40: 1862-68.
- Dalahmeh, Sahar, Sana Tirgani, Allan John Komakech, Charles B Niwagaba, and Lutz Ahrens. 2018. 'Per-and polyfluoroalkyl substances (PFASs) in water, soil and plants in wetlands and agricultural areas in Kampala, Uganda', *Science of The Total Environment*, 631: 660-67.
- Dasu, K., J. Liu, and L. S. Lee. 2012. 'Aerobic soil biodegradation of 8:2 fluorotelomer stearate monoester', *Environ Sci Technol*, 46: 3831-6.
- Dasu, K., L. A. Royer, J. Liu, and L. S. Lee. 2010. 'Hydrolysis of fluorotelomer compounds leading to fluorotelomer alcohol production during solvent extractions of soils', *Chemosphere*, 81: 911-7.
- Dasu, Kavitha, and Linda S. Lee. 2016. 'Aerobic biodegradation of toluene-2,4-di(8:2 fluorotelomer urethane) and hexamethylene-1,6-di(8:2 fluorotelomer urethane) monomers in soils', *Chemosphere*, 144: 2482-88.
- Dasu, Kavitha, Linda S. Lee, Ronald F. Turco, and Loring F. Nies. 2013. 'Aerobic biodegradation of 8:2 fluorotelomer stearate monoester and 8:2 fluorotelomer citrate triester in forest soil', *Chemosphere*, 91: 399-405.
- Dauchy, Xavier, Virginie Boiteux, Adeline Colin, Jessica Hémard, Cristina Bach, Christophe Rosin, and Jean-François Munoz. 2019. 'Deep seepage of per-and polyfluoroalkyl substances through the soil of a firefighter training site and subsequent groundwater contamination', *Chemosphere*, 214: 729-37.

- Dolfing, Jan. 2003. 'Thermodynamic Considerations for Dehalogenation.' in Max M. Häggblom and Ingeborg D. Bossert (eds.), *Dehalogenation: Microbial Processes and Environmental Applications* (Springer US: Boston, MA).
- Duchesne, A. L., Brown, J. K., Patch, D. J., Major, D., Weber, K. P., & Gerhard, J. I. 2020. Remediation of PFAS-Contaminated Soil and Granular Activated Carbon by Smoldering Combustion. *Environmental Science & Technology*, 54, 19: 12631-12640
- Ellis, DA, JW Martin, SA Mabury, MD Hurley, MP Sulbaek Andersen, and TJ Wallington. 2003. 'Atmospheric lifetime of fluorotelomer alcohols', *Environmental science & technology*, 37: 3816-20.
- Ellis, David A, Jonathan W Martin, Amila O De Silva, Scott A Mabury, Michael D Hurley, Mads P Sulbaek Andersen, and Timothy J Wallington. 2004. 'Degradation of fluorotelomer alcohols: a likely atmospheric source of perfluorinated carboxylic acids', *Environmental science & technology*, 38: 3316-21.
- EPA, US. 2007. 'Method 1614 brominated diphenyl ethers in water soil, sediment and tissue by HRGC/HRMS', *EPA*.
- Fang, Xiangguang, Qi Wang, Zhen Zhao, Jianhui Tang, Chongguo Tian, Yiming Yao, Junchao Yu, and Hongwei Sun. 2018. 'Distribution and dry deposition of alternative and legacy perfluoroalkyl and polyfluoroalkyl substances in the air above the Bohai and Yellow Seas, China', *Atmospheric Environment*, 192: 128-35.
- Felizeter, Sebastian, Michael S McLachlan, and Pim De Voogt. 2012. 'Uptake of perfluorinated alkyl acids by hydroponically grown lettuce (*Lactuca sativa*)', *Environmental science & technology*, 46: 11735-43.

- Felizeter, Sebastian, Michael S McLachlan, and Pim De Voogt. 2014. 'Root uptake and translocation of perfluorinated alkyl acids by three hydroponically grown crops', *Journal of agricultural and food chemistry*, 62: 3334-42.
- Filipovic, Marko, Andreas Woldegiorgis, Karin Norström, Momina Bibi, Maria Lindberg, and Ann-Helen Österås. 2015. 'Historical usage of aqueous film forming foam: A case study of the widespread distribution of perfluoroalkyl acids from a military airport to groundwater, lakes, soils and fish', *Chemosphere*, 129: 39-45.
- Gallen, C, G Eaglesham, D Drage, T Hue Nguyen, and JF Mueller. 2018. 'A mass estimate of perfluoroalkyl substance (PFAS) release from Australian wastewater treatment plants', *Chemosphere*, 208: 975-83.
- Galloway, Jason E, Anjelica VP Moreno, Andrew B Lindstrom, Mark J Strynar, Seth Newton, Andrew A May, and Linda K Weavers. 2020. 'Evidence of Air Dispersion: HFPO-DA and PFOA in Ohio and West Virginia Surface Water and Soil near a Fluoropolymer Production Facility', *Environmental science & technology*.
- Gao, Xiaodong, and Jon Chorover. 2012. 'Adsorption of perfluorooctanoic acid and perfluorooctanesulfonic acid to iron oxide surfaces as studied by flow-through ATR-FTIR spectroscopy', *Environmental Chemistry*, 9: 148-57.
- Ghisi, Rossella, Teofilo Vamerali, and Sergio Manzetti. 2019. 'Accumulation of perfluorinated alkyl substances (PFAS) in agricultural plants: a review', *Environmental research*, 169: 326-41.
- Giesy, John P, and Kurunthachalam Kannan. 2001. 'Global distribution of perfluorooctane sulfonate in wildlife', *Environmental science & technology*, 35: 1339-42.

- Gobelius, Laura, Jeffrey Lewis, and Lutz Ahrens. 2017. 'Plant uptake of per-and polyfluoroalkyl substances at a contaminated fire training facility to evaluate the phytoremediation potential of various plant species', *Environmental science & technology*, 51: 12602-10.
- Gonzalez, D., Thompson, K., Quiñones, O., Dickenson, E., & Bott, C. 2021. Assessment of PFAS fate, transport, and treatment inhibition associated with a simulated AFFF release within a wastewater treatment plant. *Chemosphere*, 262: 127900.
- Gottschall, N., E. Topp, M. Edwards, M. Payne, S. Kleywegg, and D. R. Lapen. 2017. 'Brominated flame retardants and perfluoroalkyl acids in groundwater, tile drainage, soil, and crop grain following a high application of municipal biosolids to a field', *Science of The Total Environment*, 574: 1345-59.
- Gribble, Matthew O, Scott M Bartell, Kurunthadain Kannan, Qian Wu, Patricia A Fair, and Diane L Kamen. 2015. 'Longitudinal measures of perfluoroalkyl substances (PFAS) in serum of Gullah African Americans in South Carolina: 2003–2013', *Environmental research*, 143: 82-88.
- Guelfo, Jennifer L, and Christopher P Higgins. 2013. 'Subsurface transport potential of perfluoroalkyl acids at aqueous film-forming foam (AFFF)-impacted sites', *Environmental science & technology*, 47: 4164-71.
- Guo, Bo, Jicai Zeng, and Mark L Brusseau. 2020. 'A Mathematical Model for the Release, Transport, and Retention of Per- and Polyfluoroalkyl Substances (PFAS) in the Vadose Zone', *Water Resources Research*, 56: e2019WR026667.
- Gurkov, Theodor D, Dora T Dimitrova, Krastanka G Marinova, Christine Bilke-Crause, Carsten Gerber, and Ivan B Ivanov. 2005. 'Ionic surfactants on fluid interfaces: determination of

- the adsorption; role of the salt and the type of the hydrophobic phase', *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 261: 29-38.
- Hale, Sarah E, Hans Peter H Arp, Gøril Aasen Slinde, Emma Jane Wade, Kamilla Bjørseth, Gijs D Breedveld, Bengt Fredrik Straith, Kamilla Grotthing Moe, Morten Jartun, and Åse Høisæter. 2017. 'Sorbent amendment as a remediation strategy to reduce PFAS mobility and leaching in a contaminated sandy soil from a Norwegian firefighting training facility', *Chemosphere*, 171: 9-18.
- Hamid, Hanna, and Loretta Y. Li. 2016. "Role of wastewater treatment plant in environmental cycling of poly- and perfluoroalkyl substances." In.
- Harding-Marjanovic, Katie C., Erika F. Houtz, Shan Yi, Jennifer A. Field, David L. Sedlak, and Lisa Alvarez-Cohen. 2015. 'Aerobic Biodegradation of Fluorotelomer Thioether Amido Sulfonate (Lodyne) in AFFF-amended Microcosms', *Environmental Science & Technology*, 49: 7666-74.
- Heydebreck, Franziska, Jianhui Tang, Zhiyong Xie, and Ralf Ebinghaus. 2015. 'Alternative and legacy perfluoroalkyl substances: differences between European and Chinese river/estuary systems', *Environmental science & technology*, 49: 8386-95.
- Hill, Christopher, Adam Czajka, Gavin Hazell, Isabelle Grillo, Sarah E Rogers, Maximilian WA Skoda, Nigel Joslin, John Payne, and Julian Eastoe. 2018. 'Surface and bulk properties of surfactants used in fire-fighting', *Journal of colloid and interface science*, 530: 686-94.
- Høisæter, Åse, Anja Pfaff, and Gijs D Breedveld. 2019. 'Leaching and transport of PFAS from aqueous film-forming foam (AFFF) in the unsaturated soil at a firefighting training facility under cold climatic conditions', *Journal of contaminant hydrology*, 222: 112-22.

- Holden, Patricia A, and Noah Fierer. 2005. 'Microbial processes in the vadose zone', *Vadose Zone Journal*, 4: 1-21.
- Houtz, Erika F, Christopher P Higgins, Jennifer A Field, and David L Sedlak. 2013. 'Persistence of perfluoroalkyl acid precursors in AFFF-impacted groundwater and soil', *Environmental science & technology*, 47: 8187-95.
- Hu, Xindi C, David Q Andrews, Andrew B Lindstrom, Thomas A Bruton, Laurel A Schaidler, Philippe Grandjean, Rainer Lohmann, Courtney C Carignan, Arlene Blum, and Simona A Balan. 2016. 'Detection of poly-and perfluoroalkyl substances (PFASs) in US drinking water linked to industrial sites, military fire training areas, and wastewater treatment plants', *Environmental science & technology letters*, 3: 344-50.
- Huang, Shan, and Peter R. Jaffé. 2019. 'Defluorination of Perfluorooctanoic Acid (PFOA) and Perfluorooctane Sulfonate (PFOS) by Acidimicrobium sp. Strain A6', *Environmental Science & Technology*, 53: 11410-19.
- ITRC. 2020. 'Interstate Technology & Regulatory Council (ITRC).', *Per- and Polyfluoroalkyl Substances (PFAS). Technical/Regulatory Guidance. Washington, DC, U.S.A. June 27, 2020.* https://pfas-1.itrcweb.org/wp-content/uploads/2020/04/ITRC_PFAS_TechReg_April2020.pdf.
- Jiao, X., Shi, Q., & Gan, J. 2020. 'Uptake, accumulation and metabolism of PFASs in plants and health perspectives: A critical review'. *Critical Reviews in Environmental Science and Technology*, 1-32.
- Jin B, Mallula S, Golovko SA, Golovko MY, Xiao F. 2020. 'In Vivo Generation of PFOA, PFOS, and Other Compounds from Cationic and Zwitterionic Per-and Polyfluoroalkyl

- Substances in a Terrestrial Invertebrate (*Lumbricus terrestris*)'. *Environmental Science & Technology*, 54: 7378-7387.
- Johnson, Ramona L, Amy J Anschutz, Jean M Smolen, Matt F Simcik, and R Lee Penn. 2007. 'The adsorption of perfluorooctane sulfonate onto sand, clay, and iron oxide surfaces', *Journal of Chemical & Engineering Data*, 52: 1165-70.
- Kannan, Kurunthachalam, Simonetta Corsolini, Jerzy Falandysz, Gilberto Fillmann, Kurunthachalam Senthil Kumar, Bommanna G Loganathan, Mustafa Ali Mohd, Jesus Olivero, Nathalie Van Wouwe, and Jae Ho Yang. 2004. 'Perfluorooctanesulfonate and related fluorochemicals in human blood from several countries', *Environmental science & technology*, 38: 4489-95.
- Ke, Yanchu, Jianfei Chen, Xiaoyan Hu, Tianli Tong, Jun Huang, and Shuguang Xie. 2020. 'Emerging perfluoroalkyl substance impacts soil microbial community and ammonia oxidation', *Environmental pollution*, 257: 113615.
- Kempisty, David M, Yun Xing, and LeeAnn Racz. 2018. *Perfluoroalkyl substances in the environment: theory, practice, and innovation* (CRC Press).
- Kennedy, Ann C, and Tami L Stubbs. 2006. 'Soil microbial communities as indicators of soil health'. *Annals of the New York Academy of Sciences*, 45,287.
- Kiaalhosseini, S., Johnson, R. L., Rogers, R. C., Renno, M. I., Lyverse, M., & Sale, T. C. 2016. Cryogenic core collection (C₃) from unconsolidated subsurface media. *Groundwater Monitoring & Remediation*, 36,4: 41-49.
- Kibbey, T. C., Jabrzemski, R., & O'Carroll, D. M. 2020. Supervised machine learning for source allocation of per-and polyfluoroalkyl substances (PFAS) in environmental samples. *Chemosphere*, 262: 126593.

- Kim, Heonki, P Suresh C Rao, and Michael D Annable. 1997. 'Determination of effective air-water interfacial area in partially saturated porous media using surfactant adsorption', *Water Resources Research*, 33: 2705-11.
- Kim Lazcano, Rooney, Youn Jeong Choi, Michael L Mashtare, and Linda S Lee. 2020. 'Characterizing and Comparing Per-and Polyfluoroalkyl Substances in Commercially Available Biosolid and Organic Nonbiosolid-based Products', *Environmental Science & Technology*, 54, 14: 8640–8648
- Kim, Myung Hee, Ning Wang, and Kung Hui Chu. 2014. '6: 2 Fluorotelomer alcohol (6: 2 FTOH) biodegradation by multiple microbial species under different physiological conditions', *Applied Microbiology and Biotechnology*, 98: 1831-40.
- Kim, Myung Hee, Ning Wang, Thomas McDonnell, and Kung-Hui Chu. 2012. 'Biodefluorination and biotransformation of fluorotelomer alcohols by two alkane-degrading *Pseudomonas* strains', *Biotechnology and Bioengineering*, 109: 3041-48.
- Kissa, Erik. 2001. *Fluorinated surfactants and repellents* (CRC Press).
- Korzeniowski, Stephen H., Robert C. Buck, David M. Kempisty, and Martial Pabon. 2019. 'Fluorosurfactants in Firefighting Foams: Past and Present.' in David M. Kampisty, Yun Xing and LeeAnn Racz (eds.), *Perfluoroalkyl Substances in the Environment: Theory, Practice, and Innovation* (CRC Press: Boca Raton, FL).
- Krepich, Scott. 2019. 'Per-and Polyfluorinated Alkylsubstances (PFAS) from Dairy and Fish Using QuEChERS, SPE, and LC–MS/MS', 15, 9, 30-33.
- Kwon, Bum Gun, Hye-Jung Lim, Suk-Hyun Na, Bong-In Choi, Dong-Soo Shin, and Seon-Yong Chung. 2014. 'Biodegradation of perfluorooctanesulfonate (PFOS) as an emerging contaminant', *Chemosphere*, 109: 221-25.

- Letcher, Robert J, Shaogang Chu, and Shirley-Anne Smyth. 2020. 'Side-chain fluorinated polymer surfactants in biosolids from wastewater treatment plants', *Journal of hazardous materials*, 388: 122044.
- Li, Fei, Xinliang Fang, Zhenming Zhou, Xiaobin Liao, Jing Zou, Baoling Yuan, and Wenjie Sun. 2019. 'Adsorption of perfluorinated acids onto soils: Kinetics, isotherms, and influences of soil properties', *Science of the total environment*, 649: 504-14.
- Li, Hu, Jian-Qiang Su, Xiao-Ru Yang, Guo-Wei Zhou, Simon Bo Lassen, and Yong-Guan Zhu. 2019. 'RNA Stable Isotope Probing of Potential Fungi Population in Paddy Soil', *Environmental Science & Technology*, 53: 4841-49.
- Li, Rui, Gabriel Munoz, Yanan Liu, Sébastien Sauvé, S. Anis Ghoshal, and Jinxia Liu. 2019. 'Transformation of novel polyfluoroalkyl substances (PFASs) as co-contaminants during biopile remediation of petroleum hydrocarbons', *Journal of Hazardous Materials*, 362: 140-47.
- Li, Yasong, Danielle P Oliver, and Pai S Kookana. 2018. 'A critical analysis of published data to discern the role of soil and sediment properties in determining sorption of per and polyfluoroalkyl substances (PFASs)', *Science of the Total Environment*, 628: 110-20.
- Liu, Chen, and Jinxia Liu. 2016. 'Aerobic biotransformation of polyfluoroalkyl phosphate esters (PAPs) in soil', *Environmental Pollution*, 212: 230-37.
- Liu, Jinxia, and Sandra Mejia-Avenidaño. 2013. 'Microbial degradation of polyfluoroalkyl chemicals in the environment: A review', *Environ Int*, 61: 98-114.
- Liu, Jinxia, Ning Wang, Robert C. Buck, Barry W. Wolstenholme, Patrick W. Folsom, Lisa M. Sulecki, and Cheryl A. Bellin. 2010. 'Aerobic biodegradation of [¹⁴C] 6:2 fluorotelomer alcohol in a flow-through soil incubation system', *Chemosphere*, 80: 716-23.

- Liu, Jinxia, Ning Wang, Bogdan Szostek, Robert C Buck, Patricia K Panciroli, Patrick W Folsom, Lisa M Sulecki, and Cheryl A Bellin. 2010. '6-2 Fluorotelomer alcohol aerobic biodegradation in soil and mixed bacterial culture', *Chemosphere*, 78: 437-44.
- Liu, Jinxia, Guowei Zhong, Wei Li, and Sandra Mejia-Avendaño. 2019. 'Isomer-specific biotransformation of perfluoroalkyl sulfonamide compounds in aerobic soil', *Science of the Total Environment*, 651: 766-74.
- Liu, Min, Gabriel Munoz, Sung Vo Duy, Sebastien Sauve, and Jinxia Liu. 2020. 'Environmental stability of nitrogen-containing polyfluoroalkyl substances in aerobic soils', *Manuscript in preparation*.
- Loganathan, Bommanna G, Kenneth S Sajwan, Ewan Sinclair, Kurunthachalam Senthil Kumar, and Kurunthachalam Kannan. 2007. 'Perfluoroalkyl sulfonates and perfluorocarboxylates in two wastewater treatment facilities in Kentucky and Georgia', *Water Research*, 41: 4611-20.
- Londono, Nathalia, Ariel R. Donovan, Honglan Shi, Matthew Geisler, and Yanna Liang. 2017. 'Impact of TiO₂ and ZnO nanoparticles on an aquatic microbial community: effect at environmentally relevant concentrations', *Nanotoxicology*, 11: 1140-56.
- Londono, Nathalia, Ariel R. Donovan, Honglan Shi, Matthew Geisler, and Yanna Liang. 2019. 'Effects of environmentally relevant concentrations of mixtures of TiO₂, ZnO and Ag ENPs on a river bacterial community', *Chemosphere*, 230: 567-77.
- Longstaffe, James G, Denis Courtier-Murias, Ronald Soong, Myrna J Simpson, Werner E Maas, Michael Fey, Howard Hutchins, Sridevi Krishnamurthy, Jochem Struppe, and Mehran Alaei. 2012. 'In-situ molecular-level elucidation of organofluorine binding sites in a whole peat soil', *Environmental science & technology*, 46: 10508-13.

- Luo, Q., S. Liang, and Q. Huang. 2018. 'Laccase induced degradation of perfluorooctanoic acid in a soil slurry', 539:241-247.
- Luo, Q., J. Lu, H. Zhang, Z. Wang, M. Feng, S. Y. D. Chiang, D. Woodward, and Q. Huang. 2015. *Laccase-Catalyzed Degradation of Perfluorooctanoic Acid*, 2.7: 198-203
- Lyu, Ying, and Mark L Brusseau. 2020. 'The influence of solution chemistry on air-water interfacial adsorption and transport of PFOA in unsaturated porous media', *Science of The Total Environment*, 713: 136744.
- Lyu, Ying, Mark L Brusseau, Wei Chen, Ni Yan, Xiaori Fu, and Yueyu Lin. 2018. 'Adsorption of PFOA at the air-water interface during transport in unsaturated porous media', *Environmental science & technology*, 52: 7745-53.
- Ma, X., Sharifan, H., Dou, F., Sun, W. 2020. Simultaneous reduction of arsenic (As) and cadmium (Cd) accumulation in rice by zinc oxide nanoparticles. *Chemical Engineering Journal*, 384: 123802.
- McGregor, Rick. 2018. 'In Situ treatment of PFAS- impacted groundwater using colloidal activated Carbon', *Remediation Journal*, 28: 33-41.
- McGuire, Meghan E., Charles Schaefer, Trenton Richards, Will J. Backe, Jennifer A. Field, Erika Houtz, David L. Sedlak, Jennifer L. Guelfo, Assaf Wunsch, and Christopher P. Higgins. 2014. 'Evidence of Remediation-Induced Alteration of Subsurface Poly- and Perfluoroalkyl Substance Distribution at a Former Firefighter Training Area', *Environmental Science & Technology*, 48: 6644-52.
- Mejia-Avenidaño, Sandra, and Jinxia Liu. 2015. 'Production of PFOS from aerobic soil biotransformation of two perfluoroalkyl sulfonamide derivatives', *Chemosphere*, 119: 1084-90.

- Mejia-Avendaño, Sandra, Gabriel Munoz, Sung Vo Duy, Mélanie Desrosiers, Paul Benoit, Sébastien Sauvé, and Jinxia Liu. 2017. 'Novel fluoroalkylated surfactants in soils following firefighting foam deployment during the Lac-Mégantic railway accident', *Environmental Science & Technology*, 51: 8313-23.
- Mejia-Avendaño, Sandra, Gabriel Munoz, Sébastien Sauvé, and Jinxia Liu. 2017. 'Assessment of the Influence of Soil Characteristics and Hydrocarbon Fuel Cocontamination on the Solvent Extraction of Perfluoroalkyl and Polyfluoroalkyl Substances', *Analytical Chemistry*, 89: 2539-46.
- Mejia-Avendaño, Sandra, Sung Vo Duy, Sébastien Sauvé, and Jinxia Liu. 2016. 'Generation of perfluoroalkyl acids from aerobic biotransformation of quaternary ammonium polyfluoroalkyl surfactants', *Environmental science & technology*, 50: 9923-32.
- Mejia-Avendaño, Sandra, Yue Zhi, Bei Yan, and Jinxia Liu. 2020. 'Sorption of Polyfluoroalkyl Surfactants on Surface Soils: Effect of Molecular Structures, Soil Properties, and Solution Chemistry', *Environmental science & technology*, 54: 1513-21.
- Mejia-Avendaño, Sandra, Guowei Zhong, and Jinxia Liu. 2015. 'Comment on "Biodegradation of perfluorooctanesulfonate (PFOS) as an emerging contaminant"', *Chemosphere*, 138: 1037-38.
- Merino, Nancy, Meng Wang, Rocio Ambrocio, Kimberly Mak, Ellen O'Connor, An Gao, Elisabeth L. Hawley, Rula A. Deeb, Linda Y. Tseng, and Shaily Mahendra. 2018. 'Fungal biotransformation of 6:2 fluorotelomer alcohol', *Remediation Journal*, 28: 59-70.
- Milinovic, Jelena, Silvia Lacorte, Anna Rigol, and Miquel Vidal. 2016. 'Sorption of perfluoroalkyl substances in sewage sludge', *Environmental Science and Pollution Research*, 23: 8339-48.

- Moody, Cheryl A, Jonathan W Martin, Wai Chi Kwan, Derek CG Muir, and Scott A Mabury. 2002. 'Monitoring perfluorinated surfactants in biota and surface water samples following an accidental release of fire-fighting foam into Etobicoke Creek', *Environmental science & technology*, 36: 545-51.
- Munoz, G., M. Desrosiers, L. Vetter, S. Vo Duy, J. Jarjour, J. Liu, and S. Sauve. 2020. 'Bioaccumulation of Zwitterionic Polyfluoroalkyl Substances in Earthworms Exposed to Aqueous Film-Forming Foam Impacted Soils', *Environmental Science & Technology*, 54: 1687-97.
- Munoz, G., P. Ray, Sandra Mejia-Avenida, S. Vo Duy, L. Tien Do, J. Liu, and S. Sauve. 2018. 'Optimization of extraction methods for comprehensive profiling of perfluoroalkyl and polyfluoroalkyl substances in firefighting foam impacted soils', *Anal Chim Acta*, 1034: 74-84.
- Munoz, Gabriel, Jinxia Liu, Sung Vo Duy, and Sébastien Sauvé. 2019. 'Analysis of F-53B, Gen-X, ADONA, and emerging fluoroalkylether substances in environmental and biomonitoring samples: A review', *Trends in Environmental Analytical Chemistry*: e00066.
- Muschket, Matthias, Nils Keltsch, Heidrun Paschke, Thorsten Reemtsma, and Urs Berger. 2020. 'Determination of transformation products of per- and polyfluoroalkyl substances at trace levels in agricultural plants', *Journal of Chromatography A*: 461271.
- Naidu, R., Nadebaum, P., Fang, C., Cousins, I., Pennell, K., Conder, J., . . . Nathanail, P. 2020. Per- and poly-fluoroalkyl substances (PFAS): Current status and research needs. *Environmental Technology & Innovation*, 19: 100915.

- Navarro, Irene, Adrián de la Torre, Paloma Sanz, Miguel Ángel Porcel, Javier Pro, Gregoria Carbonell, and María de los Ángeles Martínez. 2017. 'Uptake of perfluoroalkyl substances and halogenated flame retardants by crop plants grown in biosolids-amended soils', *Environmental Research*, 152: 199-206.
- Nguyen, T. M. H., Bräunig, J., Thompson, K., Thompson, J., Kabiri, S., Navarro, D. A., Kookana, R. S., Grimison, C., Barnes, C. M., Higgins, C. P., McLaughlin, M. J., Mueller, J. F. 2020. Influences of Chemical Properties, Soil Properties, and Solution pH on Soil–Water Partitioning Coefficients of Per- and Polyfluoroalkyl Substances (PFASs). *Environmental Science & Technology*, 54: 15883-15982.
- Nickerson, A., A. C. Maizel, P. R. Kulkarni, D. T. Adamson, J. J. Kornuc, and C. P. Higgins. 2020. 'Enhanced Extraction of AFFF-Associated PFASs from Source Zone Soils', *Environ Sci Technol*, 54: 4952-62.
- Nobels, Ingrid, Freddy Dardenne, Win. De Coen, and Ronny Blust. 2010. 'Application of a multiple endpoint bacterial reporter assay to evaluate toxicological relevant endpoints of perfluorinated compounds with different functional groups and varying chain length', *Toxicology in Vitro*, 24: 1768-74.
- O'Carroll, Denis M., Thomas C. Jeffries, Matthew J. Lee, Song Thao Le, Anna Yeung, Sarah Wallace, Nick Battye, David J. Patch, Michael J. Manefield, and Kela P. Weber. 2020. 'Developing a roadmap to determine per- and polyfluoroalkyl substances-microbial population interactions', *Science of The Total Environment*, 712: 135994.
- Oliver, Danielle P, Yasong Li, Ryan Orr, Paul Nelson, Mary Barnes, Michael J McLaughlin, and Rai S Kookana. 2020. 'Sorption behaviour of per-and polyfluoroalkyl substances (PFASs) in tropical soils', *Environmental Pollution*, 258: 113726.

- Paul, Alexander G., Kevin C. Jones, and Andrew J. Sweetman. 2009. 'A First Global Production, Emission, And Environmental Inventory For Perfluorooctane Sulfonate', *Environmental Science & Technology*, 43: 386-92.
- Peng, Sheng, and Mark L Brusseau. 2005. 'Impact of soil texture on air- water interfacial areas in unsaturated sandy porous media', *Water resources research*, 41.
- Pezeshki, SR, and RD DeLaune. 2012. 'Soil oxidation-reduction in wetlands and its impact on plant functioning', *Biology*, 1: 196-221.
- Piekarz, Arkadiusz M, Toby Primbs, Jennifer A Field, Douglas F Barofsky, and Staci Simonich. 2007. 'Semivolatile fluorinated organic compounds in Asian and western US air masses', *Environmental science & technology*, 41: 8248-53.
- Place, Benjamin J, and Jennifer A Field. 2012. 'Identification of novel fluorochemicals in aqueous film-forming foams used by the US military', *Environmental science & technology*, 46: 7120-27.
- Presentato, Alessandro, Silvia Lampis, Andrea Vantini, Flavio Manea, Francesca Daprà, Stefano Zuccoli, and Giovanni Valini. 2020. 'On the ability of Perfluorohexane Sulfonate (PFHxS) bioaccumulation by two *Pseudomonas* sp. strains isolated from PFAS-contaminated environmental matrices', *Microorganisms*, 8: 92.
- Prevedouros, K., I. T. Cousins, R. C. Buck, and S. H. Korzeniowski. 2006. 'Sources, fate and transport of perfluorocarboxylates', *Environ Sci Technol*, 40: 32-44.
- Psillakis, Eleftheria, Jie Cheng, MR Hoffmann, and AJ Colussi. 2009. 'Enrichment factors of perfluoroalkyl oxoanions at the air/water interface', *The Journal of Physical Chemistry A*, 113: 8826-29.

- Qiao, Weichuan, Zhenyu Xie, Yunhao Zhang, Xin Liu, Shuguang Xie, Jun Huang, and Lei Yu. 2018. 'Perfluoroalkyl substances (PFASs) influence the structure and function of soil bacterial community: Greenhouse experiment', *Science of The Total Environment*, 642: 1118-26.
- Rankin, Keegan, Scott A Mabury, Thomas M Jenkins, and John W Washington. 2016. 'A North American and global survey of perfluoroalkyl substances in surface soils: Distribution patterns and mode of occurrence', *Chemosphere*, 161: 333-41.
- Rauert, Cassandra, Mahiba Shoieb, Jasmin K Schuster, Anita Eng, and Tom Harner. 2018. 'Atmospheric concentrations and trends of poly-and perfluoroalkyl substances (PFAS) and volatile methyl siloxanes (VMS) over 7 years of sampling in the Global Atmospheric Passive Sampling (GAPS) network', *Environmental Pollution*, 238: 94-102.
- Ray, Jessica R, Itamar A Shabtai, Marc Feixadó, Yael G Mishaël, and David L Sedlak. 2019. 'Polymer-clay composite geomedia for sorptive removal of trace organic compounds and metals in urban stormwater', *Water research*, 157: 454-62.
- Reeves, Paul C, and Michael A Celia. 1996. 'A functional relationship between capillary pressure, saturation, and interfacial area as revealed by a pore- scale network model', *Water resources research*, 32: 2345-58.
- Reth, Margot, Urs Berger, Dag Broman, Ian T Cousins, E Douglas Nilsson, and Michael S McLachlan. 2011. 'Water-to-air transfer of perfluorinated carboxylates and sulfonates in a sea spray simulator', *Environ. Chem*, 8: 381-88.
- Rich, C. D., Blaine, A. C., Hundal, L., Higgins, C. P. Bioaccumulation of Perfluoroalkyl Acids by Earthworms (*Eisenia fetida*) Exposed to Contaminated Soils. 2015. *Environ. Sci. Technol.*, 49: 881-888.

- Ritscher, Amélie, Zhanyun Wang, Martin Scheringer, Justin M Boucher, Lutz Ahrens, Urs Berger, Sylvain Bintein, Stephanie K Bopp, Daniel Borg, and Andreas M Buser. 2018. 'Zürich Statement on Future Actions on Per-and Polyfluoroalkyl Substances (PFASs)', *Environmental Health Perspectives*, 126: 084502.
- Rosenqvist, L., R. Vestergren, E. Westberg, K. Eliaeson, K. Norström, M. Liljeberg, J. Strandberg and M. Rahmberg. 2017. 'Spridning av högfluorerade ämnen i mark från Stockholm Arlanda Airport'. Svenska miljöinstitutet 121.
- Ruan, Ting, Bogdan Szostek, Patrick W. Folsom, Barry W. Wootenholme, Runzeng Liu, Jiyan Liu, Guibin Jiang, Ning Wang, and Robert C. Buck. 2013. 'Aerobic Soil Biotransformation of 6:2 Fluorotelomer Iodide', *Environmental Science & Technology*, 47: 11504-11.
- Russell, Mark H., William R. Berti, Bogdan Szostek, and Robert C. Buck. 2008. 'Investigation of the biodegradation potential of a fluoroacrylate polymer product in aerobic soils', *Environ Sci Technol*, 42: 800-07.
- Russell, Mark H., William R. Berti, Bogdan Szostek, Ning Wang, and Robert C. Buck. 2010. 'Evaluation of PFO formation from the biodegradation of a fluorotelomer-based urethane polymer product in aerobic soils', *Polymer Degradation and Stability*, 95: 79-85.
- Sandermann Jr, Heinrich. 1994. 'Higher plant metabolism of xenobiotics: the 'green liver' concept', *Pharmacogenetics*, 4: 225-41.
- Sale, T.; Gallo, S.; Karimi Askarani, K.; Irianni-Renno, M.; Lyverse, M.; Hopkins, H.; Blotevogel, J.; Burge, S. 2021. 'Real-time soil and groundwater monitoring via spatial and temporal resolution of biogeochemical potentials'. *Journal of Hazardous Materials*, DOI: 10.1016/j.jhazmat.2020.124403.

- Schaefer, CE, DA DiCarlo, and MJ Blunt. 2000a. 'Experimental measurement of air- water interfacial area during gravity drainage and secondary imbibition in porous media', *Water Resources Research*, 36: 885-90.
- Schaefer, Charles E, Veronika Culina, Dung Nguyen, and Jennifer Field. 2019. 'Uptake of Poly- and Perfluoroalkyl Substances at the Air–Water Interface', *Environmental Science & Technology*, 53: 12442-48.
- Schaefer, Charles E, David A DiCarlo, and Martin J Blunt. 2000b. 'Determination of water-oil interfacial area during 3-phase gravity drainage in porous media', *Journal of colloid and interface science*, 221: 308-12.
- Schaefer, Charles E, Dung Nguyen, and Jennifer Field. 2020. 'Response to the Comment on “Uptake of Poly- and Perfluoroalkyl Substances at the Air-Water Interface”', *Environ. Sci. Technol.*, 54, 7021-7022.
- Schellenberger, Steffen, Christina Jonsson, Pelle Mellin, Oscar A Levenstam, Ioannis Liagkouridis, Anton Ribbenstedt, Anne-Charlotte Hanning, Lara Schultes, Merle M Plassmann, and Caiza Persson. 2019. 'Release of side-chain fluorinated polymer-containing microplastic fibers from functional textiles during washing and first estimates of perfluoroalkyl acid emissions', *Environmental Science & Technology*, 53: 14329-38.
- Scher, Deanna P., James E. Kelly, Carin A. Huset, Kitrina M. Barry, Richard W. Hoffbeck, Virginia L. Yingling, and Rita B. Messing. 2018. 'Occurrence of perfluoroalkyl substances (PFAS) in garden produce at homes with a history of PFAS-contaminated drinking water', *Chemosphere*, 196: 548-55.
- Schreiber, Lukas. 2010. 'Transport barriers made of cutin, suberin and associated waxes', *Trends in Plant Science*, 15: 546-53.

- Schultz, Melissa M., Christopher P. Higgins, Carin A. Huset, Richard G. Luthy, Douglas F. Barofsky, Jennifer A. Field. 2006. 'Fluorochemical Mass Flows in a Municipal Wastewater Treatment Facility', *Environmental Science & Technology*, 40: 7350-7357.
- Sepulvado, Jennifer G, Andrea C Blaine, Lakhwinder S Hundal, and Christopher P Higgins. 2011. 'Occurrence and fate of perfluorochemicals in soil following the land application of municipal biosolids', *Environmental Science & Technology*, 45: 8106-12.
- Sharifan, Hamidreza, Xingmao Ma, Janie McClurkin Moore, Mohammad Ruzlan Habib, and Catelyn Evans. 2019. 'Zinc oxide nanoparticles alleviated the bioavailability of cadmium and lead and changed the uptake of iron in hydroponically grown lettuce (*Lactuca sativa* L. var. Longifolia)', *ACS Sustainable Chemistry & Engineering*, 7: 16401-09.
- Sharifan, Hamidreza, Janie Moore, and Xingmao Ma. 2020a. 'Zinc oxide (ZnO) nanoparticles elevated iron and copper contents and mitigated the bioavailability of lead and cadmium in different leafy greens', *Ecotoxicology and Environmental Safety*, 191: 110177.
- Sharifan, H. 2017. 'Commentary on "Characteristics of cadmium uptake and membrane transport in roots of intact wheat (*Triticum aestivum* L.) seedlings" reported by Lian-Zhen Li, Chen Tu, Willie JGM Reijnenburg, Yong-Ming Luo'. *Environmental Pollution*, 231; 1213-1214
- Sharifan, Hamidreza, Xiaoxuan Wang, and Xingmao Ma. 2020b. 'Impact of nanoparticle surface charge and phosphate on the uptake of coexisting cerium oxide nanoparticles and cadmium by soybean (*Glycine max.*(L.) merr.)', *International Journal of Phytoremediation*, 22: 305-12.

- Sharifan, Hamidreza. 2020c. Mechanistic Insight on Transfer Rate of the Polar Organic Compounds through the Polyethersulfone Membrane', *Environmental Monitoring and Assessment*, 192: 344.
- Shaw, Dayton M. J., Gabriel Munoz, Eric M. Bottos, Sung Vo Duy, Sébastien Sauvé, Jinxia Liu, and Jonathan D. Van Hamme. 2019. 'Degradation and defluorination of 6:2 fluorotelomer sulfonamidoalkyl betaine and 6:2 fluorotelomer sulfonate by *Gordonia* sp. strain NB4-1Y under sulfur-limiting conditions', *Science of the Total Environment*, 647: 690-98.
- Silva, Jeff AK, William A Martin, Jared L Johnson, and John F. McCray. 2019. 'Evaluating air-water and NAPL-water interfacial adsorption and retention of Perfluorocarboxylic acids within the Vadose zone', *Journal of contaminant hydrology*, 223: 103472.
- Silva, J.A., Martin, W.A. and McCray, J.E., 2020a. On the potential variability of air-water interfacial adsorption coefficients of PFAS when present as a multi-component mixture. *Journal of Contaminant Hydrology*. DOI: 10.1016/j.jconhyd.2020.103731.
- Silva, J.A.K.; McCray, J.E.; Martin, W.A., 2020b. Final Report: Baseline Data Acquisition and Numerical Modeling to Evaluate the Fate and Transport of PFAS within the Vadose Zone. SERDP Project ER18-1389. Available online: <https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Emerging-Issues/ER18-1389> (accessed on 10 September 2020).
- Sima, M.W and P.R. Jaffé. 2021. A critical review of modeling Poly- and Perfluoroalkyl Substances (PFAS) in the soil-water environment. *Science of the Total Environment*, 757: 143793.

- Sleep, Julie A, and Albert L Juhasz. 2020. 'Perfluoroalkyl, fluorotelomer sulfonate, and perfluorooctane sulfonamide contamination in biosolids: Composition, co-contamination and re-use implications', *Environmental Pollution*: 115120.
- Spielvogel, Sandra, Jörg Prietzel, Jana Leide, Michael Riedel, Julian Zemke, and Ingrid Kögel-Knabner. 2014. 'Distribution of cutin and suberin biomarkers under forest trees with different root systems', *Plant and soil*, 381: 95-110.
- Stahl, T., Heyn, J., Thiele, H., Hüther, J., Failing, K., Georgii, S., Brunn, H., 2009. Carryover of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) from soil to plants. *Arch. Environ. Contam. Toxicol.* 57, 289–298
- Stahl, Thorsten, Rika Alessa Riebe, Sandy Falk, Klaus Failing, and Hubertus Brunn. 2013. 'Long-term lysimeter experiment to investigate the leaching of perfluoroalkyl substances (PFASs) and the carry-over from soil to plants: results of a pilot study', *Journal of agricultural and food chemistry*, 61: 1784-93.
- Stoiber, Tasha, Sydney Evans, and Olga V Naidenko. 2020. 'Disposal of products and materials containing per-and polyfluoroalkyl substances (PFAS): A cyclical problem', *Chemosphere*: 127659.
- Strynar, Mark, Sonia Degnino, Rebecca McMahan, Shuang Liang, Andrew Lindstrom, Erik Andersen, Larry McMillan, Michael Thurman, Imma Ferrer, and Carol Ball. 2015. 'Identification of novel perfluoroalkyl ether carboxylic acids (PFECAs) and sulfonic acids (PFESAs) in natural waters using accurate mass time-of-flight mass spectrometry (TOFMS)', *Environmental Science & Technology*, 49: 11622-30.
- Sun, Yajun, Tieyu Wang, Xiawei Peng, Pei Wang, and Yonglong Lu. 2016. 'Bacterial community compositions in sediment polluted by perfluoroalkyl acids (PFAAs) using

- Illumina high-throughput sequencing', *Environmental Science and Pollution Research*, 23: 10556-65.
- Sung, Menghau, and Bi-Hsiang Chen. 2011. 'Using aliphatic alcohols as gaseous tracers in determination of water contents and air–water interfacial areas in unsaturated sands', *Journal of contaminant hydrology*, 126: 226-34.
- Sepulvado J.G., Blaine A.C., Hundal L.S. & Higgins C.P. 2011. 'Occurrence and fate of perfluorochemicals in soil following the land application of municipal biosolids'. *Environmental Science & Technology*, 45, 8106-12.
- Szabo, Drew, Timothy L Coggan, Timothy C Robson, Matthew Currell, and Bradley O Clarke. 2018. 'Investigating recycled water use as a diffuse source of per-and polyfluoroalkyl substances (PFASs) to groundwater in Melbourne, Australia', *Science of The Total Environment*, 644: 1409-17.
- Thalheimer, Andrew H, Leah B McConney, Indra K Kalinovich, Anne V Pigott, Jennifer D Franz, Heather Taylor Holbert, Dean Mericas, and Zachary J Puchacz. 2017. *Use and potential impacts of AFFF containing PFASs at airports*.
- Tokranov, Andrea K, Nicole Nishizawa, Carlo Alberto Amadei, Jenny E Zenobio, Heidi M Pickard, Joseph C Allen, Chad D Vecitis, and Elsie M Sunderland. 2018. 'How do we measure poly-and perfluoroalkyl substances (PFASs) at the surface of consumer products?', *Environmental science & technology letters*, 6: 38-43.
- Trapp, Stefan. 2000. 'Modelling uptake into roots and subsequent translocation of neutral and ionisable organic compounds', *Pest Management Science: formerly Pesticide Science*, 56: 767-78.

- Tseng, Nancy, Ning Wang, Bogdan Szostek, and Shaily Mahendra. 2014. 'Biotransformation of 6:2 Fluorotelomer Alcohol (6:2 FTOH) by a Wood-Rotting Fungus', *Environmental Science & Technology*, 48: 4012-20.
- USEPA. 2018. 'Assessing and Managing Chemicals under TSCA', *Fact Sheet: 2010/2015 PFOA Stewardship Program*.
- Van Hamme, Jonathan D., Eric M. Bottos, Nicholas J. Bilbey, and Sharon E. Brewer. 2013. 'Genomic and proteomic characterization of *Gordonia* sp. NB4-1Y in relation to 6:2 fluorotelomer sulfonate biodegradation', *Microbiology*, 152: 1618-28.
- Vecitis, CD, H Park, J Cheng, BT Mader, and MR Hoffmann. 2008. 'Enhancement of perfluorooctanoate and perfluorooctanesulfonate activity at acoustic cavitation bubble interfaces', *The Journal of Physical Chemistry C*, 112: 16850-57.
- Venkatesan, Arjun K, and Rolf U Halden. 2013. 'National inventory of perfluoroalkyl substances in archived US biosolids from the 2001 EPA National Sewage Sludge Survey', *Journal of hazardous materials*, 252: 413-18.
- Wang, Fei, Chengshuai Li, and Kaimin Shih. 2012. 'Adsorption behavior of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) on boehmite', *Chemosphere*, 89: 1009-14.
- Wang, Fei, and Kaimin Shih. 2011. 'Adsorption of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) on alumina: Influence of solution pH and cations', *water research*, 45: 2925-30.
- Wang, N., R. C. Buck, B. Szostek, L. M. Sulecki, and B. W. Wolstenholme. 2012. '5:3 Polyfluorinated acid aerobic biotransformation in activated sludge via novel "one-carbon removal pathways"', *Chemosphere*, 87: 527-34.

- Wang, N., J. Liu, R. C. Buck, S. H. Korzeniowski, B. W. Wolstenholme, P. W. Folsom, and L. M. Sulecki. 2011. '6:2 fluorotelomer sulfonate aerobic biotransformation in activated sludge of waste water treatment plants', *Chemosphere*, 82: 853-8.
- Wang, N., B. Szostek, R. C. Buck, P. W. Folsom, L. M. Sulecki, and J. T. Gannon. 2009. '8-2 fluorotelomer alcohol aerobic soil biodegradation: pathways, metabolites, and metabolite yields', *Chemosphere*, 75: 1089-96.
- Wang, Tiejyu, Pei Wang, Jing Meng, Shijie Liu, Yonglong Lu, Jong Seong Khim, and John P Giesy. 2015. 'A review of sources, multimedia distribution and health risks of perfluoroalkyl acids (PFAAs) in China', *Chemosphere*, 129: 87-99.
- Wang, T. T., Ying, G. G., He, L. Y., Liu, Y. S., Zhao, J. L. 2020. 'Uptake mechanism, subcellular distribution, and uptake process of perfluorooctanoic acid and perfluorooctane sulfonic acid by wetland plant *A. isra orientale*'. *Science of the Total Environment*, 733(378), 139383.
- Wang, Yu, Wenguang Chang, Ling Wang, Yinfeng Zhang, Yuan Zhang, Man Wang, Yin Wang, and Peifeng Li. 2019. 'A review of sources, multimedia distribution and health risks of novel fluorinated alternatives', *Ecotoxicology and environmental safety*, 182: 109402.
- Wang, Zhanyun, Ian T Cousins, Martin Scheringer, Robert C Buck, and Konrad Hungerbühler. 2014. 'Global emission inventories for C4–C14 perfluoroalkyl carboxylic acid (PFCA) homologues from 1951 to 2030, Part I: production and emissions from quantifiable sources', *Environment international*, 70: 62-75.
- Wang, Zhanyun, Jamie C DeWitt, Christopher P Higgins, and Ian T Cousins. 2017. "A never-ending story of per-and polyfluoroalkyl substances (PFASs)?" *Environ Sci Technol*, 51: 2508-2518.

- Washington, J. W., J. Ellington, T. M. Jenkins, J. J. Evans, H. Yoo, and S. C. Hafner. 2009. 'Degradability of an acrylate-linked, fluorotelomer polymer in soil', *Environ Sci Technol*, 43: 6617-23.
- Washington, John W, Charlita G Rosal, James P McCord, Mark J Strynar, Andrew B Lindstrom, Erica L Bergman, Sandra M Goodrow, Haile K Tadesse, Andrew N Pilant, and Benjamin J Washington. 2020. 'Nontargeted mass-spectral detection of chloroperfluoropolyether carboxylates in New Jersey soils', *Science*, 368: 1103-07.
- Weathers, Tess S., Katie Harding-Marjanovic, Christopher P Higgins, Lisa Alvarez-Cohen, and Jonathan O. Sharp. 2016. 'Perfluoroalkyl Acids Inhibit Reductive Dechlorination of Trichloroethene by Repressing Dehalococcoides', *Environmental science & technology*, 50: 240-48.
- Wen, B., Li, L., Liu, Y., Zhang, H., Hu, X., Shan, X., Zhang, S., 2013. Mechanistic studies of perfluorooctane sulfonate, perfluorooctanoic acid uptake by maize (*Zea mays* L. cv. TY2). *Plant Soil* 370, 345–354.
- Wen, Bei, Yali Wu, Hongna Zhang, Yu Liu, Xiaoyu Hu, Honglin Huang, and Shuzhen Zhang. 2016. 'The roles of protein and lipid in the accumulation and distribution of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in plants grown in biosolids-amended soils', *Environmental Pollution*, 216: 682-88.
- Xiao, Feng, Bosen Jin, Svetlana A Golovko, Mikhail Y Golovko, and Baoshan Xing. 2019. 'Sorption and desorption mechanisms of cationic and zwitterionic per-and polyfluoroalkyl substances in natural soils: Thermodynamics and hysteresis', *Environmental science & technology*, 53: 11818-27.

- Xiao, Feng, Matt F Simcik, Thomas R Halbach, and John S Gulliver. 2015. 'Perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in soils and groundwater of a US metropolitan area: migration and implications for human exposure', *Water research*, 72: 64-74.
- Xin, Jia, Yang Liu, Fei Chen, Yijun Duan, Guanli Wei, Xilai Zheng, and Miao Li. 2019. 'The missing nitrogen pieces: A critical review on the distribution, transformation, and budget of nitrogen in the vadose zone-groundwater system', *Water research*: 114977.
- Yao, Yiming, Shuai Chang, Yangyang Zhao, Jianhui Tang, Hongwen Sun, and Zhiyong Xie. 2017. 'Per-and poly-fluoroalkyl substances (PFASs) in the urban, industrial, and background atmosphere of Northeastern China coast around the Bohai Sea: Occurrence, partitioning, and seasonal variation', *Atmospheric Environment*, 167: 150-58.
- Yi, Langbo, Qingzhong Peng, Deming Liu, Lulu Zhou, Chongjian Tang, Yaoyu Zhou, and Liyuan Chai. 2019. 'Enhanced degradation of perfluorooctanoic acid by a genome shuffling-modified *Pseudomonas parafulva* YAB-1', *Environmental technology*, 40: 3153-61.
- Yi, LB, LY Chai, Y Xie, QF Peng, and QZ Peng. 2016. 'Isolation, identification, and degradation performance of a PFOA-degrading strain', *Genet. Mol. Res*, 15: 235-46.
- Yi, Shan, Katie C. Harding-Marjanovic, Erika F. Houtz, Ying Gao, Jennifer E. Lawrence, Rita V. Nichiporuk, Anthony T. Iavarone, Wei-Qin Zhuang, Martin Hansen, Jennifer A. Field, David L. Sedlak, and Lisa Alvarez-Cohen. 2018. 'Biotransformation of AFFF Component 6:2 Fluorotelomer Thioether Amido Sulfonate Generates 6:2 Fluorotelomer Thioether Carboxylate under Sulfate-Reducing Conditions', *Environmental Science & Technology Letters*, 5: 283-88.

- Yoo, H., J. W. Washington, T. M. Jenkins, and J. J. Ellington. 2011. 'Quantitative Determination of Perfluorochemicals and Fluorotelomer Alcohols in Plants from Biosolid-Amended Fields using LC/MS/MS and GC/MS', *Environmental Science & Technology*, 45: 7985-90.
- Yoo, Hoon, John W. Washington, J. Jackson Ellington, Thomas M. Jenkins, and Michael P. Neill. 2010. 'Concentrations, distribution, and persistence of fluorotelomer alcohols in sludge-applied soils near Decatur, Alabama, USA', *Environmental Science & Technology*, 44: 8397-402.
- Young, Cora J, Vasile I Furdui, James Franklin, Roy M Koerner, Derek CG Muir, and Scott A Mabury. 2007. 'Perfluorinated acids in arctic snow: new evidence for atmospheric formation', *Environmental science & technology*, 41: 3455-61.
- Young, Cora J, Scott A Mabury. 2010. 'Atmospheric perfluorinated acid precursors: chemistry, occurrence, and impacts.' in, *Reviews of Environmental Contamination and Toxicology Volume 208*: 1-109
- Yu Q, Zhang R, Deng S, Huang J & Yu G. 2009. Sorption of Perfluorooctane Sulfonate and Perfluorooctanoate on Activated Carbons and Resin: Kinetic and Isotherm Study. *Water research*, 43:4:1159
- Zabaleta, Itsaso, Ekhine Bizkarguenaga, Deborah B. O. Nunoo, Lara Schultes, Juliana Leonel, Ailette Prieto, Olatz Zuloaga, and Jonathan P. Benskin. 2018. 'Biodegradation and Uptake of the Pesticide Sulfluramid in a Soil–Carrot Mesocosm', *Environmental Science & Technology*, 52: 2603-11.
- Zhang, Dong Qing, Mo Wang, Qiaochong He, Xiaojun Niu, and Yanna Liang. 2020. 'Distribution of perfluoroalkyl substances (PFASs) in aquatic plant-based systems: From

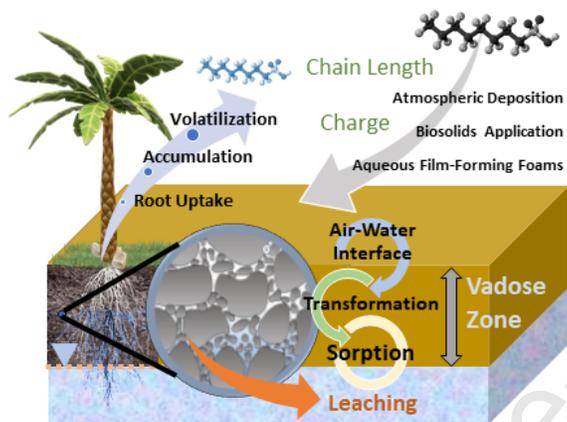
- soil adsorption and plant uptake to effects on microbial community', *Environmental pollution*, 257: 113575.
- Zhang, Dongqing, Weilan Zhang, and Yanna Liang. 2019a. 'Bacterial community in a freshwater pond responding to the presence of perfluorooctanoic acid (PFOA)', *Environmental technology*: 1-11.
- Zhang, Dongqing, Weilan Zhang, and Yanna Liang. 2019b. 'Distribution of eight perfluoroalkyl acids in plant-soil-water systems and their effect on the soil microbial community', *Science of The Total Environment*, 697: 134146.
- Zhang, L., L. S. Lee, J. Niu, and J. Liu. 2017. 'Kinetic analysis of aerobic biotransformation pathways of a perfluorooctane sulfonate (PFOS) precursor in distinctly different soils', *Environ Pollut*, 229: 159-67.
- Zhang, Ruiming, Wei Yan, and Chuanyong Jing. 2014. 'Mechanistic study of PFOS adsorption on kaolinite and montmorillonite', *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 462: 252-58.
- Zhang, Shu, Xiaoxia Lu, Ning Wang, and Robert C. Buck. 2016. 'Biotransformation potential of 6:2 fluorotelomer sulfonate (6:2 FTSA) in aerobic and anaerobic sediment', *Chemosphere*, 154: 224-30.
- Zhang, Shu, Nancy Merino, Ning Wang, Ting Ruan, and Xiaoxia Lu. 2017. 'Impact of 6:2 fluorotelomer alcohol aerobic biotransformation on a sediment microbial community', *Science of The Total Environment*, 575: 1361-68.
- Zhang, Shu, Bogdan Szostek, Patricia K. McCausland, Barry W. Wolstenholme, Xiaoxia Lu, Ning Wang, and Robert C. Buck. 2013. '6:2 and 8:2 Fluorotelomer Alcohol Anaerobic

- Biotransformation in Digester Sludge from a WWTP under Methanogenic Conditions', *Environmental Science & Technology*, 47: 4227-35.
- Zhang, Weilan, Dongqing Zhang, Dmitri V Zagorevski, and Yanna Liang. 2019. 'Exposure of *Juncus effusus* to seven perfluoroalkyl acids: Uptake, accumulation and phytotoxicity', *Chemosphere*, 233: 300-08.
- Zhang W, Pang S, Lin Z, Mishra S, Bhatt P, Chen S. 2020. 'Biotransformation of perfluoroalkyl acid precursors from various environmental systems: Advances and perspectives. *Environmental Pollution*'. 115908.
- Zhang, Y., Y. Zhi, J. Liu, and S. Ghoshal. 2018. 'Sorption of Perfluoroalkyl Acids to Fresh and Aged Nanoscale Zerovalent Iron Particles', *Environ. Sci Technol*, 52: 6300-08.
- Zhao, S., Z. Fan, L. Sun, T. Zhou, Y. Xing, and L. Liu. 2017. Interaction effects on uptake and toxicity of perfluoroalkyl substances and cadmium in wheat (*Triticum aestivum L.*) and rapeseed (*Brassica campestris L.*) from co-contaminated soil, *Ecotoxicology and environmental safety*, 137: 194-201.
- Zhao, S., T. Zhou, L. Zhu, B. Wang, Z. Li, L. Yang, and L. Liu. 2018. Uptake, translocation and biotransformation of N-ethyl perfluorooctanesulfonamide (N-EtFOSA) by hydroponically grown plants, *Environmental Pollution*, 235: 404-410.
- Zhao S, Ma X, Fang S, Zhu L. 2016. 'Behaviors of N-ethyl perfluorooctane sulfonamide ethanol (N-EtFOSE) in a soil-earthworm system: Transformation and bioaccumulation'. *Science of The Total Environment*, 554-555:186-91.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Journal Pre-proof



Graphical abstract

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.

Journal Pre-proof