A critical analysis of published data to discern the role of soil and sediment properties in determining sorption of per and polyfluoroalkyl substances (PFASs)

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HIGHLIGHTS
• Significant relationships between $K_d$ values and OC for some PFASs, but generally $R^2 < 0.40$.
• Strong relationships between $K_d$ values and OC and pH for 9 PFASs with $R^2 > 0.60$.
• Field based $K_d$ values were always larger than those measured in laboratory by batch method.
• Lack of full characterisation of sorbent properties is limiting the utility of literature data.

GRAPHICAL ABSTRACT

ABSTRACT

Widespread usage of per- and polyfluoroalkyl substances (PFASs) has caused major environmental contamination globally. The hydrophilic and hydrophobic properties of PFASs affect the sorption behaviour and suggest organic carbon may not be the only factor affecting sorption. We reviewed the quality of all data published in peer-reviewed literature on sorption of PFASs to critically evaluate the role organic carbon (OC) and other properties have in sorption of PFASs in soils or sediments. The largest data sets available were for perfluorooctanoic acid (PFOA, n = 147) and perfluorooctane sulfonic acid (PFOS, n = 178), and these analyses showed very weak correlations between sorption coefficient ($K_d$) and OC alone ($R^2 = 0.05$–$0.07$). When only laboratory-derived $K_d$ values of PFASs and OC were analysed, the $R^2$ values increased for PFOA ($R^2 = 0.24$, n = 42), PFOS ($R^2 = 0.38$, n = 69), perfluorononanoic acid (PFNA, $R^2 = 0.77$, n = 12), and perfluorodecanoic acid (PFDA, $R^2 = 0.78$, n = 13). However, the relationships were heavily skewed by one or two high OC values. Similarly, there was no significant relationship between $K_d$ values and pH for PFOS ($R^2 = 0.06$) and PFOA ($R^2 = 0.07$), across a range of environmental pH values. Our analyses showed sorption behaviour of a range of PFASs could not be explained by a single soil or sediment property. Multiple regression models better explained the sorption behaviour of a number of PFASs. Regressions of OC and pH together explained a significant proportion of the variation in $K_d$ values for 9 out of 14 PFASs and 8 of these regressions had ≥10 data points. This review highlighted that at least OC, pH and...
1. Introduction

Per- and polyfluoroalkyl substances (PFASs) were first developed in the late 1940s. A comprehensive definition of PFASs is given in Buck et al. (2011). They are aliphatic substances characterised by a partial or fully fluorinated alkyl chain and a terminal functional group (such as carboxylates, sulfonates, sulphonamides, phosphonates and alcohols) (Buck et al., 2011; Ding and Peijnenburg, 2013). A summary of structures and selected properties of PFASs reviewed is given in Supplementary material, Table S1 and the terminology used throughout is that defined in Bous et al. (2011). They found widespread applications in industry due to their unique chemistry of having both hydrophilic and hydrophobic (surfactant-like) properties. Consequently, these compounds have been produced and emitted into the environment for over 50 years (Houde et al., 2011). However, concerns about these chemicals have been growing due to their long-term persistence in the environment, potential for bioaccumulation and toxicity to human and ecological health (Giesy and Kannan, 2001; Higgins et al., 2007; Pan and You, 2010). A range of PFASs have been detected in humans, fish and wildlife world-wide (Giesy and Kannan, 2001; Houde et al., 2011; Kraft and Riess, 2015a; Kraft and Riess, 2015b), but the most common detections in wastewater treatment, fresh water and ground water systems have been of perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) (Boiteux et al., 2017; Chen et al., 2016; Lam et al., 2017; Loganathan et al., 2007; Wang et al., 2016; Yang et al., 2011). Concerns about environmental and toxicological impact of these chemicals led the 3M Company in 2000 to start phasing out production of PFOS, PFOA and related compounds (Ellefon, 2001; Kraft and Riess, 2015b). In addition, perfluoro-octanesulfonyl fluoride (PFOSF), PFOS and its salts have been added to Annex B of the Stockholm Convention on Persistent Organic Pollutants in May 2009 (UNEP, 2009).

Due to the hydrophobic and hydrophilic functionalities of these chemicals they are expected to behave differently from traditional non-ionisable organic pollutants (Renner, 2001; Villagrasa et al., 2006). There is a substantial body of literature of monitoring detections of PFASs in organisms, sediments and waterways but literature about the fate and behaviour of these chemicals in the environment is still limited. Some of the published studies on sorption behaviour of PFASs in soils and sediments draw conclusions based on a very limited set of data and therefore the role of certain soil/sediment properties (e.g. organic carbon, OC) has not been properly evaluated. So currently the environmental assessment of PFASs continues to be based on OC alone. The objective of this study was to (i) collate all available peer-reviewed data on sorption and associated soil/sediment properties, (ii) critically evaluate the quality of the data and choose the best available data for further analyses, and (iii) to establish the role of single and combinations of physico-chemical properties of soils and sediments in determining the sorption behaviour of PFASs. We believe such a critical study and synthesis is crucial for the development of a better understanding of the sorption behaviour of PFASs in soils/sediments. Details of the literature considered for this analysis is given in Supplementary material, Table S2.

2. Sources of PFASs

The surface-active properties of PFASs have made them widely used in stain- and water-resistant textiles, food packaging, fire-extinguishing formulations, pesticides, paints, personal care products and surfactant agents (Lau et al., 2007; Pevearudos et al., 2006). Consequently, the sources of PFASs are diverse and include point sources, such as industrial sites as well as diffuse sources, such as agricultural land uses where pesticides have been applied or where recycled wastewater has been used for irrigation (Clara et al., 2008; Plumlee et al, 2012; Tsai et al., 2002; Xie et al., 2013; Zareitalabad et al., 2013). Since these chemicals can act as low-viscosity vapour sealants to inhibit combustion of jet fuel, they have been widely used for decades in the formulation of aqueous fire-fighting foams commonly employed for combating fires. Subsequently, they have been commonly detected in sediments and aqueous phases in many fire-fighting locations worldwide, such as fire-fighting training sites, airports, traffic accident sites, military sites...
and some mining industries (Arias et al., 2015; Barzen-Hanson et al., 2017b; Favreau et al., 2017; Hale et al., 2017; Houtz et al., 2016; Munoz et al., 2017).

Emission through effluent from wastewater treatment plants (WWTPs) and transport to surface waters is also a possible pathway for PFASs (Clara et al., 2008). The importance of WWTPs and landfills as emission sources of PFASs has been documented worldwide (Alder and van der Voet, 2015; Arvaniti et al., 2012; Becker et al., 2010; Bossi et al., 2008; Campo et al., 2014; Chen et al., 2012; Chen et al., 2016; Chirikona et al., 2015; Filipovic and Berger, 2015; Kim et al., 2016; Loganathan et al., 2007; Sindiku et al., 2013; Subedi et al., 2014).

The increased control of production and usage of PFASs in some countries has led to a decline in levels of PFASs in the environment (Johansson et al., 2014; Hong et al., 2015; Ulrich et al., 2016). However, in other countries such as India and China, manufacturing of PFASs has increased in order to meet the growing demand for surfactants and other surface modification applications (Shan et al., 2015; Wang et al., 2015). It is conceivable that environmental dispersal of PFASs will continue to occur around the world in the foreseeable future.

3. Chemistry of PFASs

Excellent reviews of the physiochemical aspects of PFASs have been written previously (Ding and Peijnenburg, 2013; Ahrens and Bundschuh, 2014; Krafft and Riess, 2015b) and hence, their chemistry will only be briefly outlined here. An understanding of the chemistry of fluorinated surfactants must consider the three distinct structural aspects: (1) the hydrophobic “tail” that contains a high proportion of fluorine, (2) the hydrophilic group, and (3) the “spacer” organic group linking these two portions of the compound together (Buck et al., 2012). Replacing the hydrogen atoms by fluorine atoms in organic molecules conveyed a range of unique chemical properties that enabled this group of chemicals to be used for a diverse range of functions or uses that previously were not possible. Properties of these chemical include very high strength of the C–F bond, strong polarisation and greater hydrophobicity than alkyl chains of comparable length. The addition of other functional groups however has increased water solubility of these chemicals. Consequently, the functionalized fluorochromes has surfactant properties because of both hydrophobic and hydrophilic moieties (Ding and Peijnenburg, 2013; Krafft and Riess, 2015b). The key features of fluorinated surfactants 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., 2012).

4. Mechanism of sorption-desorption and their importance

A major factor controlling the fate and behaviour of chemicals in the environment is their phase partitioning behaviour such as sorption to soils and sediments. For example, sorption determines the removal, bio-availability, degradation, volatilisation and transport of organic chemicals in the environment (Weber and Miller, 1989). The sorption-desorption processes are dependent upon numerous factors including the physical and chemical properties of the chemical, the properties of the solid and solution phases that the chemical interacts with and the duration of interactions between the chemical and the sorbent phase.

One of the major sorption mechanisms for PFASs is electrostatic interaction. At environmental pH values these chemicals usually exist as anionic species due to their low pKₐ values (Burns et al., 2008; Vierke et al., 2013) and an electrostatic attraction can form between the negatively charged functional head of the PFASs and the positively charged surfaces of the adsorbents. For soils and sediments oxides provide positively charged surfaces for electrostatic interaction and these sorption sites would become increasingly important in variable charged soils. The presence of divalent cations has been found to act as a bridge between negatively charged surfaces of sorbents and negatively charged functional head of PFASs (Higgins and Luthy, 2006; Du et al., 2014). This has been found in studies where pH has been adjusted (discussed further in Section 4.2). In soils the mineral phase and organic matter contribute charged surfaces. Soil constituents usually carry both positive and negative charges and can contain both permanent- and variable-charge surfaces. The permanent-charges are fixed and are developed by isomorphous substitution of metal ions in the lattice structures of silicate clay minerals (Uehara and Gillman, 1980; Bolan et al., 1999). Variable charges in soils are developed through the dissociation of functional groups and these charges vary with solution pH, ionic strength and reactions with anions and cations. The C–F chains of these chemicals are also likely to be involved in hydrophobic interactions and in soils and sediments the organic matter can act as the hydrophobic fraction for sorption. Du et al. (2014) have reviewed the sorption behaviour of PFASs on a range of materials and illustrated the importance of various types of interactions with the solid phase and sorption mechanism in soils and sediments. The review concluded that the electrostatic and hydrophobic interactions are likely to be the dominant mechanisms of sorption of PFASs, while the hydrogen bonding and Van der Waals interactions are likely to be insignificant. Similarly, absence of conjugated groups makes π–π interactions of PFASs with soils or sediments are unlikely. A recent study (Barzen-Hanson et al., 2017b) concluded that for certain anionic, cationic and zwitterionic fluorotelomers (precursors that can be metabolized into, and degrade to PFASs) the sorption mechanisms are so complex that they cannot be predicted by bulk soil properties. The main soil/sediment components that are expected to control sorption behaviour and the published literature on the role of these factors on PFASs sorption are reviewed below.

4.1. Effect of organic carbon

Literature in 1960s and 1970s established that for typical non-ionic organic compounds soil organic matter serves as the principal sorbent phase (Goring, 1967; Lambert, 1968). Chiou et al. (1979) hypothesised that sorption by soil organic matter was essentially a phase partitioning process. Their work, and others, showed isotherms for neutral organic chemicals that were linear over a range of concentrations, indicating that for these chemicals the uptake was a process of partitioning rather than physical adsorption. The sorption of non-ionic chemicals was then assumed to be based only on the OC content of soil or sediments and led to the sorption coefficient (Kₛ) being normalized to the soil OC. This normalization is expressed as Kₛ = Kₒ/Kₒ, where Kₒ is the fraction of soil OC (Hamaker and Thompson, 1972). The Kₒ value has been used extensively in modelling behaviour of organic contaminants in soil and sediments but on a theoretical ground it is implied that organic matter behaves in the same way with the same thermodynamic characteristics for all soil types and that the adsorption isotherm is linear (Calvet, 1989). However, many studies since have established that not only OC content but the chemistry of OC has a strong bearing on sorption of most organic compounds and that the Kₒ approach is a highly simplified representation of sorption of even non-ionic organic compounds in soils and sediments (Ahmad et al., 2001; Wauchope et al., 2002).

As mentioned earlier, PFASs are atypical of organic compounds and encompass a range of complex hydrophobic, hydrophilic, surfactant type behaviour and surface active properties (Ding and Peijnenburg, 2013; Krafft and Riess, 2015b). A limited number of studies have considered sorption of PFASs on soils and sediments with the majority of studies focussing on PFOS (23 papers) and PFOA (16 papers). Some studies have found strong relationships between sorption of the PFASs and OC. For example, Higgins and Luthy (2006) found strong relationships (R² > 0.9, n = 5) between sorption of PFOS, PFNA (Perfluorononanoic acid), MeFOSAA (N-methyl perfluorooctane sulfonamidoacetic acid), PFOA (Perfluorooctanoic acid), PFDA (Perfluorodecanoic acid), PFUnDA (Perfluoroundecanoic acid), and ETFOSAA (N-ethyl...
perfluorooctane sulfonamidoacetic acid) and OC content for all chemicals except PFOA, where there were insufficient data for determining the relationship. Others have also found statistically significant relationships between sorption of PFASs and OC (Ahrens et al., 2011; Chen et al., 2012; Chen et al., 2013; You et al., 2010) but some of these studies have been limited by being conducted at a fixed pH of 7.0 (You et al., 2010) or by using only a small number of soils or sediments (Ahrens et al., 2011). In other cases the relationship was strongly skewed by one sediment with a high OC content and removal of this value resulted in a weaker and often insignificant relationship (Higgins and Luthy, 2006; You et al., 2010; Milinovic et al., 2015).

However, numerous studies have observed that simple correlations with soil OC content do not hold for all systems. Becker et al. (2008) did not find a correlation of the PFASs content of the sediments to TOC, and suggested that sorption of PFOA and PFOS was partially controlled by electrostatics as well as other factors, such as the pH of water and sediment and water temperature. Pan and You (2010) found only a weak relationship between field-determined PFOS sorption values onto river sediments and TOC, Zhu et al. (2014) found significant correlations between OC content of the sediment and Kd values for PFNA, PFDA and PFHxS, but not for perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluorooctanoic acid (PFOS), PFOA, perfluoroundecanoic acid (PFUnDA), perfluorobutane sulfonic acid (PFBS) or PFOS. Kwadijk et al. (2010) similarly determined Kd values for PFNA, L-PFOA, PFNA, PFDA, PFBS, PFOS and L-PFOS based on field measurements of sediments and surface waters and only Kd values for PFOS and FPOA correlated significantly with OC content. So the published data about the relationship between sorption of PFASs and OC in sediments and soils is not consistent and there is a need to analyse the entire published dataset together.

### 4.1.1. Our findings based on entire set of literature data

Initially, an assessment of the quality of the literature data was made before inclusion within the collation and analysis. Details of the data assessed is given in Table S2 (Supplementary material). Some data were excluded from the assessment where the units for sorption coefficients were given as L/g and, when converted to L/kg for consistency, the data were found to be unusually high and inconsistent with the rest of the literature. Data for soils and sediments only were considered and the data for pure mineral phases or artificial soils were excluded. When pH was measured in the surface water (field measurement) it was not included in the analysis. In one manuscript, pH was only measured at point of zero charge and hence pH data could not be included for further analyses. In addition, data from column leaching experiments has also been excluded due to the dependence of Kd values from these studies on several factors including flow rate and the sediment depth at which samples were collected. For example, in Vierke et al. (2014) there was approximately a 0.5 to 93-fold difference in Kd values for several PFASs depending on whether the water sample was collected at 40 cm or 80 cm depth of the sediment column.

A collation of all the published sorption data for a range of PFASs and various soil and sediment properties found generally weak relationships between Kd values and OC. The simple regression relationships between literature Kd values for numerous PFASs and soil properties are given in Supplementary material, Table S3 and examples are shown in Fig. 1 for PFOS and Fig. 2 for PFNA. Significant (P < 0.05) relationships for chemicals with >10 data points were found between OC and Kd values for PFOS (n = 178) (Fig. 1), PFOA (n = 147), PFNA (n = 87) (Fig. 2), PFDA (n = 57), PFHpA (n = 54), PFHxA (n = 50) and FOSA (perfluorooctane sulphonamide) (n = 26). However, for all these relationships the R² values were ≤0.35, except for FOSA where R² = 0.70 (Supplementary material, Table S3). The relationship for PFNA (R² = 0.34) was highly significant (P < 0.001) but was heavily levered by a few very high OC and Kd values. Removal of these high values (OC > 10% and Kd > 100 L/kg) resulted in the relationship becoming insignificant (R² = 0.07) (Fig. 2). The strongest relationships (P < 0.001) were found between Kd values for PFUnDa, EtFOSAA and MeFOSAA and OC (R² ≥ 0.80, 0.87 and 0.98, respectively) but the sample size for each of these chemicals was very small (n ≤ 8) (Supplementary material, Table 2). Furthermore, the relationship between Kd values for EtFOSAA and MeFOSAA and OC was heavily levered by one high OC value (9.66%) and removal of this value resulted in the relationship not being significant (R² = 0.46 and 0.82, respectively) (Supplementary material, Table S3). The above observations are consistent with studies based on small datasets where correlations have been noted to be significant (e.g. Ahrens et al., 2011). When all the published data is considered together, OC content alone failed to explain the variation of sorption parameters of PFASs and suggested that other properties in addition to OC may play a significant role in governing sorption behaviour of these chemicals.
4.2. Effect of pH

The sorption of ionisable chemicals would be expected to be dependent upon a range of soil properties. For ionisable solutes sorption isotherms are dependent upon the pH of the aqueous solution and the saturating cation on the sorbent surface. Calvet (1989) discussed the effect of ionic composition on adsorption and the effects on sorption of PFASs are reviewed by Du et al. (2014). PFASs are weakly acidic chemicals and with increasing pH the proportion of anionic molecule increases resulting in decreased sorption (Calvet, 1989; Weber and Miller, 1989; Lee et al., 1990; Kah and Brown, 2006). In addition to the effect on the charge characteristics of the molecule, changes in pH can also affect the surface properties of the sorbent. As pH increases the average net surface charge on mineral particles becomes less positive (Johnson et al., 2007). Thus, any solution parameters such as pH or ionic strength would be expected to affect the sorption behaviour of any chemicals that are ionisable. Given the hydrophilicity of the sulfonate or carboxylate head groups of PFASs it would be expected that electrostatic effects will influence sorption (Higgins and Luthy, 2006; Du et al., 2014).

In addition, certain PFASs may be present in cationic, anionic or zwitter-ionic state and hence the electrostatic interactions sensitive to ambient pH are expected to be important. Higgins and Luthy (2006) found sorption of the anionic PFASs, PFDS, EtFOSAA, PFOS and PFNA, decreased with increasing pH (5.7 to 7.5). Johnson et al. (2007) found that as the pH increased the average surface charge on goethite and kaolinite became less positive and sorption of the anionic PFOS decreased due to stronger electrostatic repulsion (Du et al., 2014). You et al. (2010) studied PFOS sorption on one sediment at two pH values (7.0 and 8.0) and three different CaCl$_2$ concentrations. They found $K_d$ values almost doubled from 47.86 L/kg to 87.10 L/kg with increasing pH from 7 to 8. However, other studies have found only weak or no relationship between sorption and pH. For example, Milinovic et al. (2015) found no relationship between sorption of PFOS, PFOA and PFBS and pH for six sediments ranging in pH from 4.6 to 8.0. Kwadijk et al. (2013) found PFOS sorption increased from pH 4 to 6 but there was little difference in sorption values with further pH increases. More recently, Barzen-Hanson et al., (2017a) observed that $K_d$ of anionic 8:2 fluorotelomer sulfonic acid decreased with increasing pH but pH had no effect on sorption of 6:2 fluorotelomer sulfonic acid. Field-based determinations of $K_d$ values for PFOA, L-PFOA, PFNA, PFDeA, PFBS, PFOS and L-PFOS also showed no relationship between $K_d$ values and pH of the overlying water column (Kwadijk et al., 2010).

4.2.1. Our findings from the entire set of literature data

A collation of all the literature $K_d$ data and pH was more limited with datasets containing $>$15 points available only for PFOS, PFOA, PFNA and PFDA (Supplementary material, Table S3). The largest dataset available was for PFOS (n = 27) and PFOA (n = 36). There was no significant relationship for $K_d$ values and pH for PFOS (pH range 2.5 to 8.5, $R^2 = 0.06$, Fig. 3) or PFOA (pH range 4.5 to 10.0, $R^2 = 0.07$, Supplementary material, Table S3). After the initial assessment, the data from Zhang et al. (2012) and Li et al. (2011) were excluded because in these field studies pH was measured in the overlying surface water and was not the pH of the sediment. Even after the removal of this data the relationship of $K_d$ and pH was not significant for PFOS and PFOA. While the relationships between $K_d$ values and pH for EtFOSAA ($R^2 = 0.57$, n = 10), MeFOSAA ($R^2 = 0.67$, n = 10) and PFDS ($R^2 = 0.65$, n = 10) (Supplementary material, Table S3) were significant (P < 0.05) they were limited by small datasets.

4.2.2. Sorption of ionised and neutral species of PFASs

For chemicals that can be ionised, the solution pH affects the proportion of ionised and neutral species present. When the solution pH and $pK_a$ of the chemical are equal the proportion of the neutral and the charged species of the chemical are equal. As the pH decreases below the $pK_a$ of the chemical an increasing proportion of PFASs is in the neutral form and as the pH increases above the $pK_a$ of the chemical an increasing proportion of the chemical is in the anionic form. For most soils, the soil surface exhibits a net negative charge at environmentally relevant pH values. The theory and application of this approach to estimating soil-water distribution coefficients of ionic pesticides is well documented in Lee et al. (1990). The dominant sorption mechanism for hydrophobic, ionisable organic compounds depends on the degree of dissociation, which is a function of the soil-solution pH and the chemical's $pK_a$ value (Lee et al., 1990).

When it is assumed that only the neutral species are sorbed and that the OC of the sorbent predominantly determines sorption of the chemical, the sorption coefficient can be expressed as $K_{oc}$. However, Lee et al. (1990) proposed that sorption of ionisable organic chemicals may be better explained by accounting for the sorption of both the neutral
and ionised forms, as described by the equation:

$$K_{oc,p} = K_{oc,n} \delta_n + K_{oc} (1-\delta_n) \quad (1)$$

where the subscript p is the predicted value, n is the neutral form, and i is the ionised form.

$$\delta_n = \left(1 + 10^{pH - pK_a}\right)^{-1} \quad (2)$$

This approach was applied to those PFASs where there was a sufficiently large dataset of literature $K_d$ values and accompanying soil OC and pH data. The highest number of observations were available for PFOA ($n = 33$) and hence we tested the above theory on this compound.

The pKa values for PFASs in the literature are contentious, e.g. reported values of the pK$_a$ for PFOA range from 0.5 (Vierke et al., 2013) to 3.8 (Burns et al., 2008). The lower the pK$_a$, the lesser is its relevance to the ambient conditions in the environment. Therefore, for this analysis we used the highest reported value to assess if pH and OC combined would explain the sorption data available from the literature (generally above pH 4.5). Assuming pK$_a$ for PFOA as 3.8 (Burns et al., 2008) 50% of the chemical will be in a neutral form and 50% in charged form at solution pH of 3.8. At pH 5.8 over 95% of the chemical would be in an ionised form and in this situation the majority of the sorption would be controlled by ionic interactions with the sorbent. From Eq. (2) $\delta_n$ was calculated and the log $K_{oc}$ value at pH > 6.8 (where ~99.9% of PFOA would be in the ionised form) was calculated as the average log $K_{oc}$ value from available literature data. From Eq. (1) $K_{oc,p}$ was then calculated and the predicted log $K_{oc}$ value determined (Fig. 4). While there is no literature sorption data for pH values < 4.5 it can be seen that even when this approach is used the sorption data is still scattered around the predicted $K_{oc}$ value. If a lower literature pK$_a$ value for PFOA was used (i.e. 0.5, Vierke et al., 2013) the chemical would be fully dissociated under typical environmental conditions and the predicted $K_{oc}$ line would be shifted to the left in Fig. 5. This suggests that pH and OC together are also not sufficient to explain the sorption of PFASs.

4.3. Effect of index cations and ionic strength

The cations in solution, such as Ca$^{2+}$, Na$^+$, Mg$^{2+}$ and K$^+$, can also affect the sorption behaviour of PFASs. Higgins and Luthy (2006) studied the effect of Ca$^{2+}$ and Na$^+$ on sorption of anionic PFASs and found the average increase in log $K_d$ per unit [Ca$^{2+}$] was 0.36 ± 0.04. However, there was no significant increase in sorption of the PFASs studied with increasing concentrations of Na$^+$. They interpreted the effects of Ca$^{2+}$ on sorption as a reduction in the charge present on the organic matter. Similarly, Chen et al. (2012) found that PFOS sorption increased with increasing concentrations of Ca$^{2+}$ and Mg$^{2+}$, with a rate of change of approximately 0.50 and 0.52 log units per log unit [Ca$^{2+}$] and [Mg$^{2+}$], respectively. They found PFOS sorption increased by a factor of 2 with increasing Na$^+$ concentration but found no changes in sorption with increasing K$^+$. You et al. (2010) found sorption of PFOS increased by a factor of 3 as the CaCl$_2$ concentration increased from 0.005 mol/L to 0.5 mol/L at pH 7.0, and by a factor of 6 at pH 8.0. Chen et al. (2013) also observed increased sorption of PFOS and PFDA with increasing concentration of Ca$^{2+}$, and increased sorption of PFOS and PFOA with increasing concentration of Na$^+$. The increased sorption of the anionic PFOS with increased concentration of CaCl$_2$ has been attributed to the neutralization of the negative charge on the sediment surface and decreased electrostatic repulsion and the salting-out effect of the increased content of dissolved ions (You et al., 2010). The salting out effect occurs when the water molecule becomes more ordered and compressible in the presence of dissolved ions and the cavity volume available to accommodate the neutral solutes decreases (Turner and Rawling, 2001). Consequently, the aqueous solubility of organic chemicals was inversely related to the content of dissolved ions (You et al., 2010). Others have also described a mechanism where divalent cations, such as Ca$^{2+}$, Mg$^{2+}$ and Cu$^{2+}$, could form a bridge between the anionic functional groups in soil organic matter and the anionic organic pollutants (Hyun and Lee, 2005).

By contrast to other studies though Kwadijk et al. (2010) determined $K_d$ values for PFOA, L-PFOA, PFNA, PF'DCA, PFBS, PFOS and L-PFOS based on field measurements and found no relationship between $K_d$ values and Ca$^{2+}$. Hong et al. (2013) considered only salinity and found significant ($P < 0.001$) positive relationships between field-determined $K_d$ values for PFOA, PFDA, PF'DoDA, PFOS and PFDS and increasing salinity.

4.3.1. Our findings from the entire set of literature data

A collation of literature sorption data for PFOS and PFOA found no significant relationship with Ca$^{2+}$ ($R^2 = 0.11$, $n = 32$ and $R^2 = 0.14$, $n = 7$, respectively) and or with Na$^+$ ($R^2 = 0.05$, $n = 23$ and $R^2 = 0.08$, $n = 6$, respectively) (Supplementary material, Table S4). Significant ($P < 0.05$) regressions with Ca$^{2+}$ were only found for EtFOSAA ($R^2 = 0.71$, $n = 10$) and PFDS ($R^2 = 0.42$, $n = 10$). One difficulty experimentally with assessing the impact of ionic strength as noted by Higgins and Luthy (2006) is that variations in ionic strength can also
change pH, thus making it difficult to identify the role of individual parameters on sorption.

4.4. Effect of clay content, cation exchange capacity (CEC) or anion exchange capacity (AEC)

Given the importance of electrostatic interaction in the sorption of PFASs it would be expected that the soil components that carry a surface charge enabling electrostatic interaction, namely the mineral and OC fractions, would be important factors in the sorption process. While no studies in the literature have reported the surface charge characteristics of the soils or sediments used in the sorption studies of individual PFASs a small number of studies (4) have reported clay content. The absence of specific soil or sediment surface charge data being reported in the studies most likely reflects that the determination of this property is not a routine laboratory measurement and the majority of sorption studies have been conducted using soils from temperate regions that predominantly carry a net negative surface charge. A more routine laboratory measurement is CEC, which is a measure of the ability of the soil or sediment to exchange cations. Since PFASs exist as anionic compounds at environmental pH values an inverse relationship with CEC would be expected. The AEC of a soil measures the capacity of the soil to exchange anions which would be more relevant to explain sorption behaviour of PFASs, but this is not a routine chemical measurement and few studies reported this property.

4.4.1. Our findings from the entire set of literature data

While soils that carry a variable charge (and can potentially become positively charged under certain pH conditions) develop under intensive weathering in subtropical and tropical regions or from volcanic ash parent material (Qafoku et al., 2004) not all tropical soils will carry a variable charge. Six studies (Chen et al., 2013; Guello and Higgins, 2013; Miao et al., 2017; Milinovic et al., 2015; Pico et al., 2012; Zhang et al., 2012) had one or more soils from a tropical region or could potentially carry a variable charge but there was insufficient information from the published literature to include their surface charge characteristics in the assessment.

Only four studies (n = 32) included clay content in their description of soil properties and there were only four chemicals (PFBS, PFOA, PFOS and PFDA) with >10 data points (Table S4, Supplementary material). A significant (P < 0.05) relationship between K_d and % clay was found only for PFPeA (R^2 = 0.88, n = 6) but the sample size was extremely small. While clay content is not a measure of the surface charge of the soil it is an indication (along with OC content) of potential binding sites for electrostatic interaction. The CEC is a measure of the sorbents ability to sorb cations and an inverse relationship would be expected for the electrostatic interaction of these anionic substances and soil or sediment surfaces at environmental pH values. However, again very few studies reported CEC. A significant (P < 0.05) relationship was found only for PFBS sorption (R^2 = 0.73, n = 6). For PFOA, which had a decent data size (n = 18), CEC alone only accounted for 30% of the sorption variability (Supplementary material, Table S4).

The above shows that when various soil properties are considered individually in isolation the sorption behaviour of PFASs in soils and sediments cannot be explained satisfactorily. Often soil properties are dependent on each other and correlated. For example, it is common that soils with higher clay content will be richer in OC. Similarly CEC depends on organic matter content, clay content and pH. It is therefore prudent that the role of multiple soil/sediment properties is considered simultaneously to explain sorption behaviour, especially for PFASs given their complex chemistry.

5. Effect of multiple soil properties on sorption behaviour

Given the lack of relationships between sorption values for a range of PFASs and single properties of soils and sediments traditionally considered important for sorption (namely OC and pH), multiple regressions were conducted to determine whether several properties combined could explain the sorption data. While a more detailed statistical approach, such as principal component analysis (PCA), would have been ideal the data provided in the published studies on the soil or sediment properties were limited. For example, the largest dataset with 3 soil properties reported was 29 for PFOA (%OC, pH and %clay), followed by 18 for PFOA (%OC, pH and CEC). The largest dataset where 4 soil properties were reported was 9 for PFOS (%OC, pH, %clay and CEC). Hence, despite the attractiveness of the PCA approach, we could not use it for the available dataset.

A conceptual diagram (Fig. 6) depicts the range of possible sorption mechanisms for the main PFASs found environmentally (the carboxylic and sulfonic acids). Using the combined data (with ≥10 K_d values) from those studies that included both pH and OC for soils or sediments the results of multiple regressions are presented in Table 1. Statistically significant (P < 0.05) regressions were found for PFOS, PFOA, PFNA, PFDA, PFUnDA, PFDS, MeFOSAA, and EfFOSAA. Statistically significant (P < 0.05) regressions were also found for several chemicals but the dataset was limited (≤10), namely PFPeA, EfFOSAA, MeFOSAA and PFDS (Table 1).

There were even fewer studies that included pH and clay or CEC or AEC. Studies with ≥10 data points that included clay were only available for PFBS, PFOA, PFOS and PFDA, and that included CEC were only available for PFOS and PFOA. Significant (P < 0.05) multiple regressions were only found for regressions of K_d values for PFPeA with pH and clay, for PFOS with pH and CEC, and for PFOA, EfFOSAA and PFDS for pH and AEC. A greater number of chemicals had highly significant (P < 0.01) regressions when OC and % clay, or OC and CEC or OC and AEC were considered (Table S4, Supplementary material). Significant regressions between K_d values and OC and clay were found for PFOS, PFOA, MeFOSAA, PFNA, PFDA, PFUnDA and PFPeA (Table 1). Also, while the regressions were not statistically significant due to the small sample size high R^2 values (>0.9) were also found for K_d values of EfFOSAA and PFDS and OC and clay (Table 1). The limited number of values in the regression made statistical analysis difficult but these findings would suggest that consideration of clay content as well as OC and pH is likely to be crucial in explaining sorption behaviour of PFASs and should be further investigated. This also highlights that in future studies the full characterisation of both mineral and organic phases of sorbents need to be included to allow a more comprehensive assessment.

Significant (P < 0.05) relationships were also found between OC and Ca concentration in solution for PFOS, EfFOSAA, MeFOSAA, PFDS, PDfA and PFUnDA (Supplementary material, Table S6) but only PFOS had >10 data points (R^2 = 0.71, n = 28). Similarly strong relationships were found between OC and Na^+ for PFOS, EfFOSAA, MeFOSAA, PFDS, PFDA and PFUnDA and for OC and Mg^2+ for PFOS (Supplementary material, Table S5). However, again only PFOS had >10 data points. For PFOS the R^2 for the relationship between K_d values and OC and Na^+ was 0.76 (n = 19) and OC and Mg^2+ was 0.93 (n = 11). These latter relationships however, include parameters that are not solely soil or sediment properties which would make them less useful for deriving predictive properties.

Clearly, the limited amount of data currently available in literature that is amenable to multiple regression precludes the development of any meaningful multiple regression model to elucidate the combined role of soils/sediments properties in PFASs sorption. However, the significant relationships between K_d values for several PFASs and OC, pH and clay suggests that they together better explain sorption behaviour than OC alone.

6. Comparison of field- and laboratory-derived K_d values for single soil properties

Some studies have derived K_d values using the ratio of concentration of chemicals in sediments and concentrations in overlying water
columns collected in the field. Others have used traditional laboratory, batch sorption studies to determine \( K_d \) values. For PFOS, PFOA, PFNA and PFDA, \( K_d \) values determined using field-derived data are consistently higher than those determined using laboratory-derived data. The median values of log \( K_d \) for the four compounds for field-derived data were 1.6, 4.0, 1.9 and 1.7 times higher, respectively, compared with the median values of laboratory-derived data (Fig. 5).

When only field-derived data were considered, significant relationships \( (P < 0.05) \) between \( K_d \) and OC were found for PFBA, PFPeA, PFHxS, PFHxA, PFHpA, PFOA, PFNA and PFDA (\( R^2 = 0.11, 0.17, 0.09, 0.22, 0.05, 0.34 \) and 0.45, respectively) (Supplementary material, Table S6) but the amount of variance that could be explained by OC alone was low as indicated by the low \( R^2 \) values. When only the laboratory-derived \( K_d \) values were considered, for those chemicals where there were >10 data points, significant \( (P < 0.05) \) regressions between \( K_d \) and OC were found for PFOS (\( R^2 = 0.38, n = 69 \)), PFOA (\( R^2 = 0.24, n = 42 \)), PFNA (\( R^2 = 0.77, n = 12 \)) and PFDA (\( R^2 = 0.78, n = 13 \)). For all four chemicals however, the relationships were heavily levered by one or two high OC values and removal of these high values resulted in the relationship being insignificant (Supplementary material, Table S6).

The OECD 106 standard protocol for the adsorption – desorption of chemicals (OECD, 2000) requires an equilibrium period of 24 h. A problem with using field measurements to derive \( K_d \) values is that the concentration of the chemical in the water column is potentially continually changing with water flow and equilibrium may not have been achieved. In addition, as well as varying temporally the concentration in the water column can also vary spatially depending upon sample depth. For example, Ahrens et al. (2010) showed at one location the PFBA concentration (the most abundant PFASs in their study) in water ranged from about 15 to 22 ng/L with water collected at 0.5 m, 6 m and 11 m depth but at a second location the concentration in water

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**Table 1**

<table>
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<tr>
<th>Chemical</th>
<th>Carbon chain length</th>
<th>OC and pH</th>
<th>Significance</th>
<th>( R^2 )</th>
<th>OC and % clay</th>
<th>Significance</th>
<th>( R^2 )</th>
<th>OC and pH and % clay</th>
<th>Significance</th>
<th>( R^2 )</th>
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<td>6</td>
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<td>0.50</td>
<td>NS</td>
<td>11</td>
<td>0.59</td>
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<td>*</td>
<td>6</td>
<td>0.91</td>
<td>*</td>
<td>6</td>
<td>0.91</td>
<td>NS</td>
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<td>NS</td>
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<td>0.99</td>
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<tr>
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<td>12</td>
<td>0.92</td>
<td>**</td>
<td>7</td>
<td>0.93</td>
<td>*</td>
<td>7</td>
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</tbody>
</table>

NS = not significant.

* \( P < 0.05 \).

** \( P < 0.01 \).

*** \( P < 0.001 \).
was 20 ng/L at 0.5 m, 15 ng/L at 10 m and approximately 9 ng/L at 20 m depth, which is a 2.2 fold difference depending upon sampling depth. This variation in the value for the concentration in water (the numerator in the calculation of K_d) will affect the final value obtained. The same trend was also seen for PFOA and PFNA, the next most abundant PFASs analysed in their study. This would indicate concentrations can vary depending upon sampling depth of water column which is an additional factor in the field-derived values. Often the depth of sediment sampling was not given but sediment properties would also expect to change with sampling depth and hence affect the field-derived K_d values. An additional issue for comparing field- and laboratory-derived K_d values is that under laboratory conditions the contact time for the sorption interactions between the chemical and the sorbent is usually short (only a few days) while in the field the contact time is unknown but often much longer. Therefore field ageing may be an important factor that should be kept in mind while comparing the field- and laboratory-based data.

7. Knowledge gaps

This review has highlighted that the behaviour of PFASs in the environment is more complex than can be explained by a single soil or sediment property and it is not appropriate to express the sorption behaviour of these chemicals normalized over the OC content of the sorbent (K_OC). An assessment of the published data has shown that neither OC, pH nor clay content alone could explain the sorption behaviour of the PFASs. This is consistent with recent findings on sorption mechanisms of certain fluorotelomers, where Barzen-Hanson et al. (2017b) concluded that given the complexity, their sorption could not be predicted by bulk soil properties. Further work is required to assess a wider range of soils across a broader spectrum of OC, clay and pH values to determine whether the significant relationships suggested from the multiple regression of the collated data will be relevant. A large amount of published data could not be used in multiple regression assessment due to lack of adequate characterisation of the soil or sediment. For example, the greatest dataset for sorption values was available for PFOS (n = 178) and there was OC data for all these K_d values but of these only 27 sorbents had pH values. A conspicuous lack in the additional issue for comparing field- and laboratory-derived K_d values is that under laboratory conditions the contact time for the sorption interactions between the chemical and the sorbent is usually short (only a few days) while in the field the contact time is unknown but often much longer. Therefore field ageing may be an important factor that should be kept in mind while comparing the field- and laboratory-based data.

such an assessment is crucial for development of a multivariate sorption model.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2018.01.167.

References


