

Key properties governing sorption-desorption behaviour of poly- and perfluoroalkyl substances in saturated and unsaturated soils: a review

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Handling Editor: Balwant Singh

Received: 10 August 2022 Accepted: 3 November 2022 Published: 16 December 2022

Cite this:

Kookana RS et al. (2023) Soil Research, **61**(2), 107–125. doi:10.1071/SR22183

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ABSTRACT

Poly- and perfluoroalkyl substances (PFAS) have been widely used worldwide over the last seven decades in >200 diverse industrial applications. Thousands of different PFAS have been used in a wide range of products, such as food packaging, water-repellent and stain-resistant clothing and fire-fighting foams. Partially due to their extreme stability and high mobility, PFAS are now ubiquitous in the environment. Due to their prolonged persistence, some PFAS have been added to the list of persistent organic pollutants. Sorption is one of the fundamental processes that governs environmental fate and effects of organic chemicals. In recent years, a significant body of literature has been published on sorption of PFAS in soils. However, there are conflicting reports about the soil or sediment properties that may be used to predict the mobility of PFAS in the soil environment. This is not surprising because PFAS have complex chemical properties (anionic, cationic and zwitterionic charges together with surface active properties) that influence their sorption-desorption behaviour. Additionally, PFAS show a fluidwater interfacial adsorption phenomenon and such interfaces offer additional retention mechanisms in unsaturated or oil-contaminated soils. In this review, we analyse the literature on sorption and desorption of PFAS to evaluate the dominant soil and solution properties that govern their sorption-desorption behaviour in saturated and unsaturated soils. We also identify the knowledge gaps that need to be addressed in order to gain a sound understanding of their sorption-desorption behaviour in saturated as well as unsaturated soils.

Keywords: adsorption, air-water interfacial adsorption, desorption, perfluoroalkyl substances, PFAS, polyfluoroalkyl substances, sorption-desorption mechanism, vadose zone soils.

Introduction

Manufactured over a period of seven decades, several thousand poly- and perfluoroalkyl substances (PFAS) have been introduced in the market globally (Organisation for Economic Co-operation and Development (OECD) 2018). Industrial usage of >1400 different PFAS (with >8000 unique known structures) have been noted to span across >200 diverse applications. Applications of PFAS range from food packaging, water-repellent and stain-resistant clothing to fire-fighting foams (Evich *et al.* 2022). The diverse range of applications reflect their unique chemical properties (e.g. amphiphilicity and thermal stability) which are, in part, responsible for the environmental concern they engender. Because of their extreme stability (C–F being a very strong bond) and high mobility, PFAS are now ubiquitous in the environment. Soils and sediments often serve as sinks for these chemicals (Brusseau *et al.* 2020; Sharifan *et al.* 2021; Wallis *et al.* 2022). Maximum reported concentrations of PFOS and perfluorooctanoic acid (PFOA) in soils from different countries have been presented in Table 1.

While bioaccumulation potential, endocrine disruption and other adverse outcomes for ecological and human health have been identified for PFAS, a full understanding of their toxicological properties is not yet clear (Fenton *et al.* 2021; Evich *et al.* 2022). However, due

Type of site	Locations	Maximum PFOA concentration (μg/kg)	Maximum PFOS concentration (μg/kg)
AFFF source zones	USA	50 000	373 000
Airports	Australia	6400	84 200
	Norway	75	17 400
Crash site	Canada	29	9.3
Fire training area	Australia	3200	460 000
	Norway	141	8924
	Sweden	219	8520
	USA	11 484	36 534
PFAS manufacturing	Belgium	114	7800
	China	50	2583
PFAS industrial park	China	5.3	0.4
Global median concentration (µg/kg)	-	83	8722

Table I. Maximum concentrations of PFOA and PFOS found in soil at contaminated sites in various countries, based on the data compiled by Brusseau et al. (2020).

AFFF, aqueous film-forming foam.

to their prolonged persistence, perfluorooctane sulfonic acid (PFOS) and its salts, perfluorooctane sulfonyl fluoride (PFOSF), PFOA and its salts and related compounds have been added to the list of Persistent Organic Pollutants (POPs) under the Stockholm Convention (United Nations Environment Program (UNEP) 2009). Some other PFAS are currently under consideration for listing.

Sorption-desorption, or partitioning to solid surfaces, is one of the fundamental processes that governs environmental fate and effects of organic chemicals. Partitioning not only determines transport and mobility of chemicals but also influences their bioavailability and uptake and thus moderates their effects on the environment. In recent years, numerous studies have been published on PFAS sorption in soils and sediments. However, a vast majority of these have focussed on perfluoroalkyl acids (PFAAs, e.g. PFOA and PFOS), perhaps because these were among the compounds that were regulated first, including their placement on the Stockholm Convention's List of POPs.

There are conflicting reports in the literature on what soil properties may be used as predictors of PFAS partitioning in the soil environment. This is not surprising as PFAS have complex chemistries including various ionic states (anionic, cationic and zwitterionic charges) and surface active properties that influence their partitioning. Sorption or partitioning is often represented via a partitioning/distribution coefficient, or K_d value, where K_d represents the ratio of soil and solution concentrations. Initially, there were attempts to treat PFAS as

conventional POPs and utilise organic carbon (OC)-based partition coefficients ($K_{oc} = K_d/f_{oc}$, where f_{oc} is the fraction of OC in soil). This has been an attractive approach for conventional POPs, as it allowed extrapolation of data among soils based on f_{oc} in soil, which is a commonly measured soil property. However, as the database on PFAS grew it became clear that no single soil property could accurately predict the K_d of PFAS in soils (e.g. Li *et al.* 2018). In recent years, the database on sorption of PFAS in soils has grown markedly (e.g. Knight et al. 2019; Umeh et al. 2021) thus allowing a better understanding of the role of soil properties in governing their behaviour in saturated and unsaturated soils. It is noteworthy that the processes contributing to retention of PFAS in soils differ in soils depending on their degree of saturation (Brusseau 2019). Therefore, the partitioning behaviour of PFAS in saturated and unsaturated soils can be vastly different.

The principal aim of this study is to identify the soil and solution properties that are crucial in determining the partitioning behaviour of PFAS in saturated and unsaturated soils. Here, we analyse the literature to identify the most important properties controlling the retention of PFAS in saturated and unsaturated soils. The findings have a direct bearing on predictions of the mobility of PFAS from source zones in contaminated soils and their transport to ground and surface water. We believe this review will help facilitate the choice of relevant soil properties in transport models for prediction of the fate of PFAS in the soil environment. Recent studies on modelling of transport behaviour of PFAS in historically contaminated soils have highlighted the importance of sorption data under saturated as well as unsaturated conditions in predicting the mobility of PFAS in the real world (Wallis et al. 2022).

The chemistry of PFAS is markedly different from other POPs

The OECD (Organisation for Economic Co-operation and Development (OECD) 2018) recently released a revised definition of PFAS as 'PFAS are fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom without any H/Cl/Br/I atom attached to it'. The PFAS generally have a hydrophobic 'tail' that contains a high proportion of fluorine (C–F chain), a hydrophilic head-group (e.g. carboxylate and sulfonate) and in many cases a 'spacer' organic group linking these two portions of the compound together (Buck *et al.* 2011). Replacing the hydrogen atoms (in a hydrocarbon chain in organic molecules) by fluorine atoms rendered a range of unique chemical properties that enabled this group of chemicals to be used for a diverse range of functions and applications mentioned above.

The PFAS, being a large group of substances (polymers and non-polymers) as solid, liquid and gases, have a broad range

of physical, chemical and biological properties (Buck et al. 2021). The chemical properties of PFAS are very different from conventional organic compounds, especially the other POPs and nonpolar compounds. Unique properties of these chemicals include very high strength of the C-F bond, strong polarisation and greater hydrophobicity than alkyl chains of comparable lengths. The addition of functional head-groups increases their water solubility. Consequently, a functionalised fluorochemical has surfactant properties because of both hydrophobic and hydrophilic moieties (Ding and Peijnenburg 2013; Krafft and Riess 2015). The key features of fluorinated surfactants also include their surface activity in both aqueous solvent systems, reduced surface tension, which results in superior wetting, spreading and levelling properties for all types of surfaces, effective emulsification in specialty applications, and extreme stability both chemically and thermally (Buck et al. 2011).

Many of the PFAS compounds (e.g. carboxylates and sulfonates) are present in the anionic form (Table 2) over the environmentally relevant pH range (4–9). These PFAAs are highly water-soluble and consequently have greater mobility in the environment. The most common detections

in wastewater treatment, fresh water and ground water systems have been of anionic PFAS such as PFOS, PFOA and perfluorohexanoic acid (PFHxA). Given that the C–F chain makes PFAS hydrophobic, their partitioning properties depend on the chain length. However, several PFAS containing amide and sulfonamido headgroups are cationic in nature (Table 2). Furthermore, some PFAS (e.g. fluorotelomer sulfonamido betaines, FtSaBs) are zwitterions. For example, perfluorooctane amidoalkyl betaine (PFOAB), in addition to a positive charge in its structure ($-N^+(CH_3)^{2-}$), contains other ionisable functional groups which theoretically can result in four species with different charges. Clearly, PFAS have more complex chemistries than conventional POPs.

Key processes or mechanisms determining **PFAS** sorption in soils

Solid-phase adsorption is a well-recognised process and perhaps the dominant contributor to the sorption behaviour of PFAS in soils, in both saturated as well as unsaturated soils. Because of their complex chemistry (e.g. amphiphilic

Table 2. Chemical structures of some PFAS with diverse chemistries and charge characteristics.



and surfactant properties as well as surface activity), the sorption mechanisms of PFAS in soils are more complex than many conventional organic chemicals, especially the non-ionic and highly hydrophobic organic chemicals such as POPs. A variety of mechanisms are responsible for their retention in soils, namely hydrophobic interactions (especially for long C–F chain compounds), electrostatic interactions (especially for ionic and ionisable compounds) and other mechanisms, including fluid–fluid interfacial adsorption as well as absorption and physical retention in inner pores of the solid-phase matrix (Fig. 1). These are discussed in more detail in the following sections. However, a direct evidence base for various mechanisms is still limited due to the relatively small number of mechanistic studies. Additionally, often low concentrations of many of these compounds in the environment makes spectroscopic investigations of the mechanisms difficult.

Electrostatic interactions

As mentioned earlier, PFAAs are anionic in nature, the PFAS containing amide and sulfonamido headgroups are cationic and the FtSaBs are zwitterionic. Therefore, electrostatic interactions of these PFAS with soil solid surfaces can play a dominant role in partitioning (Gao and Chorover 2012; Du *et al.* 2014; Barzen-Hanson *et al.* 2017; Mejia-Avendaño *et al.* 2020).

In soils, many aluminosilicate or phyllosilicate minerals carry permanent negative charges and thus offer significant adsorption sites for positively-charged PFAS (e.g. cationic



Fig. 1. Various mechanisms contributing to partitioning of PFAS in saturated and unsaturated soils. H, hydrophobic; E, electrostatic interactions; I, interfacial adsorption; and P, physical entrapment.

or zwitterionic compounds) in soils. Organic matter, Fe and Al oxides and edges of phyllosilicate minerals such as kaolinite, have significant amounts of pH-dependent surface charge. The Fe and Al oxides can carry positive charge below their point of zero charge (pH \sim 8). Therefore, soils rich in these sorbents, particularly Fe and Al oxides (such as in highly weathered soils in tropical and subtropical regions) can electrostatically adsorb PFAS from soil solution. In contrast, the negatively charged PFAS (e.g. PFAAs with a carboxylic acid or sulfonic acid head group) are repelled by the net negatively-charged adsorption sites on clay minerals and thus are generally adsorbed in smaller amounts than cationic or zwitterionic PFAS (depending on their hydrophobic chain lengths) in soils. The substantial body of literature on adsorption of dissolved humic acids on clay minerals may be relevant in understanding the nature of electrostatic interactions that anionic PFAS may undergo during the partitioning process in soils (Feng et al. 2005). Various mechanisms that drive the adsorption of humic acids on clay minerals (e.g. cation bridges, ligand exchange, anion exchange, van der Waals interactions and hydrophobic effects) may be involved in PFAA adsorption.

Du et al. (2014) in their review on sorption behaviour of PFAS concluded that, although a range of mechanisms are potentially relevant for partitioning of PFAS in soils, the electrostatic and hydrophobic mechanisms are expected to be dominant players. They argued that hydrogen bonding, van der Waals and $\pi-\pi$ interactions of PFAS in soils and sediments are likely to be insignificant. Lu et al. (2016), while studying the adsorption behaviour of PFOS on nanosized inorganic oxides (Al₂O₃, Fe₂O₃, SiO₂ and TiO₂), noted that coexisting metal ions (Cu^{2+} and Pb^{2+}) significantly enhanced the adsorption of PFOS on nano-oxides, through a cation bridging effect. The authors ascribed this to metallic cations forming inner-sphere complexes with nano-oxides and thus converting the neutral or negatively charged sites into positively charged sites that adsorbed PFOS anions. The PFOS molecule has been reported to replace the hydroxyl group on Al₂O₃ by ligand exchange (Wei et al. 2017).

Gao and Chorover (2012) reported that the sulfonate headgroup in PFOS forms outer-sphere complexes with haematite surfaces. This is one of the few spectroscopic studies on adsorption mechanisms, albeit the study had to employ PFAS concentrations in the range of 0.25–1 mM, which is several orders greater than those found in the environment. Campos-Pereira *et al.* (2020) in their adsorption study on 12 PFAS on ferrihydrite, using X-ray absorption near-edge structure (XANES), found no evidence of the formation of inner-sphere complexes. However, the strong pH-dependence of sorption of PFAS on ferrihydrite in their study was ascribed to the change in zeta potential of ferrihydrite surface with pH.

Recently, Loganathan and Wilson (2022) provided molecular-level insights into the adsorption of short- and long-chain PFAS molecules in mesopores of kaolinite clay through simulations and computations. They concluded that the PFAS molecules were exclusively adsorbed onto the hydroxyl surface of kaolinite. However, the interfacial adsorption and the coordination environment was strongly influenced by the nature of functional groups and hydrophobic chain length of the PFAS. These findings may apply to other minerals with basal hydroxyl groups (e.g. gibbsite).

Hydrophobic interactions

As mentioned earlier, the hydrophobicity of PFAS increases with the hydrophobic C-F chain length and consequently their partitioning on hydrophobic surfaces in soils, such as on soil organic matter, can become significant, especially for long-chain compounds (Fig. 2). Indeed, sorption of some long-chain anionic PFAAs (>C8) in soils may be primarily due to hydrophobic interactions with organic carbon, as the anionic headgroup would not favour adsorption to negatively charged mineral (or organic) surfaces. In contrast, the adsorption of short-chain compounds and ionic or ionisable compounds is primarily driven by the electrostatic interactions with charged surfaces in soil (Nguyen et al. 2020). Hydrophobic interactions between PFAS and the soil solid phase may be influenced by factors such as the ionic strength of the soil solution through salting out effects (Fig. 1) or polyvalent cations in soil solutions that may neutralise the negative charge on the headgroup, thus facilitating hydrophobic interactions of the PFAS tail with uncharged surfaces on soil solids.

Interfacial accumulation

The PFAS are surface active agents by design, i.e. they can readily form films at fluid-fluid interfaces (such as waterhydrocarbon and air-water). This process can impart additional opportunity for PFAS to accumulate at the air-water interface, which can potentially result in greater retention of PFAS in unsaturated soils. For a range of hydrocarbon surfactants, a significant adsorption on the air-water interface has been observed (e.g. Kim et al. 1998). Because PFAS are fluorinated surfactants they are more surface active than hydrocarbon surfactants and hence this retention process may be significant for PFAS in unsaturated soils (Brusseau 2019). In soils contaminated by PFAS, as well as other nonaqueous-phase liquids (NAPLs), water-hydrocarbon interfacial processes become important and the accumulation of PFAS at the NAPL-water interface may also contribute to the overall retention of PFAS by soils. The relative contribution of interfacial adsorption to overall retention of PFAS in unsaturated soils depends on their solid-phase sorption and degree of saturation in soils. As the solid phase sorption of PFAS increases (such as with increasing chain-length or favourable charge properties) the relative contribution of interfacial adsorption is expected to diminish (Brusseau 2019).



Fig. 2. Box plots of \log_{10} transformed K_d values for 29 PFAS in up to 10 soils as a function of perfluorinated C-chain length for PFCAs, PFSAs and FASAs (coloured) together with other PFAS and zwitterions (grey). The boxes and whiskers represent median and minimum to maximum values, respectively. n = 3 for C11 PFCA, n = 2 for 9Cl-PF3ONS, n = 9 for zwitterions and n = 10 for remaining compounds; n is the number of soils. Reproduced from Nguyen *et al.* (2020), with permission from the American Chemical Society. Copyright the American Chemical Society.

Other retention mechanisms

Other processes that could result in PFAS entrapment in soils include micelle and hemimicelle formation at soil/water surface (at high PFAS concentrations) as well as absorption and physical retention in inner pores of the solid-phase matrix. For example, PFOA can form hemimicelles on an adsorbent surface at 0.01-0.001 times its critical micelle concentration of 15 700 mg/L (Kissa 2001). In relation to physical entrapment, in a study on PFOS and its alternative 6:2 polyfluorinated ether sulfonate (F-53B) in a soil incubated over 240 days, Zhu et al. (2021) observed the formation of non-extractable residue of the two compounds that resisted solvent extraction and alkaline hydrolysis. However, they noted that the residues of both compounds underwent different stages of incorporation (decline in extractable fraction) and remobilisation (increase in extractable fraction). The authors ascribed the formation of nonextractable residue in the case of PFOS to the covalent bonding (via the head group) and strong adsorption (via the tail group), and in the case of F-53B to physical entrapment (sequestration). The remobilisation was attributed to the decomposition of organic matter in soils. Although sequestration of residues of POPs has been commonly observed (Alexander 2000), definitive work on this phenomenon for PFAS is currently lacking.

In addition, accumulation and retention of PFAS can occur at the fluid–fluid interface under both saturated (such as NAPL–water) as well as unsaturated conditions (air–water interfaces), as shown in Fig. 1. Although the partitioning into the air phase (soil atmosphere) has been found to be a significant contributor towards the retention of volatile aromatic compounds in soils (Kim *et al.* 1998), this phenomenon is expected to be insignificant for most PFAAs, which have low volatility (i.e. the Henry's constant *H* in the range of 10^{-3} even in protonated form and lower in anionic form). In contrast, the *H* values for some fluorotelomers are much higher (up to 10 000), and for these compounds partitioning into the soil atmosphere from the aqueous phase may be significant.

Factors affecting sorption of PFAS in soils under saturated conditions

The solid-phase sorption in saturated soils is one of most studied process in the literature on organic contaminants and several reviews have been published on sorption of PFAS in soils and sediments (e.g. Zareitalabad *et al.* 2013; Du *et al.* 2014; Li *et al.* 2018; Sharifan *et al.* 2021).

Sorbate chemistry

Chemistry of PFAS is the single most important property determining their sorption to soils. As mentioned earlier, PFAAs are expected to be anions at ambient pH in most soils with a hydrophobic tail of various C-F chain length (e.g. C4–C12). Their amphiphilic nature is a strong determinant of their partitioning behaviour. Being anionic, they are repelled from negatively-charged surfaces, especially clay minerals. In contrast, PFAAs are attracted by the net positive charge such as those on Al and Fe oxides commonly present in tropical soils, especially in subsoils. There is now a large body of literature on PFAS that demonstrates the dependence of sorption in soils and sediments on the chain length of PFAAs. In addition, the nature of the headgroup of PFAAs (such as carboxylic acid or sulfonic acid) also influences their sorption behaviour, with sulfonates showing greater sorption than corresponding carboxylates (e.g. Higgins and Luthy 2006; Campos Pereira et al. 2018; Nguyen et al. 2020). Higgins and Luthy (2006) noted 0.5-0.6 log unit increase in PFAS partition coefficient on sediments with each increase in CF2 moiety. Similarly, Campos Pereira et al. (2018) reported an increase in PFAS sorption of the order of 0.60 and 0.83 log Koc units per CF2 moiety for perfluorocarboxylates and perfluorosufonates, respectively.

Recently, Nguyen *et al.* (2020) examined the sorption behaviour of a range of PFAS with diverse chemistry (Fig. 2). Their work showed a strong dependence of sorption of PFAAs on their chain length as well as headgroup. Similarly, while the zwitterions showed greater sorption than their corresponding PFAAs analogues, their sorption was also affected by the nature of functional group. It is noteworthy that new (replacement) PFAS (such as GenX and ADONA) also showed low sorption to soils, generally in the range shown by C_4 - C_5 PFAAs. Sometimes, the partitioning process of polyfluorinated PFAS could be so complex that their sorption behaviour may not be predicted by soil properties alone (Barzen-Hanson *et al.* 2017).

Soil organic matter and its chemistry

The K_{oc} value has been used extensively in modelling behaviour of organic contaminants in soil due to ease of extrapolation of data between soils based on a single soil property (OC content) and its relationship with chemical parameters such as octanol–water partition coefficient (K_{ow}). However, many studies have since established that the K_{oc} approach is a highly simplified representation of sorption of even non-ionic organic compounds in soils and sediments (Ahmad *et al.* 2001). However, as mentioned earlier, PFAS are atypical of organic compounds and encompass a range of complex hydrophobic, hydrophilic, surface activity and surfactant-type behaviour which makes it difficult to even measure their hydrophobicity via K_{ow} .

Results from studies on the role of OC in PFAS sorption in soils are not consistent. While some studies have reported significant correlations with soil OC contents (e.g. Milinovic et al. 2015; Oliver et al. 2020a), others have observed that a simple correlation with soil OC does not hold for all systems (e.g. Li et al. 2018; Knight et al. 2019) and it may depend on PFAS chemistry (long-chain versus short-chain) and other factors. In the study by Milinovic et al. (2015), four of the six soils studied contained OC in the range of 3.9-39.0% and the carbon-rich soil perhaps had a stronger leverage on the correlation. The study by Oliver et al. (2020a) employed 19 estaurine coastal sediment samples containing OC in the range of 0.1-11.0%, with a narrow range of pH (6.2-7.7) and high salinity (electrical conductivity of 25.6-46.7 mS/cm). Li et al. (2018) evaluated the relative role of solid phase properties on sorption of PFAS in soils as well as sediments, based on a review of published data. The largest datasets available were for PFOA (n = 147) and PFOS (n = 178), and these analyses showed that OC content of soils and sediments only explained $\leq 10\%$ variance in K_d of these two compounds. However, this dataset was drawn from various studies on sediments as well as soils, and the methods employed in soil or sediment characterisation were not consistent. The diversity of the sources may have been one reason for such poor correlation with OC in the dataset examined by Li et al. (2018). Since then, two major studies on sorption of PFAS employing a large number of soils have been reported, wherein the soils were characterised in a single laboratory. Knight et al. (2019) studied sorption of radiolabelled PFOA (14C) on 100 Australian soils with diverse physico-chemical properties (e.g. OC range 1-3.5% and silt + clay content range 5-88%) and found that the K_d values did not correlate well with any single soil property. Although OC had the highest R^2 value ($R^2 = 0.36$), it only explained about one-third of the variation in PFOA sorption in these soils. Similarly, in a subsequent study on sorption of PFOS on a set of 114 soils from Australia and Fiji, Umeh et al. (2021) found that while total OC showed a significant positive relationship with K_d , it accounted for approximately 35% of variance in PFOS sorption in soils. In both studies, while OC could not explain some two-thirds of variance in sorption of PFOA and PFOS, it still had the dominant effect on sorption of these two PFAAs. The importance of soil OC may increase with increasing size and hydrophobicity of PFAS (Nguyen et al. 2020). Generally, OC contents decline rapidly with depth in soil profiles. The K_d of PFOA also showed a decline with depth in Australian soils (Fig. 3). This shows that OC content, although not the sole predictor, is an important factor affecting sorption of PFAS in soils.

Carbon chemistry is also expected to play a role in the sorption of PFAS. For example, activated carbon is a very effective sorbent of most PFAS and hence routinely employed in removing PFAS from groundwaters using 'pump and treat'



Fig. 3. The K_d values of ¹⁴C-PFOA in 100 Australian soils with depth in soils. Box plots represent the minimum, median, interquartile range and maximum. Significant differences between depths are denoted with different letters. Samples were considered outliers when they extended more than three box lengths from the edge of the box and are marked with an asterisk. Reproduced from Knight *et al.* (2019), with permission from Elsevier. Copyright Elsevier.

method and also for stabilisation of soils (Kabiri et al. 2021; Kah et al. 2021). In a study on 14 PFAS sorption to an organic soil, Campos Pereira et al. (2018) concluded that most long-chain PFAS are preferentially sorbed on highly condensed domains of the humin fraction and sorption is affected by the net charge, and hence pH. In another study, Campos-Pereira et al. (2022), while investigating the role of carbon chemistry (using ¹³C nuclear magnetic resonance spectroscopy) in sorption of a range of PFAS in three organic soil samples, observed a positive relationship between sorption and the contents of carbohydrates (i.e. O-alkyl carbon) and a negative relationship with pH. Zhao et al. (2014), in a study on sequentially extracted humic substances from a peat soil, found an inverse relationship between PFAS sorption and the contents of aromatic OC as well as phenolic and carboxylic moieties. Oliver et al. (2020a) found no correlation between sorption of PFOS and PFHxS with any of the carbon structures in 19 estuarine sediments.

Umeh *et al.* (2021) compared the sorption of PFOS by total OC and nonoxidisable organic matter in some soils by treating the soils with persulfate. They found that the K_d of PFOS in treated soils was 2–6 times greater than in untreated soils and concluded that soil organic matter quality also plays an important role in PFAS sorption. This is consistent with previous studies by Zhang *et al.* (2015) and Campos Pereira *et al.* (2018), wherein the humin fraction accounted for most of the PFOS sorption in contrast to humic and fulvic acids. Proteinaceous carbon has also been found to favour the sorption of some long-chain PFAAs in soils (Li *et al.* 2019). Overall, organic carbon in soils remains one of the most important soil properties affecting PFAS sorption. However, the soil mineral matter may also contribute

significantly to the sorption of PFAS, especially in soils with low OC or for cationic and zwitterionic PFAS.

Soil minerals (including clays) and their charge characteristics

In a study on 29 PFAS (representing a range of chemistries and charge characteristics) in 10 soils, Nguyen et al. (2020) found that sorption of PFAS in soils decreased in the order zwitterions > sulfonamides > telomers > PFSAs > PFCAs > ethers (Fig. 2). Mejia-Avendaño et al. (2020) carried out a batch sorption study on five anionic, three zwitterionic and one cationic PFAS in five soils. They observed that cationic PFAS (a perfluorooctaneamide ammonium compound) showed an order of magnitude greater sorption than PFOA (an anion). Furthermore, sorption behaviour of some PFAS (e.g. zwitterionic perfluorooctane sulfonamidoalkyl betaine due to its marked change in speciation at around neutral pH) was pH dependent in this study. Adsorption of PFAAs on soils in this study and that by others has been found to be insensitive to pH as they remain anionic in the pH range of most soils (e.g. Oliver et al. 2020b).

Barzen-Hanson et al. (2017) examined the sorption behaviour of aqueous film-forming foams (AFFF) containing anionic FtSs, zwitterionic FtSaBs and cationic 6:2 fluorotelomer sulfonamido amine (FtSaAm) in six soils with varying physico-chemical properties. They observed the greatest sorption of 8:2 FtSaB followed by 8:2 FtS, 6:2 FtSaB and 6:2 FtS. Within each class of compounds, sorption increased with increasing fluorinated chain-length. The increase in log K_d with increasing C–F chain length showed that hydrophobic binding was also contributing to the sorption of these PFAS. For compounds with comparable chain lengths, sorption was dependent on the molecular size, molecular weight and charge properties of compounds. The cationic 6:2 FtSaAm was completely sorbed in all but one soil. A comparison of sorption among various compounds showed that not only the number of positive charges, but also the position of the charge and the net charge of PFAS played role in determining the extent to which the compound was sorbed by the soils.

In another study on sorption of PFOS (an anionic compound) in 114 soils (mostly from the tropical regions of Australia and Fiji), Umeh *et al.* (2021) observed that variable charge soils carrying net positive charge showed higher sorption than the other soils. Many Fijian soils (63%) showed PFOS K_d values greater than the median value (28 L/kg), whereas only 35% of Australian soils exceeded this value. The sorption behaviour of various PFAS in these studies and in others (reviewed by Li *et al.* (2018)) is consistent with the electrostatic interactions driven by the permanent negative charge on aluminosilicates and pH-dependent charges on organic matter and Al and Fe oxides/hydroxides in soils.

Soil solution chemistry (pH, ionic strength, cations and DOC)

Soil solution chemistry can have a major effect on the sorption behaviour of PFAS in soils. For example, pH, ionic strength and the nature of polyvalent cations as well as dissolved organic carbon (DOC) can significantly influence the overall net charge of the soil solid phase (e.g. reduced negative electrostatic potential on organic matter). Dissolved organic matter has been found to interact with PFAS molecules or sorption surfaces (e.g. soil and activated carbon) and affect their partitioning onto the solid phase (e.g. Jeon et al. 2011; Oi et al. 2022). The work by Higgins and Luthy (2006) on sorption of PFAS on sediments noted a strong relationship with electrostatic potential for sediment organic matter. Polyvalent cations in soil solution (and on the soil exchange complex) have been found to affect the sorption behaviour of PFAS, through their influence on the electrostatic interactions with the soil solid phase (e.g. negative charge on soil OC and aluminosilicates). Polyvalent ions can enhance PFAS sorption through cation-bridging (e.g. of anionic PFAAs) and through complexation with soil minerals. While monovalent cations such as Na⁺ and K⁺ in solution have been found to have little effect on PFAS sorption, polyvalent ions such as Ca²⁺, Mg²⁺, Fe²⁺ and Al³⁺ have been found to enhance the sorption of PFAS in soils (Higgins and Luthy 2006; Campos Pereira et al. 2018; Cai et al. 2022). Cai et al. (2022) studied the sorption of 18 anionic PFAS (with varying chain lengths and headgroups) in two soils in the presence of a range of ionic strengths of three cations (Na⁺, Ca²⁺ and Mg²⁺). They observed that, at equimolar concentrations, Ca²⁺ and Mg²⁺ were more effective than Na⁺ in enhancing the sorption of several PFAS. The effect of cations was insignificant for some short-chain compounds (e.g. PFPeA, GenX and ADONA). This indicates that the enhancement of sorption involved hydrophobic interactions which were more prominent in the case of long-chain compounds. The K_d of PFAS increased linearly with increasing cation concentration. The authors ascribed this effect to the interplay of electrostatic and hydrophobic interactions, both favouring sorption at higher ionic strengths of divalent cations through reduction of the intramolecular repulsion of anionic PFAS and neutralising the negative surface charge on soil solids with increasing concentration of cations.

The effect of cations may become even more complex in soils with pH-dependent charge (Oliver *et al.* 2020*b*) and for cationic PFAS. For example, sorption of cationic PFAS (perfluorooctane-amido quaternary ammonium salt (PFOAAmS)) decreased with increasing concentration of Ca²⁺ (Mejia-Avendaño *et al.* 2020). Contaminants co-existing with PFAS in soil may affect PFAS sorption in both saturated and unsaturated soils. Co-contaminants may include DOC, hydrocarbon surfactants, NAPLs and other sorbates (such as mixture of PFAS, DOC and metals). Column studies on activated carbons and anion exchange resins have demonstrated that DOC competes with PFAS for sorption sites on sorbents employed to remove PFAS from water (McCLeaf *et al.* 2017). The presence of humic acid on clay mineral surfaces has been found to inhibit adsorption of PFOS (Zhang *et al.* 2014). The addition of P in soil solution has also been found to reduce the sorption of PFOS in a soil in the presence as well as absence of organic matter and ferric oxides (Qian *et al.* 2017).

Effect of co-contaminants in PFAS products on sorption

Firefighting activities over decades have employed AFFF with a complex composition of fluorinated surfactants, hydrocarbon surfactants, organic solvents, polymers and other additives (Interstate Technology and Regulatory Council (ITRC) 2020). Indeed, hydrocarbon surfactants in AFFFs are more abundant (5-10%) than PFAS (0.9-1.5%) and these can co-exist with PFAS in soil as well as in contaminated groundwaters (García et al. 2019). The presence of hydrocarbon surfactants at higher concentrations than PFAS in AFFF and their greater surface activity means that cocontaminants can make a major difference in the retention of PFAS in saturated and unsaturated soils. However, most PFAS sorption studies in soils have been conducted using very simple systems. Often a single PFAS compound has been studied in the absence of co-contaminants, such as hydrocarbon surfactants. Additionally, during the electrochemical fluorination process both linear and branched isomers of PFASs are produced and their reactions with sorbing surfaces are different (McCleaf et al. 2017). Therefore, their field transport behaviour in both saturated and unsaturated soils may be quite different (Nickerson et al. 2021; Sharifan et al. 2021).

Based on a leaching study of historically contaminated soils, Høisæter *et al.* (2019) hypothesised that complex mixtures of AFFF affect the retention behaviour of PFAS in field-contaminated soils. Similarly, leaching experiments showed that longer chain PFAS can effectively displace the shorter chain PFAS from sorption sites in soil columns (e.g. Gellrich *et al.* 2012). However, the effect of co-contaminants has not been fully investigated so far.

Metals and PFAS can be released simultaneously into the surrounding environment, especially because some fluorinated surfactants (e.g. PFOS) are used as the chrome mist suppressant in the plating industry (Li *et al.* 2019). Although PFOS has been reported to form surface-bound complexes with haematite and copper (e.g. Gao and Chorover 2012), the effect of transition metals on sorption of PFAS in soils has not been investigated. Overall, a sound understanding of the effects of co-contaminants on PFAS sorption in soils is lacking.

Additional factors affecting PFAS retention in unsaturated soils

A range of processes could contribute to the retention of PFAS in unsaturated soils (Brusseau 2018). These may include sorption and partitioning occurring on the solid phase as discussed above, but also air-phase interactions and in NAPLs, as shown in Fig. 1. Thus a combination of several processes may determine the mobility of PFAS in unsaturated soils. The soil physical and chemical properties (mineralogy, particle size and organic matter content), PFAS properties (chain length and polarity) and NAPL physical and chemical properties (solubility, viscosity, density and solvency power) together will determine the relative importance of the interfacial processes in affecting PFAS mobility. Rarely do PFAAs and NAPLs exist as single compounds in the subsurface; more commonly consisting of multicomponent mixtures with perhaps a few dominant compounds dictating the behaviour or toxicity. However, the interaction between chemicals and the competition for interfacial or solid phase sorption sites is the subject of ongoing research.

Effect of PFAS chain length and functional groups on interfacial adsorption

Adsorption at the air-water interface (AWA) is directly dependent on the C-F chain length of the compound. This is because AWA depends on the surface activity of the compound which is strongly dependent on the C-F chain length and its concentration in solution (Costanza et al. 2019; Silva et al. 2019). Lyu et al. (2022) reported an excellent linear relationship between $\log K_{ai}$ (air-water adsorption coefficient) and the number of fluorinated carbons for perfluoro carboxylates with chain lengths in the range of 3-9 (Fig. 4). With each additional fluorinated carbon, they observed an approximately 0.46 log unit increase in K_{ai} . However, when K_{ai} was incorporated into the retardation factor, the relationship showed that for short chain compounds the interfacial adsorption did not significantly contribute to the retardation of PFAS transport in unsaturated soils (Fig. 4). Simulations carried out by Guo et al. (2022), using a screening model on six different soils, showed that the retention in unsaturated soils was strongly dependent not only on the chain length of PFAS but also the type of functional group present (e.g. carboxylates versus sulfonates).

Effect of degree of saturation in soils

Several studies have compared the movement of PFOS and PFOA through soil and sand columns under saturated and unsaturated conditions (Lyu *et al.* 2018; Brusseau *et al.* 2019). They noted that movement of PFAS through these columns was universally slower under unsaturated conditions than when the soil or sand was saturated with water (Fig. 5).



Fig. 4. Air–water adsorption coefficient (K_{ai}) and fraction of total retention contributed by air–water adsorption for perfluoroalkyl acids of different chain length as measured during transport experiments under unsaturated conditions (degree of saturation 0.68–0.70). Based on data from Lyu et *al.* (2022).



Fig. 5. Breakthough curves of PFOS under saturated (SAT) and unsaturated (UNSAT) conditions (degree of saturation 0.66) during transport through a sand, relative to a non-reactive tracer (NRT). The solid lines represent model simulations. Reproduced from Brusseau *et al.* (2019) with permission from Elsevier. Copyright Elsevier.

This retarded movement has been ascribed to the AWA phenomenon. Brusseau *et al.* (2019), for example, observed that PFOS movement, as represented by the retardation factor (which is a measure of delayed movement of chemical in comparison to water or a conservative, non-interacting chemical), was four times slower in unsaturated than in saturated sand. However, PFOA was only 1.4 times slower through the sand, but the conditions were not directly comparable as the water saturation was higher in the PFOA

instance and therefore interfacial area was likely smaller. The AWA as well as the movement of PFAS in unsaturated soils may also be influenced by the immobile domains of water as the soils become unsaturated and the measurement of AWA by simple retardation factor may not be straightforward (Hasan *et al.* 2020; Stults *et al.* 2021).

Effect on soil texture and grain size

The relative contribution of air–water interface towards the retention of PFAS in unsaturated soils is likely to depend on soil properties determining the total interfacial area. Brusseau *et al.* (2019) observed that although their soil had a larger specific AWA than sand, the contribution of air– water interfacial interaction was larger in sand (due to its lower solid-phase sorption) than in the soil with greater sorption potential for PFAS. In other words, with increasing sorption capacity of the solid phase in a soil (such as through electrostatic or hydrophobic interactions), the relative role of interfacial adsorption is expected to diminish.

In another study, Lyu *et al.* (2018) noted that the effect of unsaturated conditions on the rate of movement of PFOA was affected by the size of sand grains. The authors noted that in a fine sand (average grain size of 0.35 mm) the retardation of PFOA was significantly higher under unsaturated than saturated conditions but this difference was very small in a coarser sand with average grain size of 1.2 mm. The lower retardation (faster movement) of PFOA in the coarser sand at the same level of water saturation of pores was ascribed to the smaller AWA and thus lower contribution of accumulation at the air–water interface. This was further supported by model simulations carried out by Guo *et al.* (2022) on transport of PFAS through six different soils, wherein greater retardation factors of PFAS were noted in sandy soils than fine-grained soils.

Effect of solution pH, ionic strength and type of cations on the air-water interfacial accumulation

In addition to soil texture, soil solution properties have been noted to influence the relative PFAS adsorption or accumulation at the air-water interface. These include water quality, i.e. pH and salinity of water (ionic strength), multiple species as well as the concentration of PFAS in the solution. For example, Costanza et al. (2019) and Lyu and Brusseau (2020) observed that the presence of salts in solution (ionic strength) as well as solution pH affected the interfacial interactions and movement of PFOA through soil columns. However, pH had a much smaller effect than ionic strength on PFOA movement through unsaturated columns (Lyu and Brusseau 2020). As the ionic strength of the solution increased, the movement of the PFOA became slower or more retarded under unsaturated conditions. This is because the surface tension of PFAS in solution is lower in saline water than in pure water. Similarly, Silva et al. (2019) compared the surface tension isotherms of several perfluoro carboxylates at different ionic strengths and noted that the surface tension of these carboxylates not only depends on the C-F chain length and PFAS concentration, but also on the ionic strength. In synthetic groundwaters, the surface tension decreased more markedly as the chain length and concentration of perfluoroalkyl carboxylic acid increased and consequently the K_{ai} as well as adsorption energy increased with compound chain length. The effect of ionic composition on surface tension and on K_{ai} was examined by Brusseau and Van Glubt (2019), Li et al. (2021) and Le et al. (2022). These studies showed that salt concentration and type have a strong influence on retention and mobility of PFAS in unsaturated soils. Based on transport studies in soil columns maintained at different degree of moisture saturation, Lyu and Brusseau (2020) reported that air-water retention of PFOA doubled as the ionic strength increased from 0.001 to 0.1 M. Similarly, the presence of CaCl₂ in background solution increased PFOA retention by 67% in an unsaturated soil compared to that in the presence of NaCl. Most studies have been conducted in the presence of simple systems employing a monovalent salt such as NaCl. Modelling studies (e.g. Le et al. 2022) have highlighted, through an example, that the failure to account for the effect of divalent cations can significantly underestimate the retention of PFAS in unsaturated systems.

Effect of competing sorbates

As in the case of saturated soils, several co-contaminants can influence not only the solid-phase sorption (as measured in saturated soil) but also the interfacial adsorption in unsaturated soils. These may include other surfactants that enter the soils contaminated by AFFF, PFAS mixtures, DOC and other organic and inorganic contaminants. Several reports in the literature show that co-existing anionic hydrocarbons can perturb the surface activity of PFAS and thus can affect their AWA. Brusseau and Van Glubt (2019) reported that anionic hydrocarbons as co-contaminants can markedly increase the critical micelle concentration of PFOA and PFOS. Costanza et al. (2020) observed that AFFF showed greater interfacial activity than PFOA, PFOS or perfluorooctane sulfonamide (FOSA). Similarly, Lyu et al. (2022) observed that sodium dodecyl benzene sulfonate (a hydrocarbon surfactant) was preferentially adsorbed at the air-water interface and thus competed with the interfacial accumulation of PFOA in an unsaturated sand. In contrast, the co-existing hydrocarbons in AFFF can have a synergistic effect on enhancing the accumulation at the NAPL-water interface (Costanza et al. 2020).

The presence and size of alkali metal ions in solution can alter the surface activity of PFAS. At comparable concentrations, surface activity of NH_4 -PFOA was reported to be greater due to its smaller hydrated radius than Li-PFOA with larger hydrated radius (Brusseau and Van Glubt 2019). Consistent with this, PFOA showed greater retardation in column experiments in the presence of Ca^{2+} than Na^+ and the retardation increased with increasing ionic strength (Li *et al.* 2021).

Relative importance of interfacial accumulation in relation to total retention in unsaturated soils

As a synthesis from several studies in the literature, Brusseau (2019) developed a generic nomograph to illustrate the relative role of interfacial processes (air-water and oil-water combined) to the total retention of PFAS. He demonstrated that the importance of interfacial adsorption will depend on the inherent ability of soil to retain PFAS through watersolid phase interactions. While, consistent with our previous work (Li *et al.* 2018), recognising the limitation of the K_{oc} approach for PFAS (i.e. assuming only organic carbon controls the sorption of PFAS), for ease Brusseau used K_{oc} as an indicator of the sorption on the solid phase. The other parameter needed was the specific fluid-fluid interfacial area $(A_{nw} \text{ in } \text{cm}^2/\text{cm}^3)$, which represents the combined effect of degree of saturation of the geological media, such as soil and the PFAS molecule. Using these two parameters, Brusseau (2019) developed the nomograph for an estimation of the relative role of AWA in the total retention of PFAS (Fig. 6). This shows that the relative role of interfacial adsorption could be as small as <5% to as high as 85%, depending on the conditions related to the geological media, its degree of saturation and the PFAS chemical.

The f_{oc} is an easy-to-measure property and is usually part of basic characterisation of a soil and therefore is often a readily available parameter for most soils. However, there



Fig. 6. Generic nomograph developed by Brusseau (2019) describing the relative role of air/oil-water interfacial adsorption for the total retention of a given PFAS by geological media. The X-axis represents the fraction of organic carbon in soil or geologic media and the Y-axis the specific fluid-fluid (air-water or oil-water) interfacial area (A_{nw}) with units of cm⁻¹. Australian soils on an average have about 1% organic carbon ($f_{oc} = 0.01$) (adapted from Brusseau 2019).

are different methods in the literature to measure A_{nw} (Brusseau 2019), and these methods do not always give the same value for that parameter. Nevertheless, this level of uncertainty may or may not matter, depending on the geological conditions. Many surface soils, such as in Australia generally, have $f_{\rm oc}$ in the range 0.01–0.02. This often declines exponentially to about 1/10 at a depth of about 0.5-1 m for subsurface soil, and one can assume f_{oc} of about 0.001 down to the water table and perhaps lower than this in aquifer sediments. In terms of air-water interfacial area, Brusseau (2019) reported measured A_{nw} values for the range of PFOA of 24-68 cm⁻¹ for sand at 0.76 saturation and for PFOS of 120-140 cm⁻¹ for a sand and a soil at 0.66 saturation. The nomograph (Fig. 6) shows that, in an unsaturated subsurface soil (with $f_{oc} = 0.001$), this combination may have a significant contribution of airwater interfacial adsorption to the total retention below and above the line of 0.35 for both PFOA and PFOS. It will be interesting to compare the predictions from this nomograph with the measured values in future studies.

Desorption and leaching behaviour of PFAS

Desorption to water from solid surfaces in soil

Most studies have focussed on sorption behaviour of PFAS in soils with only a limited number studying both the sorption and desorption aspects (e.g. Milinovic et al. 2015; Wei et al. 2017; Xiao et al. 2019). Despite the low sorption affinity of PFAAs in soils (especially the short-chain compounds), their sorption is not always reversible (Zhao et al. 2014; Milinovic et al. 2015; Wei et al. 2017). On sequentially extracted humic substances, Zhao et al. (2014) observed that sorption of PFHxS on humin was not as reversible as from humic acids. The PFOS sorption on sediments has been found to be hystereric and its irreversibility increased with increasing salinity (You et al. 2010). Indeed, a significant sorption-desorption hysteresis has been noted in studies on a range of PFAS ranging from PFAAs to cationic and zwitterionic compounds. For example, Xiao et al. (2019) in their sorption-desorption studies on cationic (PFOAAmS) and zwitterionic (PFOAB) PFAS in five soils, noted a more pronounced hysteresis in sorption-desorption isotherms of PFOAB than in the case of PFOAAmS. However, the degree of hysteresis was dependent on soil type. The authors could not rule out the possible transformation of PFOAB during their study, which may have contributed to sorption-desorption hysteresis (Xiao et al. 2019).

Leaching of PFAS through soils is obviously dependent on their desorption behaviour. Laboratory studies based on batch or column leaching procedures conducted under saturated conditions have shown that PFAS, particularly anionic PFAS, can easily leach from contaminated soils (Bräunig *et al.* 2019, 2021; Kabiri *et al.* 2022). Unlike sorption studies, leaching/desorption studies typically follow standard leaching methods that have been developed either to classify waste for disposal or to understand leaching mechanisms/ behaviour, with method selection based on jurisdictional regulatory guidance. These methods vary based on procedural factors including leaching mode (batch or column), liquid-to-solid ratio, leaching solution conditions (pH, conductivity and solution chemistry), frequency and duration of leaching.

Desorption behaviour of PFAS is generally consistent with results from sorption studies (Nguyen et al. 2020), with desorption behaviour in soil influenced by PFAS chemistry, soil properties and solution conditions. This was evident in recent work on desorption and leaching of a broad range of PFAS (21 PFAS) from 12 AFFF-contaminated soils (Kabiri et al. 2022). In this study, short-chain PFAS (CF2-chain length \leq 7) were readily desorbed from soil (Fig. 7). Desorption was not affected by the leaching conditions including liquidto-solid ratio, leaching duration, frequency or batch versus column leaching procedures. In comparison, long-chain PFAS were more resistant to desorption, particularly under acidic conditions. Indeed, some of the long-chain PFAS including PFUnDA, PFDoDA, PFTrDA, PFTeDA and 10:2 FtS did not desorb from the soils under any circumstances. The PFAS functional head group also affected desorption from soil with greater desorption in following the order: carboxylic acids > sulfonic acids > sulfonamide head groups, given the same C-F chain length. A column desorption and leaching test showed that long-chain PFAS desorb and leach to a lesser extent than short-chain compounds. The desorption of longchain PFAS varied markedly with soil properties. For example, there was greater PFAS desorption from sandy than clay-rich soils (Kabiri *et al.* 2022).

The above discussion suggests that, compared to short-chain PFAS, long-chain PFAS (including long-chain precursors) tend to accumulate in the soil and can serve as a significant pool and long-term source for PFAS leaching. Indeed, long-chain PFAS, especially PFOS, can resist complete leaching even with repetitive extraction (Kabiri *et al.* 2022). The less extractable PFAS could be entrapped or protected by soil components (e.g. minerals or organic carbon) in meso- or micro-pores in a process known as ageing or physical entrapment (Fig. 1), thus inhibiting their desorption. Clearly, these aspects need further investigations.

It is important to note that most desorption/leaching studies on PFAS have been performed under saturated conditions. Considering increased sorption of PFAS under unsaturated conditions, the role of the air-water interface in controlling PFAS desorption/leaching also needs to be considered.

Desorption to water from air-water and NAPL-water interfaces in soil

The PFAS accumulated at the air-water interface in unsaturated soils are released back when water saturation



Fig. 7. Boxplot of the percentage of total PFAS desorbed with varying CF₂-chain lengths by acidic and alkaline solutions from 12 AFFF-contaminated soils using the Australian Standard Leaching Procedure (ASLP). The boxes, bars and whiskers represent quartiles, median and minimum to maximum values (n = 12), respectively. Asterisk * indicates that the marked PFAS were only detectable at alkaline pH (PFDA and FOSA), and were below the method detection limit in the acidic pH desorption solutions. Note that values of >100% desorbed are the result of total PFAS concentrations in the soil being greater and precision smaller than the method detection limits for the same compounds in the desorption solutions, particularly for those compounds with low total concentrations in soil. Reproduced from Kabiri et *al.* (2022), with permission from the American Chemical Society.

increases as a result of advancement of a wetting front, for example after a rain event. Through model simulations, Brusseau and Guo (2022) demonstrated that the PFAS adsorbed at the air-water interface were released to pore water and thus increased the pore-water concentrations of long-chain PFAS (such as PFOA and PFOS). For short-chain compounds this effect was minor. Clearly more work is needed on desorption behaviour of PFAS under unsaturated conditions. Pore water extracted from soils (e.g. through suction lysimeters) under field conditions may inform the real world desorption and leaching behaviour of PFAS in soils (Rayner et al. 2022). Studies on transport behaviour of PFAS at contaminated sites under field conditions indicate desorption of PFAS leading to both downward and upward movement in the soil profile, depending on the prevailing conditions (Wallis et al. 2022).

Integrated role of soil properties for sorption and desorption

It is evident from the literature that, unlike other organic compounds, the sorption processes are much more complex and soil OC content, or any other single soil property, may not be solely responsible for sorption of PFAS, except in the case of highly hydrophobic PFAS (Li *et al.* 2018). A study on sorption of anionic, cationic and zwitterionic fluorotelomers (precursors that can be metabolised into and degrade to PFAS) concluded that the sorption mechanisms are so complex that they cannot always be predicted easily (Barzen-Hanson *et al.* 2017). Studies have shown that often several properties need to be considered together to explain PFAS sorption behaviour in soils (e.g. Li *et al.* 2018; Knight *et al.* 2019; Umeh *et al.* 2021).

Based on a review of data, Li et al. (2018) found significant relationships between K_d values and OC plus clay contents for PFOS ($R^2 = 0.76$, n = 15), PFOA ($R^2 = 0.43$, n = 29), *N*-MeFOSAA ($R^2 = 0.96$, n = 5), PFNA ($R^2 = 0.87$, n = 9), PFDA ($R^2 = 0.84$, n = 11), PFUnDA ($R^2 = 0.92$, n = 7) and PFPeA ($R^2 = 0.91$, n = 6). Although the limited number of observations available by 2018 indicated that OC content, clay content and pH needed to be considered together in explaining the sorption behaviour of PFAS in soils, more work on a larger set of well-characterised soils is necessary. Li et al. (2018) also noted that in many sorption studies on PFAS, the soils or sediments used in the studies were not fully characterised and sometimes even the basic properties (such as pH) were missing, thus limiting the value of sorption data obtained in such studies. Subsequently, Knight et al. (2019) investigated the role of various soil properties - OC, pH (CaCl₂), particle size distribution, electrical conductivity, chloride, cation exchange capacity, exchangeable cations $(Ca^{2+}, Na^{+} and K^{+})$ and exchangeable sodium percentage – together to explain the variation of PFOA K_d measured in

100 surface and subsurface soils (Table 3). Their statistical analysis of the data showed that K_d was only significantly affected by OC content, silt+clay content (P < 0.05) and pH (P = 0.06) approaching the critical *t*-value (Table 3). Inclusion of pH only marginally improved the quality of their multiple linear regression model (R^2 increased from 0.61 to 0.63). More recently, Umeh et al. (2021) conducted a major study on sorption of PFOS using a set of wellcharacterised 114 soils (Table 3), including for some soil properties that have rarely been measured, such as anion exchange capacities. Their multiple linear regression (MLR) analysis revealed that the combination of total OC, oxalateextractable Al, anion exchange capacity, pH and silt (in the order of importance) accounted for approximately half of the total variation in PFOS K_d values across soils. Inclusion of these predictor properties in an artificial neural network model (trained on a subset of soils) provided satisfactory prediction of PFOS K_d in these soils.

Most of the above studies were conducted on anionic perfluoroalkyl acids (e.g. PFOA and PFOS). Limited studies on sorption of zwitterionic or cationic PFAS (e.g. FtSaB and FtSaAm) have shown that their sorption behaviour is principally driven by electrostatic interactions such as cation exchange. Barzen-Hanson *et al.* (2017) noted significant and very strong positive correlations of sorption coefficients with the cation exchange capacity of soil. For zwitterionic 6:2 FtSaB and 8:2 FtSaB, they noted *R* values of 0.94 and 0.99, respectively. However, such correlations were absent for anionic FtS, while the cationic FtSaAm was totally sorbed in five out of six soils. No correlation with OC or anion exchange capacity was noted for FtS or FtSaB.

Which soil properties matter most

The analysis above shows that the key soil properties that govern partitioning behaviour of PFAS depend strongly on the chemical characteristics of the PFAS molecule. Given the huge diversity in PFAS chemistry (surfactants to nonsurfactants, from anions to zwitterions and cations and from non-polymers to polymers), it is presumptive to expect that the same set of properties will be applicable to all chemistries. Most existing literature is on sorption of PFAAs (e.g. PFOS and PFOA), and a handful of zwitterions and other PFAS, perhaps because these have received the most regulatory attention so far. Therefore, the following discussion is largely related to the PFAA group of PFAS. Additionally, the mechanisms governing partitioning, and therefore factors affecting it, differ in saturated and unsaturated soils.

In saturated soils, the current body of literature shows that firstly no single soil property can adequately explain the sorption behaviour of PFAS on the soil solid-phase. Total OC content of soil is one of major properties governing

Soil property	PFOA K _d (all soils, n = 100) Knight et al. (2019)	PFOA K_d (surface soils only, $n = 21$) Knight et al. (2019)	PFOS K _d (all soils, <i>n</i> = 114) Umeh et al. (2021)	PFOS Log K_d (all soils, n = 114) Umeh et al. (2021)
Total organic carbon (%) (all soils)	0.60*	0.45*	0.50*	0.51*
pH (CaCl ₂ or BaCl ₂)	-0.21*	-0.21*	-0.37*	-0.39*
Electrical conductivity (dS/m)	0.24	0.39	0.61*	0.39*
Sand (%)	-0.16	-0.82	-0.09	-0.23*
Silt (%)	0.19	0.55	0.19*	0.31*
Clay (%)	0.09	0.72	0.02	0.14
Silt + Clay (%)	0.16*	0.82*	nd	nd
Cation exchange capacity (cmol _c /kg)	0.23	0.64	0.03	0.11
Anion exchange capacity (cmol _c /kg)	nd	nd	0.40*	0.35*
Oxalate extractable aluminium (meq/g)	nd	nd	0.55*	0.60*
Oxalate extractable iron (meq/g)	nd	nd	0.42*	0.47*
Carbonates	-0.03	0.27	nd	nd
Exchangeable Ca ²⁺ (cmol _c /kg)	0.45	0.59	nd	nd
Exchangeable K ⁺ (cmol _c /kg)	0.26	0.70	nd	nd
Sum of polyvalent cations (Al ³⁺ , Ca ²⁺ , Fe ²⁺ , Mg ²⁺ , Mn ²⁺ , Zn ²⁺) in mg/kg soil	nd	nd	0.08	0.03
Dissolved organic carbon (mg/L)	nd	nd	0.11	0.16

Table 3. Simple correlation coefficients (r) observed between distribution coefficients (K_d values) of PFOS and PFOA and individual soil properties.

Data drawn from two studies (Knight *et al.* 2019; Umeh *et al.* 2021) employing at least 100 soils each. Knight *et al.* (2019) used 100 surface and subsurface soils from temperate region of Australia (with low levels of sesquioxides), and Umeh *et al.* (2021) used 54 Australian soils (including 26 soils from the tropical region of Queensland) and 60 Fijian soils (all tropical soils). Most of these soils had elevated levels of sesquioxides (median value of 3 g/kg). The MLR model for PFOS based on statistically significant soil properties (total organic carbon, anion exchange capacity, oxalate extractable Al and pH) developed by Umeh *et al.* (2021) resulted in a R^2 of 0.52 (n = 109) for prediction of PFOS K_d . In the case of MLR model (based on organic carbon, silt + clay and pH) by Knight *et al.* (2019) for prediction of PFOA K_d in surface soils more accurately ($R^2 = 0.74$; n = 21). *Significant at P < 0.05.

nd, not determined.

the sorption of PFAAs and its importance increases with increasing PFAS chain-length or molecular size. That is, the longer the chain length, the more hydrophobic is the tail of the PFAS molecule, leading to a greater role for OC in partitioning. However, several studies show that OC content could explain only about one-third of the total variation in sorption of PFAAs in soils. The other important predictors of K_d of PFAS include particle size distribution, oxalateextractable Al and Fe contents (especially in tropical soils) and solution chemistry. The solution chemistry is important in terms of pH, ionic strength as well as the nature and concentrations of polyvalent cations such as Ca^{2+} , Mg^{2+} and Al³⁺. The presence of co-contaminants such as AFFF constituents, DOC and other organic and inorganic contaminants (e.g. metals) can potentially affect PFAS sorption. It is noteworthy that the properties that govern the partitioning behaviour of PFAS in saturated soils do not directly extrapolate to sediments. For example, in the case of marine and estuarine sediments, due to their high salinity, buffered pH and narrower particle size distribution, the OC content alone may be a stronger predictor of PFAS partitioning (Oliver *et al.* 2020*a*).

In unsaturated soils, in addition to the solid-phase sorption (as in saturated soils), AWA can contribute significantly to the retention of PFAS in soils. For some short-chain PFAS, which do not show significant solid-phase sorption (e.g. PFBA and PFBS), the main mechanism of their retention is interfacial accumulation. The K_{ai} of PFAAs is strongly dependent on the chemistry (surface activity) of the PFAS, the air–water interfacial area in the unsaturated soil (i.e. degree of saturation and texture of soil) and the solution chemistry (e.g. ionic strength and polyvalent cations).

Knowledge gaps

The work on sorption–desorption behaviour of PFAS remains limited, considering the diverse chemistry of compounds in this class and their myriad applications. Hence the following knowledge gaps are by no means exhaustive.

- 1. The importance of soil properties in explaining partitioning is very much dependent on PFAS chemistry. Most published work is on PFAAs and data for cationic, zwitterionic and precursor compounds (polyfluorinated compounds) are very limited.
- 2. Laboratory partitioning studies using defined compounds in isolation do not mimic field contamination because AFFF are complex mixtures of hydrocarbon surfactants and fluorinated surfactants. Furthermore, field soils may have other co-contaminants. Partitioning behaviour in the presence of co-contaminants is lacking under both saturated and unsaturated conditions.
- 3. Field-based measurements of partitioning should be attempted to obtain empirically driven sorption–desorption parameters.
- 4. Direct evidence for sorption mechanisms of PFAS on soil surfaces is lacking, partly due to the low abundance of these contaminants in most soils, which precludes the use of the many spectroscopic techniques able to provide mechanistic evidence.
- 5. Studies on reversibility of sorption reactions, either at solid surfaces or at air–NAPL–water interfaces are rare. The degree to which natural attenuation of PFAS and the appearance of non-extractable residues might reduce long-term risks to the environment is not known.
- 6. A wider range of soil types, with stronger solid-phase partitioning, should be used in studies of partitioning under unsaturated conditions, to determine the relative importance of air-water interfacial retention on overall partitioning. Most studies so far have deliberately employed sandy soils with little solid-phase sorption affinity for PFAS.
- 7. The measurement of air–water interfacial accumulation is difficult and requires complex laboratory techniques simpler methods are needed to allow wider investigation of this phenomenon.
- 8. Sorption and desorption processes together determine the partitioning and mobility of contaminants in the soil environment. So far little work is available in the published literature on the desorption behaviour of PFAS in soils.
- 9. Unlike convention nonpolar organic compounds for which K_{ow} and K_{oc} -based predictions of partitioning coefficients in soils provide a reasonable estimate of mobility, these parameters are clearly neither appropriate nor adequate for surface active chemicals such as PFAS. New predictive approaches (e.g. quantitative structure activity relationships) are needed where characterisation of PFAS structure and/or chemistry can be used to predict mobility in the environment.

Abbreviations

ADONA = Dodecafluoro-3H-4,8-dioxanoate AFFF = Aqueous film forming foams

- $A_{nw} =$ Fluid–fluid interfacial area
- AWA = Adsorption at the air–water interface
- DOC = Dissolved organic carbon
- F-53B6:2 = Chlorinated polyfluorinated ether sulfonate
 - $f_{\rm oc}$ = Fraction of organic carbon
 - FASA = Perfluoroalkane sulfonamide
 - FOSA = Perfluorooctane sulfonamide
 - FtS = Fluorotelomer sulfonic acid
 - FtSaB = Fluorotelomer sulfonamido betaine
- FtSaAm = Fluorotelomer sulfonamido amine
- GenX = 2,3,3,3-Tetrafluoro-2-
 - (heptafluoropropoxy)propanoic acid K_{ai} = Air–water adsorption coefficient
 - $K_{ai} = \text{All-water ausorption coefficient}$
 - $K_{\rm d}$ = Distribution coefficient
 - K_{oc} = Distribution coefficient based on organic carbon
 - K_{ow} = Octanol–water partition coefficient
- NAPL = Non-aqueous-phase liquid
- *N*-MeFOSAA = *N*-methyl perfluorooctane sulfonamidoacetic acid
 - OC = Organic carbon
 - PFAAs = Perfluoroalkyl acids
 - PFAS = Poly- and perfluoroalkyl substances
 - PFBA = Perfluorobutanoic acid
 - PFBS = Perfluorobutane sulfonic acid
 - PFCA = Perfluoroalkyl carboxylic acid
 - PFDA = Perfluorodecanoic acid
 - PFDoDA = Perfluorododecanoic acid
 - PFHxA = Perfluorohexanoic acid
 - PFHxS = Perfluorohexane sulfonic acid
 - PFNA = Perfluornonanoic acid
 - PFOA = Perfluorooctanoic acid
 - PFOAB = Perfluorooctane amidoalkyl betaine
 - PFOAAmS = Perfluorooctane-amido quaternary ammonium salt
 - PFOS = Perfluorooctane sulfonic acid
 - PFOSF = Perfluorooctane sulfonyl fluoride
 - PFPeA = Perfluoropentanoic acid
 - PFSAs = Perfluoroalkane sulfonic acid
 - PFTeDA = Perfluorotetradecanoic acid
 - PFTrDA = Perfluorotridecanoic acid
 - PFUnDA = Perfluoroundecanoic acid
 - pK_a = Acid–base dissociation constant
 - POP = Persistent organic pollutant
 - XANES = X-ray absorption near-edge structure

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Data availability. Data used to generate the results in the paper are available in the public domain.

Conflicts of interest. The authors declare no known conflicts of interest.

Declaration of funding. The research work did not receive any specific funding. However, CSIRO and the University of Adelaide offered in-kind support to the project.

Acknowledgements. The authors are thankful to Professor Balwant Singh, the Editor-in-Chief of Soil Research, for inviting this contribution, and to the three anonymous reviewers for their constructive comments and suggestions for improving the quality of the manuscript. Authors are thankful to various publishers for permitting the use of copyright material.

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