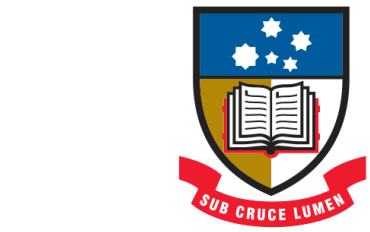

THE UNIVERSITY of ADELAIDE

Fate and Bioavailability of Per- and Poly-Fluorinated Substances (PFASs) in Soils

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Table of contents

Thesis abstract

Per- and poly-fluorinated substances (PFASs) are a group of compounds with similar structures and have a unique set of properties which make them resistant to biodegradation, available to bioaccumulate, and potentially toxic to many organisms in the environment. Yet there is currently limited information on the fate and bioavailability of PFASs in the soil environment. The thesis investigates the sorption and bioavailability of three commonly reported perfluoroalkyl acids (PFAAs) in a wide range of soils with varying properties and determines if sorption coefficients and bioaccumulation can be predicted from soil properties and are affected by residence time in soil.

Preliminary studies found that sorption of ^{14}C-perfluoroocatanioc acid (PFOA) was considerable on common laboratory consumables, e.g. centrifuge tubes and syringe filters. In contrast to reports in the literature, sorption losses on polypropylene tubes were found to be significantly higher than on glass tubes. Sorption losses were also significant using syringe filter membranes. This highlights that significant errors can occur, creating analytical bias during routine laboratory procedures.

Sorption (K_d) of perfluorooctane sulphonic acid (PFOS), ^{14}C-PFOA and perfluorohexane sulphonic acid (PFHxS) was investigated in a wide range of Australian soils with varying properties. Modelling was conducted to determine if soil properties could predict sorption coefficients using two modelling strategies: multiple linear regression (MLR) using traditional laboratory chemical analyses of soils; and diffuse reflectance Fourier transform mid-infrared spectroscopy coupled to partial least squares regression (DRIFT-PLSR). The sorption coefficients for all three compounds were at the lower end of the ranges previously reported, perhaps due to the low amounts of organic carbon (OC) and alkaline pH of many Australian soils. The retention of PFOA was weak in all soils, but even more so in subsoils, indicating that PFOA could easily be leached through surface- and sub-soil horizons into ground-waters. The retention of PFOS and PFHxS was not affected by soil depth. The sorption of all three PFAAs was influenced by their structural differences and different soil properties. The sorption of PFOA was positively affected by OC and silt-plus-clay content, PFOS sorption was positively correlated to OC content and negatively correlated to pH and PFHxS sorption was positively correlated to OC content, clay content and concentrations of exchangeable cations. DRIFT-PLSR modelling indicated that soils dominated with quartz and pyrophyllite minerals had a low affinity for PFOA sorption. The DRIFT-PLSR modelling of PFOS and PFHxS sorption was unreliable, likely due to the low and narrow range of K_d values found. For PFOA modelling, similar results were found between the MLR and DRIFT-PLSR modelling strategies which suggested that DRIFT-PLSR could be used as a quicker and cheaper technique to predict sorption compared to traditional laboratory analyses of soil coupled with MLR.

The aging and bioavailability of the same three PFAAs was investigated in 20 soils varying in physicochemical properties. The soils were spiked with PFOS, PFOA and PFHxS and incubated for up to six-months. A second batch of soils was spiked with the same compounds at the same rate creating 'aged' and 'freshly spiked' soil treatments. These soils were planted with *Phaseolus vulgaris* seeds and uptake of the PFAAs into plant shoots was determined. Over the six-month incubation period sampling of porewater was also conducted. Concentrations of the three PFAAs in soil porewater and in plant tissues did not significantly and consistently change (p >0.05) with increasing time of soil contact with the PFAAs. This indicates that significant aging of PFAAs does not occur in soils, a behaviour unlike other persistent organic pollutants (POPs) e.g. polyaromatic hydrocarbons. The sorption affinity of all three PFAAs in these soils was PFHxS<PFOA<PFOS and the inverse relationship was observed for bioaccumulation factors (BAFs) in bean plants, PFHxS>PFOA>PFOS, indicating that PFASs with low sorption have a greater potential to bioaccumulate in terrestrial plants. The lack of any significant effect of time of soil:chemical contact on partitioning or bioavailability to plants indicates that these chemicals are not only resistant to degradation but will remain bioavailable over time, unlike other POPs.

The results of this thesis show that while the sorption and bioavailability of PFASs in soils are affected by both soil properties and type of PFAS present, they are not affected by time of residence in soil. These data have the potential to be used by regulators to better manage contaminated soils and the risk assessment of any further contamination from those sites into surface- or ground-waters or the uptake by plants.

Declaration

I Emma Knight, certify that this work contains no material which has been accepted for the award of any other degree or diploma in my name, in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text.

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I acknowledge the support I have received for my research through the provision of an Australian Government Research Training Program Scholarship.

Emma Knight

Date 05/04/2020

List of publications

Publications arising from this thesis

1. Knight ER, Janik LJ, Navarro DA, Kookana RS, McLaughlin MJ. 2019. Predicting partitioning of radiolabelled ^{14}C-PFOA in a range of soils using diffuse reflectance infrared spectroscopy. *Science of the Total Environment* **686**, 505-13.

2. Lath S, Knight ER, Navarro DA, Kookana RS, McLaughlin MJ. 2019. Sorption of PFOA onto different laboratory materials: Filter membranes and centrifuge tubes. *Chemosphere* **222**, 671-8.

3. Knight ER, Bräunig J, Janik LJ, Navarro DA, Kookana RS, Mueller J, McLaughlin MJ. 2019. An investigation into the long-term binding and uptake of PFOS, PFOA and PFHxS in soil-plant systems. *(Submitted and revised in the Journal of Hazardous Materials).*

Conference proceedings

1. Knight ER, Janik L, Navarro D, Kookana RS, McLaughlin MJ. 2018. Oral presentation: The sorption of perfluorooctanoic acid (PFOA) and perfluorohexane sulphonate (PFHxS) in Australian soils. *What's in our Water (WiOW) Symposium. Emerging Contaminants in the Environment*. 29-31 October. Canberra, Australia.

2. Knight ER, Janik L, Navarro D, Kookana RS, McLaughlin MJ. 2018. Poster presentation: The sorption of perfluorooctanoic acid (PFOA) in Australian soils. *The Eleventh International Conference on Remediation of Chlorinated and Recalcitrant Compounds*. 8-12 April. Palm Springs, United States of America.

3. Knight ER, Janik L, Navarro D, Kookana RS, McLaughlin MJ. 2017. Oral presentation: The sorption of PFOA in Australian soils. *Society of Environmental Toxicology and Chemistry (SETAC) Australasia Conference. The Role of Environmental Toxicology and Chemistry in a Changing Environment*. 4-6 September. Gold Coast, Australia.

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Structure of thesis

The chapters in this thesis are presented as a combination of published papers, manuscripts prepared for submission or unpublished works written in manuscript style. In addition are introductory and summary chapters that will not be submitted for publication.

Chapter 1 provides an introduction and overview of the current literature on the sorption, uptake and bioavailability of perfluoroalkyl substances (PFASs) in soil – plant systems. The research gaps are highlighted in this chapter and includes the aims of this thesis.

Chapter 2 comprises work that has been published in *Chemosphere*. By using radiolabelled carbon-14-perfluorooctanoic acid (PFOA) this paper draws attention to the PFAS -analytical errors and biases that can occur due to sorption losses to regular laboratory materials, such as plastic and glass tubes and syringe filter membranes. The paper has been formatted as such to maintain consistency with the other chapters in this thesis.

Chapter 3 comprises of a paper that has been published in *Science of the Total Environment*. It investigates the sorption (K_d) of radiolabelled ^{14}C-PFOA in 100 Australian soils. The soil properties and soil spectra were modelled against measured sorption coefficients to assess which soil properties were influencing the sorption of PFOA the greatest. The paper has been formatted as such to maintain consistency with the other chapters in this thesis.

Chapter 4 comprises of work that investigates the sorption (K_d) of perfluorooctane sulphonic acid (PFOS) and perfluorohexane sulphonic acid (PFHxS) in 172 Australian soils. In a similar way to Chapter 3, the soil properties and soil spectra were modelled against sorption coefficients to assess which soil properties were influencing sorption the greatest.

Chapter 5 comprises of work that is being prepared for submission to *Science of the Total Environment*. This chapter investigates the long-term binding and bioaccumulation of three PFASs (PFOS, PFOA and PFHxS) in 20 different soils over a six-month time period. The sorption (K_d) and bioaccumulation factors (BAFs) are modelled with soil properties and soil spectra to understand which soil properties are influencing sorption and bioaccumulation the greatest.

Chapter 6 comprises a summary of the outcomes from the chapters in this thesis and the recommendations for future research in this field.

Chapter 1. Introduction and Literature Review

1. Introduction

Per- and poly-fluorinated substances (PFASs) are a large group of similarly structured compounds that have been in use globally for several decades, and this has led to an accumulation of these substances in the environment. It has become apparent over the last two decades that these chemicals pose a risk to humans, animals and the environment (Shi et al. 2008, Hu et al. 2011, DeWitt et al. 2012). The PFASs, along with their precursor compounds, are ubiquitous in the environment from frequently being used in aqueous film forming foams (AFFFs) and in the manufacturing processes for flame- and water-resistant clothes, carpets and textiles and non-stick frying pans (Richardson and Kimura 2015). Their persistence, bioaccumulative nature, mobility and potential toxicity have meant that the two most detected PFASs, perfluorooctanoic acid (PFOA) and perfluorooctane sulphonic acid (PFOS), have been placed on the Stockholm Convention's list of persistent organic pollutants (POPs). This Convention is a global treaty that aims to protect human health and the environment from POPs that do not degrade easily, have become widespread and accumulate in tissues. Once on the Convention's list, action is taken to reduce, eliminate and/or prohibit the use of those POPs and therefore reduce environmental contamination. In the United States, the phase out of PFOS began in the early 2000s. The 3M company, a major producer of PFAAs in their weather proofing product for clothes, Scotchgard™, voluntarily chose to phase out the use of PFOS in their manufacturing processes in 2000 (USEPA 2000, Weppner 2000). Prior to, and after the announcement of the phase out, there has been a focus on understanding the fate and potential effects of these compounds on human and environmental health, especially as concentrations of these compounds are found in a wide range of matrices; human blood serums, soils, the atmosphere and waterways (Moody and Field 2000, Llorca et al. 2012, Cousins et al. 2016, Brusseau et al. 2020).

2. Chemical structure and formation

Perfluoroalkyl acids (PFAAs) are a subset of PFASs and have a carbon (C) atoms that are fully saturated with fluorine (F) atoms and a functional group attached at one end of the C-F chain. The chemical structure means that they have affinity with both hydrophilic and hydrophobic substrates and have an amphiphilic nature which also leads to their persistence and mobility within the environment (Figure 1 and Table 1).

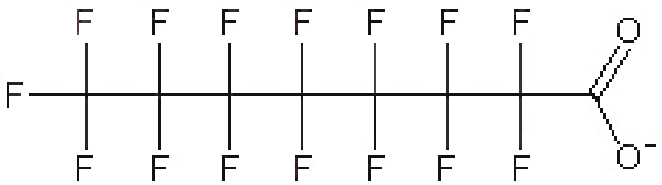

Figure 1: Chemical structure of perfluorooctanoic acid (PFOA).

These man-made substances can be formed by two manufacturing processes; electrochemical fluorination and telomerisation (Houde et al. 2006, Fujii et al. 2007). Electrochemical fluorination is where an electric current displaces hydrogen atoms (H) from a hydrocarbon with F atoms (Hekster et al. 2003). The process was used to produce perfluorooctane sulphonyl fluoride (PFOSF) products including linear and branched isomers and short chain impurities (Hagen et al. 1981). PFOSF was used to generate perfluoroalkyl sulphonamide alcohols which are known to degrade through both biotransformation and abiotic oxidation (Xu et al. 2004, D'Eon et al. 2006) into perfluoroalkyl sulphonic acids (PFSAs). Both PFOS and perfluorohexane sulphonic acid (PFHxS) are examples of perfluorosulphonic acids (PFSAs) (Houde et al. 2006). The second process, telomerisation, is where pentafluoro-iodoethane is reacted with tetrafluoroethylene compounds to produce a mix of perfluoroalkyl iodides (Schultz et al. 2003). These iodides are then used to make a selection of telomer products including fluorotelomer alcohols (FTOHs) (Schultz et al. 2003). The FTOHs can easily be converted into fluorotelomer carboxylic acids (FTCAs) and perfluorocarboxylates (PFCAs); including PFOA (Hagen et al. 1981, Schultz et al. 2003, Dinglasan et al. 2004) (Figure 1). The physico-chemical properties of PFOA, PFHxS and PFOS, can be found in Table 1. It is important to note that all three PFAAs in most environmental conditions are in an anionic form, inferred from their low proton dissociation constants (pKa) (Table 1).

Table 1: The physico-chemical properties of the PFAAs; PFOA, PFOS and PFHxS.

Characteristics	**PFOA**	**PFOS**	**PFHxS**
Chemical formula	$C_8HF_{15}O_2$	$C_8HF_{17}O_3$	$C_6HF_{13}O_3S$
Molecular weight (g/mol)	414.07	500.13	400.11
Solubility in water (mg/L)	Limited*	Limited*	Limited*
Speciation (pKa)	0, 1.5, 3.8[a], 2.8[b], 2.8[c]	-3.27[d]	0.14[e]

[a](Goss 2007), [b](Burns et al. 2008), [c](Brace 1962), (López-Fontán et al. 2005, Kutsuna and Hori 2008), [d]Calculated value from ACD/I-Lab Web Service (Brooke et al. 2004), [e]Calculated values from the SPARC calculator (Hilal et al. 1995, Steinle-Darling and Reinhard 2008), *based on experimental observations using technical grade powders.

3. Behaviour in the environment

The behaviour of PFASs in the environment is expected to be dependent on several factors, including the PFAS species and their concentrations as well as the surrounding environment's geological features, including soil type and chemical characteristics. For instance, highly contaminated sites such as fire-fighting training grounds (FFTGs) or manufacturing sites will have greater amounts of PFAA run-off and leaching than other sites. Therefore, it is important to better understand how PFAAs behave once they are in the environment, especially as the use of PFAAs in manufacturing processes are being removed and replaced by other similar, usually shorter chain length, more bioaccumulative PFAAs (Weppner 2000, Sánchez et al. 2011, Wang et al. 2013). In Australia, highly contaminated sites include FFTGs and defence sites, as no manufacturing of PFAAs has occurred in Australia (Wang et al. 2014). However, the phasing out of PFAAs in industry and banning the use of PFAA products, for example in South Australia and Queensland, including those in AFFFs, means that there will be lower direct emissions of PFAAs into the environment. However, the persistent nature of PFAAs means they are still present in the environment long after use is discontinued, further indicating that understanding how these chemicals behave once in the soil environment is important. Current studies have investigated many different sorption and partitioning aspects, predominately in sediments and aqueous environments, but there is still limited information on these aspects in soils (Wang et al. 2011, Milinovic et al. 2015).

3.1 Sorption

Sorption of PFAAs in soils and sediments is complex due to a number of physico-chemical characteristics of both PFAAs and soils, including; PFAA functional group; length of the C-chain, octanol-water partitioning coefficient (K_{ow}) and different soil properties including; organic carbon (OC), pH and clay content (Higgins and Luthy 2006, Li et al. 2018). For instance, the K_{ow} describes a partitioning ratio of the measured concentration of a substance in either the hydrophilic (water) or hydrophobic (octanol) phases (Equation 1).

$$K_{ow} = \frac{[C_{octanol}]}{[C_{water}]} \quad (1)$$

The higher the K_{ow} value the more attracted the substance is to octanol, while a lower value indicates a hydrophilic interaction. However, the use of the K_{ow} for PFAAs to determine their fate in the environment is uncertain due to the film forming properties of these compounds which prevents the use of standard methods to measure the K_{ow} (Giesy et al. 2006, Houde et al. 2006, Krafft and Riess 2015). The reason for this could be due to the surface properties of the compounds making

assessment of the K_{ow} impractical as the PFAA does not separate like other substances and instead forms a third layer (OECD 2002, Brooke et al. 2004).

Other parameters are necessary for determining the fate of PFAAs in the soil environment, such as the soil-water partitioning coefficient (K_d) (Equation 2) and OC-normalised soil-water partitioning coefficient (K_{oc}) (Equation 3) (Ahrens et al. 2011). The K_{oc} is where the K_d is divided by the OC content in the soil, meaning the K_d is normalised to the total OC content in the soil to give the K_{oc}. This normalisation is predominantly based on OC being the main driver of sorption of hydrophobic organic compounds. Both the K_d and the K_{oc} follow the same relationship as the K_{ow}; low values represent high mobility while high values represent low mobility (Ahrens et al. 2011). There is a limited number of reported equilibrium parameters for PFAAs in the literature for soils and sediments and, of those, the K_d values vary by approximately two orders of magnitude; Log K_d values -0.7–120 L/kg for PFOS and -1.16–0.96 L/kg for PFOA, as found in a review article of sorption coefficients for PFOS and PFOA by (Zareitalabad et al. 2013) (Table 2) (Johnson et al. 2007, Ferrey et al. 2009, Ahrens et al. 2011, Zareitalabad et al. 2013, Milinovic et al. 2015).

$$K_d = \frac{[C_{soil}]}{[C_{water}]} \quad (2)$$

$$K_{OC} = \frac{[K_d]}{[OC_{content\,\%}]} \quad (3)$$

The variation in reported K_d values indicates that there are numerous factors influencing the sorption behaviour of PFAAs in soils (Milinovic et al. 2015). In contrast, the mean Log K_{oc} values in the literature for PFOS and PFOA are quite similar, 3.0 and 2.8 with coefficient of variations of 21% and 32%, respectively, which indicates that at least some of the variation observed in K_d values is due to varying soil properties (Table 2) (Zareitalabad et al. 2013). It should be noted that the K_{oc} has been widely used to describe partitioning of PFAAs in water and sediments (Higgins and Luthy 2006, Chen et al. 2009, Ahrens et al. 2011, Li et al. 2012) as well as for many other organic contaminants, including polycyclic aromatic hydrocarbons (PAHs), like naphthalene (Xing 1997, Hawthorne et al. 2006) due to the greater sorption observed with soils with higher OC content. For instance, research by Ahrens et al. (2011) indicated that sorption of PFOA, PFOS, and perfluorooctane sulphonamide (PFOSA) to sediments was lower in sandy sediments with a low OC fraction (f_{oc}) than those with less sandy sediments with higher f_{oc}s. However, there is debate as to whether the K_{oc} is a useful predictor of sorption of ionic or ionisable PFAAs to organic matter because it does not account for specific polar interactions of the charged compounds within a complex matrix. It has therefore been suggested that it is more reasonable to use K_d values rather than K_{oc} values (Giesy et al. 2006, Xiao 2015). More recently, a review article using published sorption data by Li et al. (2018) found that OC

content alone could explain only approximately 5% or 7% of the variation of sorption of PFOA and PFOS in soils, respectively. This finding also suggests that there are potentially a range of soil properties, as well as OC content, that are influencing the sorption of PFAAs to soil.

Table 2: Equilibrium parameters of the PFAAs, PFOA and PFOS in soil or sediment matrices from different countries found in the published literature. Table reprinted from Chemosphere, Vol 91, Zareitalabad, P., J. Siemens, M. Hamer, and W. Amelung, Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) in surface waters, sediments, soils and wastewater–a review on concentrations and distribution coefficients, Pages No., 725-732, Copyright (2013), with permission from Elsevier.

Sample	$\log K_d$ ($\log l\ kg^{-1}$)	$\log K_{OC}$	References
PFOS			
Five sediments with C_{org} of 0.56–9.66%, dithionite–citrate–bicarbonate extractable iron of 116–1025 μmol/g	–	2.7	Higgins and Luthy (2006)
Ottawa sand standard	2.81	–	Johnson et al. (2007)
Kaolinite	5.31	2.4	Johnson et al. (2007)
Goethite	7.88	–	Johnson et al. (2007)
High iron sand standard	8.90	–	Johnson et al. (2007)
Lake Michigan sediment	7.52	2.4–2.6	Johnson et al. (2007)
Clay	18.3	2.8	3 M corp. cited in Johnson et al. (2007)
Clay loam	9.72	2.6	3 M corp. cited in Johnson et al. (2007)
Sandy loam	35.3	3.1	3 M corp. cited in Johnson et al. (2007)
River sediment	7.42	2.8	3 M corp. cited in Johnson et al. (2007)
Water treatment sludge	120	2.5	3 M corp. cited in Johnson et al. (2007)
Paddy soil (0.91% C_{org}) at c(water) = 5.0 $\mu g\ l^{-1}$	–	3.3	Chen et al. (2009)
Crude oil spiked to soil	–	4.2–4.4	Chen et al. (2009)
Oil-derived black carbon (diesel soot), c(water) = 5–50 $\mu g\ l^{-1}$ at pH = 5.05	–	3.0–3.1	Chen et al. (2009)
Aquifer sediment Washington County, USA (t = 0)	0.1	2.5	Ferrey et al. (2009)
Aquifer sediment Washington County (t = 574 d)	−0.7	2.8	Ferrey et al. (2009)
Taihu Lake	–	2.9 ± 0.6	Yang et al. (2011)
Sediment 1	1.2	4.7	Ahrens et al. (2011)
Sediment 2	1.2	3.0	Ahrens et al. (2011)
Sediment 3	1.9	3.8	Ahrens et al. (2011)
Average PFOS ($\log l\ kg^{-1}$)		3.0	
Standard deviation PFOS ($\log l\ kg^{-1}$)		0.7	
Coefficient of variation PFOS (%)		21	
Median PFOS ($\log l\ kg^{-1}$)		2.8	
PFOA			
Five sediments with C_{org} of 0.56–9.66%, dithionite-citrate-bicarbonate extractable iron of 116–1025 μmol/g	–	2.1	Higgins and Luthy (2006)
Aquifer sediment Washington County, Minn., USA (t = 0)	−0.01	3.5	Ferrey et al. (2009)
Aquifer sediment Washington County (t = 574 d)	−1.16	2.3	Ferrey et al. (2009)
Sediment 1	0.96	4.5	Ahrens et al. (2011)
Sediment 2	0.67	2.5	Ahrens et al. (2011)
Liao river sediment	–	2.3 ± 0.4	Yang et al. (2011)
Taihu Lake sediment	–	2.3 ± 0.6	Yang et al. (2011)
Yangtse sediment CQ	−0.77	1.5	Li et al. (2012)
Yangtse sediment ZG	−0.62	1.4	Li et al. (2012)
Yangtse sediment WH	−0.72	1.3	Li et al. (2012)
Yangtse sediment NJ	−0.89	1.3	Li et al. (2012)
Yangtse sediment CMW	−0.82	1.3	Li et al. (2012)
Yangtse sediment CME	−0.92	1.6	Li et al. (2012)
Average PFOA ($\log l\ kg^{-1}$)	–	2.1(2.8)	
Standard deviation PFOA ($\log l\ kg^{-1}$)	–	1.0(0.9)	
Coefficient of variation PFOA (%)	–	45(32)	
Median PFOA ($\log l\ kg^{-1}$)	–	2.1(2.3)	

Values in brackets excluding values of Li et al. (2012).

Sorption of PFAAs can also be affected by the length of the C-chain, thus also playing a role in their fate. For instance, one study found that for each C-F_2 moiety the K_d value increased by approximately by 0.5–0.6 logarithmic (Log) units for both PFSAs and PFCAs in sediments (Higgins and

Luthy 2006). Similarly, Milinovic et al. (2015) suggested that for each C-F_2 moiety the Log K_{oc} value increased by approximately 0.4 Log units in soils. It is thought that the increase in chain length increases the hydrophobic interactions with soil OC and thus sorption (Zhao et al. 2014a, Milinovic et al. 2015). However, a small sample of six data points and one soil with a very high OC content means the data presented in the study of Milinovic et al. (2015) are not comprehensive. Sepulvado et al. (2011) conducted a laboratory batch desorption study using biosolid PFAA-contaminated field samples and found that the leaching potential for short-chain PFAAs was greater than for long-chain PFAAs and that concentrations of PFAAs decreased with depth, irrespective of biosolid loading rates. This finding suggests that depth within the soil profile (and hence changes in associated soil properties) may play an important role in understanding the fate of PFAAs in the environment. In soil cores taken from sandy and silty loam soils amended with PFAA-contaminated biosolids, they found PFOS present up to 120 cm depth (Sepulvado et al. 2011). However, the study did not report on other soil characteristics such as pH and OC content which limits the interpretation of the results.

The list of properties that can affect sorption of PFAAs to soils is extensive and includes parameters such as OC content, texture, pH and exchangeable cation concentrations in the soil. For example, it has been found that for most PFCAs, (C_{5-13}), partitioning decreases with increasing pH (Ullberg 2015). However, most research conducted to date has concentrated on the bioaccumulation of PFAAs by organisms or sorption to sediments (Higgins et al. 2007, Nakayama et al. 2008, Joung et al. 2010). The limited research that has been performed on soils has often focused on PFAA sorption by one or two soil types which does not provide a comprehensive understanding of PFAA mobility or transport within soil systems (Higgins and Luthy 2006, Ahrens et al. 2011, Li et al. 2012). However, it is important to develop knowledge about the partitioning and transport of PFAAs in many soils with varying characteristics (Milinovic et al. 2015) as it will likely deliver useful information for risk assessment of these compounds in the future.

The binding mechanisms of PFAAs in soils is expected to largely be influenced by hydrophobic interactions of the C-F chain with other hydrophobic materials, like OC, whereas electrostatic interactions of the PFAA functional group are likely weaker and interact with positively charged mineral or organic phases as well as cations in the soil solution (Du et al. 2014, Li et al. 2018)(Figure 2). For instance, it is likely as the C-F chain length increases, the hydrophobicity of the molecule also increases, which in turn increases the hydrophobic interactions in the soil, that lead to an increase in K_d values observed in the literature (Higgins and Luthy 2006, Sepulvado et al. 2011, Milinovic et al. 2015). One study also investigated sorption of several PFAAs on different OC soil fractions and found that the longer chained PFAAs were preferentially binding to humin fraction (insoluble), unlike short chained PFAAs that also bind to fulvic and humic acids fractions (Pereira et al. 2018). This study also

highlights that electrostatic interactions are likely more important for shorter chain PFAAs, in terms of sorption in soils and potentially why shorter chain PFAAs are more mobile in the environment.

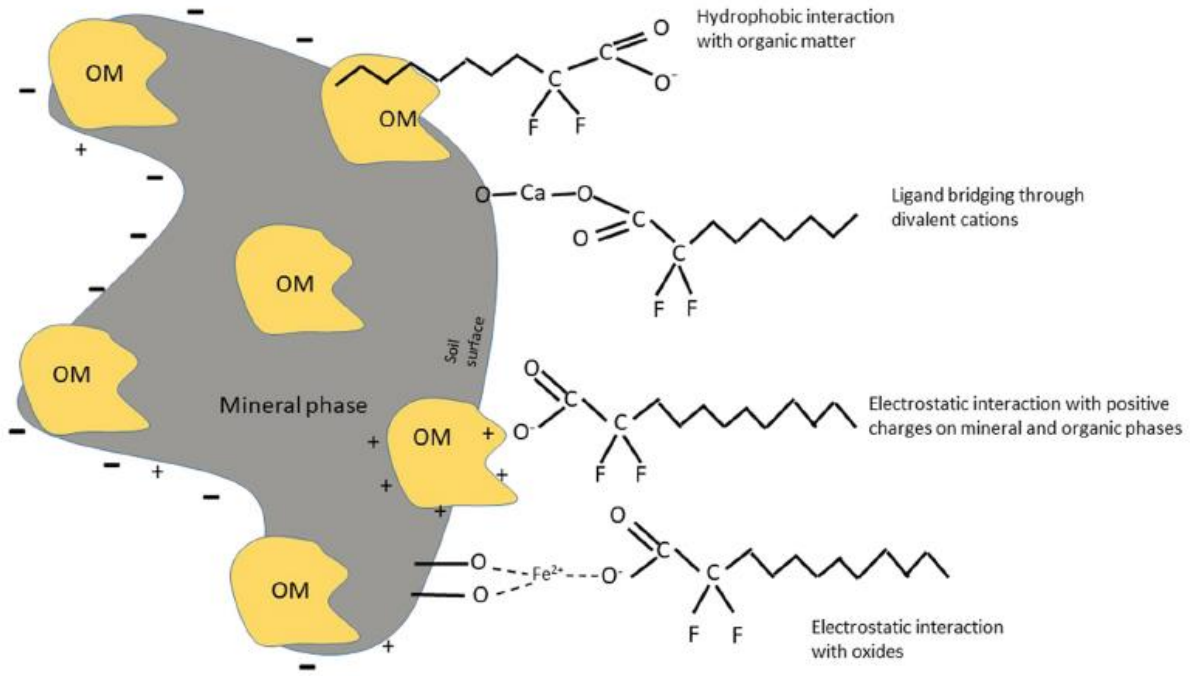

Figure 2: A conceptual model of possible PFCA binding mechanisms in soils. It is assumed PFSAs would have similar binding mechanisms. Figure is reprinted from Science of the Total Environment, vol 628, Li, Y., D. P. Oliver, and R. S. Kookana, A critical analysis of published data to discern the role of soil and sediment properties in determining sorption of per and polyfluoroalkyl substances (PFASs), Pages No., 110-120, Copyright (2018), with permission from Elsevier.

3.1.1 Modelling sorption by diffuse reflectance infrared spectroscopy

Due to the complex sorption interactions occurring in the soil in the presence of PFAAs, it would be beneficial to model or predict how multiple soil characteristics are influencing sorption together and particularly in a diverse set of soils, providing there is a reasonable correlation between soil properties and K_d values. Usually this would include extensive wet chemistry analysis of the soil, which can be both inefficient and expensive. In terms of modelling or predicting the K_d values from soil properties, diffuse reflectance mid-infrared spectroscopy coupled with partial least squares regression analysis (DRIFT-PLSR) (Nguyen et al. 1991), could provide a cost-effective, more efficient alternative that incorporates both mineral and organic soil components. The use of PLSR in conjunction with DRIFT spectroscopy means that the quantitative complexity of interpreting soil spectra, obtained from DRIFT, can be reduced. The chemometric technique, PLSR, assumes that there is a linear relationship between predictor variables and measured variables (e.g. spectral peaks

versus K_d values) and reduces the number of independent variables from spectra to a smaller number of predictor variables (PLSR x-loading weights). The DRIFT-PLSR technique was first described by Haaland and Thomas (1988).

Soil chemical characteristics, such as soil carbon content, moisture retention, particle size, pH, and carbonates have previously been successfully predicted using DRIFT-PLSR (Janik and Skjemstad 1995, Janik et al. 2016b, a). DRIFT-PLSR has also previously been used to predict K_d values for other organic contaminants, such as the pesticides diuron and atrazine, where organic matter, quartz (sand) and clay influenced sorption in a wide range of soils, including surface- and sub-soils (Forouzangohar et al. 2008, Kookana et al. 2008, Janik et al. 2015a, b). The studies also highlighted that the regression coefficients from the DRIFT-PLSR approach were greater than those found for the K_{oc} approach. However, this type of prediction has not been investigated for PFAAs, even though it is likely that PFAA sorption will likely be affected by multiple soil characteristics (Li et al. 2018) and the DRIFT-PLSR modelling technique could be a cheaper and time-efficient strategy.

3.2 Aging and desorption

Aging and desorption are important because for a contaminant to become bioavailable to plants and then to bioaccumulate, it needs to be in solution either from direct or immediate sources or from desorption from solid particles. Aging is the process whereby the longer the contact time of the contaminant with soil, the higher chance that the contaminant will become less bioavailable over time, by moving deeper into the soil matrix sites that are not easily accessed (Alexander 2000). For many other organic contaminants, including naphthalene, anthracene, phenanthrene, fluoranthene, pyrene, atrazine and 4-nitrophenol (Hatzinger and Alexander 1995, Kelsey and Alexander 1997, Chung and Alexander 1998, Tang et al. 1998), this process is a significant and important in determining their potential exposure and bioavailability (Alexander 2000). For instance, the mineralisation of atrazine and phenanthrene was found to be significantly lower after incubation for 200 days in 16 different soils (Chung and Alexander 1998). However, the rate of mineralisation in the soils was markedly different, for both compounds; between 9.6–35.0% for phenanthrene and 48.4–89.8% for atrazine (Chung and Alexander 1998). These results suggest that the bioavailability of these compounds varies not only over time but depends also on soil properties.

Depending on the environmental conditions there is the potential for desorption of organic chemicals to occur. Compared to sorption, desorption is generally a slower process where it is thought that longer-chain PFAAs are particularly slower to desorb from soils than shorter-chain PFAAs (Sepulvado et al. 2011). The process of desorption can be affected by the type of sorbent and

its properties; concentration and characteristics of PFAAs; presence of other contaminants and environmental conditions (Pan et al. 2009).

Most desorption and sorption studies are conducted using a batch equilibrium methodology whereby soil, water, chemical of interest and sometimes an electrolyte like calcium chloride are placed in a tube and shaken for 24–48 hours and then the concentration of the chemical in solution is measured. This can then be repeated several times to see if desorption of the chemical occurs from those same soils (Yu et al. 2010). This can also then be related to irreversible binding or aging of the chemical in the soil. Ahrens et al. (2011) conducted a batch equilibrium experiment spiking concentrations of PFOA in sediments and after shaking samples for 24 hours found that PFOA concentrations in the aqueous phase increased when the f_{oc} was low, which indicated desorption of PFOA concentrations from the sediment to the aqueous phase. Desorption was not an aspect that was specifically being determined in this study nor was it reasoned why there might have been an increase in concentration; such as contamination in the sediment sample. Sepulvado et al. (2011) also conducted a batch equilibrium experiment in the laboratory using field samples amended with biosolids and found that leaching potential for shorter chain PFAAs is higher than those of longer chain length. Another batch equilibrium study examined the desorption of spiked additions of PFOS and PFOA in six soils (varying organic matter 0.2–39%) and found that PFOS sorption was highly irreversible, <13% desorption, where PFOA had 24–58% desorption (Milinovic et al. 2015). However, desorption hysteresis was observed with PFHxS in humic substances indicating that irreversible binding had occurred (Zhao et al. 2014a).

There are therefore few data to determine if irreversible binding of PFAAs in soils occurs. This is important information to determine the longer-term fate and bioavailability (to plants and soil organisms) of PFAAs in soil.

3.3 Bioavailability to plants

Concentrations of PFASs have been found in many aquatic and terrestrial organisms and the adverse effects are suspected to cause cancer, endocrine disruption and immune-toxicity (Martin et al. 2003, Kannan et al. 2004, Higgins et al. 2007, DeWitt et al. 2012, Vaughn et al. 2013, Corsini et al. 2014). Once PFASs are in the human body they are slowly removed without transforming into secondary products (Lau et al. 2007). Human intake of PFASs is most likely through the consumption of food and water and secondarily through the inhalation of air and suspended dust particles, food contact with food packaging and some cookware (Tittlemier et al. 2007). However, the concerns for the bioaccumulative nature of PFASs in humans make it essential to understand their bioavailability and uptake by other organisms too. Significant concentrations of PFASs, in particular PFCAs, were found

in a variety of fruits, vegetables and cereals as well as salt and sweets in Italy, Norway, Belgium and the Czech Republic (Herzke et al. 2013, D'Hollander et al. 2015). The uptake of PFASs by plants has been demonstrated in laboratory experiments where uptake through plant roots is controlled by both the plant species and physico-chemical properties and speciation of the compounds; as well as soil properties, temperature and concentration (Zhao et al. 2013).

Zhao et al. (2013) investigated the uptake of PFOS by wheat plants in a hydroponic experiment where factors of pH, temperature, salinity and PFOS concentration were considered. As the solution pH increased from 6 to 10 the concentration of PFOS taken up by wheat roots decreased from >1200 mg/kg to 500 mg/kg, respectively. The concentration of PFOS in the shoots was approximately 900 mg/kg less than in the roots at all pH values. As the concentration of PFOS in the water increased, the concentration in the roots also increased. The concentrations of PFOS in the wheat seedlings also significantly increased with increase in temperature from 20–30 °C and increased with increasing salinity (sodium chloride) in the hydroponic water, 0.03–7.25 practical salinity units (psu). The concentrations in plants reported by Zhao et al. (2013) are much higher than those measured in any other soil-based or field experiments examining plant uptake (Ghisi et al. 2019), and are a result of the unrealistically high exposure concentration in the hydroponic solutions – 1 mg/L – most soil solutions or waters, even at highly contaminated sites, would have concentrations 3–5 orders of magnitude lower than this (Zareitalabad et al. 2013, Ghisi et al. 2019, Zhang et al. 2020).

In a similar way to sorption, the concentrations of PFAAs found in plants can be affected by the type and chain length of the PFAAs. In one study, lettuce grown in soil amended (5% w/w) with PFAA-spiked compost (final nominal soil concentration of 500 µg/kg) for 12–14 weeks found that concentrations of PFOA were taken up and accumulated in the edible part of lettuce plants more than PFOS (Bizkarguenaga et al. 2016). In another study investigating a larger variety of PFAAs, maize was grown for 128 days in soil spiked with 0.25 mg/kg or 1.00 mg/kg PFAAs and the authors found that the measured concentrations of PFAAs in the maize straw decreased significantly with an increase in PFAA chain length (Krippner et al. 2015). Even more interestingly, the four-fold difference in initial spiking concentration led to a four-fold increase in concentrations of PFCAs (≥C6) and PFSAs (≥C6) in the maize straw, except for PFOS where an eight-fold increase in concentration was found in the straw. The PFCAs were always found in higher concentrations in the maize straw than PFSAs, and only PFCAs (≤C8) were detected in the maize kernels (Krippner et al. 2015). This study highlighted a number of different factors influencing the uptake of PFAAs in maize, and potentially more broadly in other plant species i.e. that uptake is dependent on the concentration initially in the soil, the PFAA type (e.g. PFCA or PFSA), PFAA chain length as well as the species of plant grown.

Unlike other organic contaminants with bioaccumulative mechanisms which bind to lipids in the human body, PFAAs bind to proteins in the liver and serum (Conder et al. 2008). The same connection between proteins, lipids and PFAAs has also been identified in plants (Wen et al. 2016). Maize, soybean, mung bean, radish, lettuce, alfalfa and ryegrass were grown in biosolid-amended soils where root concentration factors (RCFs) were plotted against protein or lipid contents in roots. The data indicated where protein concentration was high, the concentration of PFOA or PFOS was also high (Figure 3). A linear relationship was found between PFAA concentration in plants and plant protein content, whereas the opposite was true for RCFs and lipid content (Wen et al. 2016). This relationship also infers that different plant species have different capabilities to accumulate PFAAs e.g. mung bean, a legume, accumulated more PFOA and PFOS than maize, a non-legume. Uptake of PFAAs from soils into plants is an important pathway in determining potential human exposure to PFAAs. Thus, understanding how different plant and soil properties affect accumulation of PFAAs by plants is critical to accurate risk assessments at contaminated sites.

The use of bioaccumulation factors (BAFs) can also be a way to understand the uptake of PFAAs into plants, where concentration in the plant parts, C_{plant} (mg/kg) is divided by the concentration in the soil, C_{soil} (mg/kg) (Equation 4).

$$BAF = \frac{[C_{plant}]}{[C_{soil}]} \quad (4)$$

The BAF values can also be affected by several factors, similar in respects to the sorption of PFAAs in soils, including plant species and soil properties as well as the PFAA chain length, functional group and concentration (Ghisi et al. 2019). These factors can cause a large variation in reported BAF values, with values ranging from 0.003–8.82 for PFOS and 0.002–7.52 for PFOA, from a collation of published BAF values reported in Ghisi et al. (2019). However, this variation in one study was reduced by calculating the BAF values on the basis of soil organic matter, for wheat grown in bio-solid amended soils (Wen et al. 2014). Ghisi et al. (2019) also noted that the accumulation in plants was significantly affected by the soil amendment used and suggested that this was due to a specific interaction with organic matter. For lettuce grown in biosolid-amended PFAA-contaminated soils, the BAFs decreased by approximately 0.3 Log units per C-F_2 moiety (Blaine et al. 2014). It would be reasonable from these results to assume that similar soil properties are influencing BAF values, as with K_d values, yet inversely. However, this relationship may not be linear. For instance, Blaine et al. (2014) also found that the uptake of short-chained PFASs (C4 and C5) in lettuce was greater at 2% soil OC content than the other two OC content treatments, 0.4% and 6%. Other factors such as leaching, earthworm presence and position of the PFAS in the soil has also been suggested to

influence the accumulation of PFASs in plants (Stahl et al. 2009, Gellrich et al. 2012, Zhao et al. 2014b). For example, Zhao et al. (2014b) found an increase in accumulation of PFCAs (≤C7) in wheat plants and a decrease in accumulation of PFSAs (C >7) with the presence of earthworms in the soil. The use of BAF values are important for regulators to effectively set the limits for safe consumption of food or animal products. However, the current BAF values are limited to the most common PFASs, PFOS and PFOA. Even with these PFASs, there is not a clear understanding of the many factors that potentially have a combined effect on plant uptake.

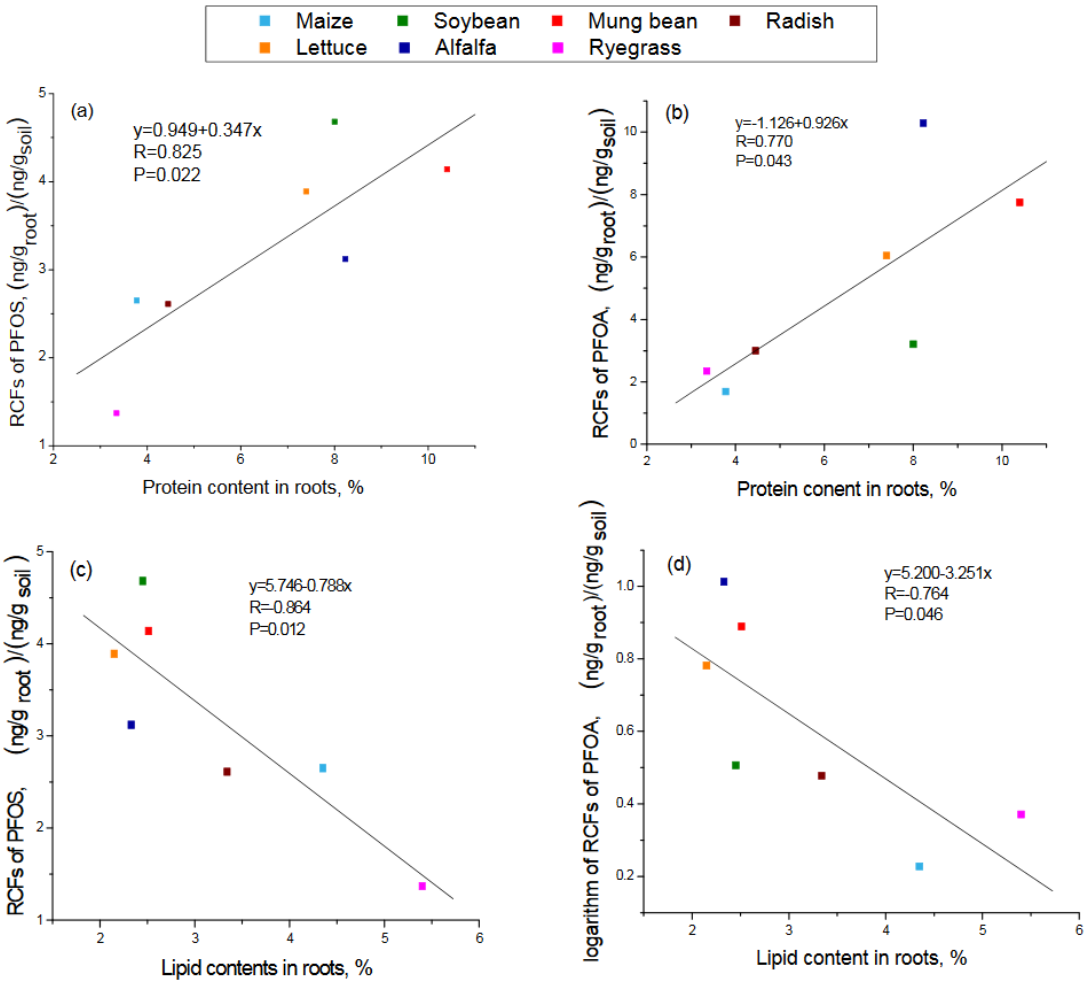

Figure 3: The relationship between protein (a and b) and lipid (c and d) contents in plant roots compared to root concentration factors (RCFs) of PFOS (a and c) and PFOA (b and d). Figure is reprinted from Journal of Environmental Pollution, Vol 216, Wen, B., Y. Wu, H. Zhang, Y. Liu, X. Hu, H. Huang, and S. Zhang., The roles of protein and lipid in the accumulation and distribution of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in plants grown in biosolids-amended soils, Pages No., 682-688, Copyright (2016)m with permission from Elsevier.

4. Summary of research gaps

In the environment, soil can be both a source and a sink for contaminants, including PFAAs, to potentially accumulate or transfer through the ecosystem or higher up the food chain. This potential transfer creates a greater risk of exposure to humans, other organisms and in the food we consume. It is therefore important to understand the fate and uptake of these substances in soil and plants. It is clear from the literature that PFAAs are unusually complex substances to work with and their sorption and bioavailability will depend on a number of independent characteristics in the soil and plant environment, including but not limited to the physico-chemical properties of the PFAA, PFAA species, soil type and characteristics as well as plant species.

In terms of sorption, having a range of soils with differing characteristics would provide a clearer understanding of how soil properties, other than OC, might influence sorption. These same soil properties may influence whether aging of PFAAs occurs in soils, yet no evidence regarding the significance of aging has been investigated. Plant uptake expressed as BAF values of PFAAs from freshly spiked and aged soils could identify whether or not aging is important for long-term bioavailability of these compounds.

5. Aims and objectives

The focus of this research was to carry out a comprehensive study on the fate of three PFASs, in particular PFOA, PFOS and PFHxS, in the soil environment – their sorption behaviour, aging, and potential uptake by plants.

The aims and objectives of this thesis are:

1) To investigate sorption and the soil properties influencing sorption the greatest:
    a. Establish sorption coefficients in a wide range of soils for PFOA, PFOS and PFHxS; and
    b. Identify and model the soil properties influencing sorption using MLR and DRIFT-PLSR.
2) To evaluate the aging and bioavailability of PFOS, PFOA and PFHxS in soils:
    a. Establish if aging occurs in soils;
    b. Measure the uptake of PFAAs by plants; and
    c. Identify and model the soil properties influencing uptake, expressed as BAF values, using MLR and DRIFT-PLSR.

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Chapter 2. Sorption of PFOA onto different laboratory materials: Filter membranes and centrifuge tubes

Highlights

- Sorption of PFOA on to lab-ware can cause analytical bias during routine procedures.
- Filtrations of PFOA solutions can lead to underestimation of dissolved concentrations.
- Sorption losses of PFOA onto polypropylene tubes was greater than on glass tubes.
- Sorption losses decreased when concentrations of PFOA in test solutions increased.

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Overall percentage (%)	20%		
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By signing the Statement of Authorship, each author certifies that: 1) the candidate's stated contribution to the publication is accurate (as detailed above); 2) permission is granted for the candidate in include the publication in the thesis; and 3) the sum of all co-author contributions is equal to 100% less the candidate's stated contribution.

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1. Abstract

Measurement and reporting of concentrations of contaminants of emerging concern such as per- and polyfluoroalkyl substances (PFASs), including perfluorooctanoic acid (PFOA), is an integral part of most investigations. Occurrence of sorption losses of PFAS analytes onto particular laboratory-ware (e.g. glass containers) has been suggested in the published literature but has not been investigated in detail. We examined sorption losses from aqueous PFOA solutions in contact with different commonly-used materials in filter units and centrifuge tubes (glass and plastics). Sorption of PFOA onto different filter membrane types ranged from 21–79% indicating that filtration can introduce a major source of error in PFOA analysis; pre-treatment of filter membranes with phosphate or methanol solutions did not improve PFOA recovery. Substantial adsorption of PFOA was also observed on tubes made from polypropylene (PP), polystyrene (PS), polycarbonate (PC), and glass where losses observed were between 32–45%, 27–35%, 16–31% and 14–24%, respectively. Contrary to suggestions in the literature, our results indicated that the greatest sorption losses for PFOA occurred on PP, whereas losses on glass tubes were much lower. Variations in ionic strength and pH did not greatly influence PFOA recovery. When PFOA concentrations were increased, the percent recovery of PFOA increased, indicating that binding sites on tube-walls were saturable. This study draws attention towards analytical bias that can occur due to sorption losses during routine procedures and highlights the importance of testing the suitability of chosen laboratory-ware for specific PFAS analytes of interest prior to experimental use.

2. Introduction

Perfluorooctanoic acid (PFOA) and other related per- and poly-fluoroalkyl substances (PFASs) have been recognised as contaminants of emerging concern due to their ubiquitous and persistent nature in the environment, as well as their bioaccumulative properties. As a result, these chemicals are being studied extensively with respect to their human and ecological toxicity (Hekster et al. 2003, Sundström et al. 2011) their occurrence, fate and transport in different environmental compartments (Hansen et al. 2002, Ahrens et al. 2015), as well as management and remediation strategies (Ochoa-Herrera and Sierra-Alvarez 2008, Ross et al. 2018). At various stages of such laboratory and field studies, the PFAS analytes being researched come in contact with a variety of apparatus that are usually made from glass, steel or plastics. The most common apparatus in any study are sampling and storage containers, including a range of tubes, vials and bottles. Others examples include disposable polystyrene (PS) well-plates used as exposure-vessels for toxicity assays, glass aquariums for fish toxicity tests, as well as disposable filtration membranes used for

the separation of aqueous phases from solid or particulate matrices prior to analysis.

Regardless of the types of experiments conducted, one aspect that is commonly cited in the methods' section of several published studies relates to the use of sample containers made of particular materials. Specifically, several studies exclude the use of equipment made from glass in experimental or analytical protocols involving PFASs (Hansen et al. 2002, Ahrens et al. 2015). The justification regularly provided for this is that glass adsorbs PFAS analytes. The USEPA and ISO methods, which are the most widely accepted test methods for PFAS analytes, also stipulate that PFAS standards, extracts and samples should not come in contact with any glass containers or pipettes (ISO 2009, Shoemaker et al. 2009). They recommend that polypropylene (PP) containers be used for all sample, standard and extraction preparation and storage, and suggest that other plastics may be used if they meet quality control requirements (Shoemaker et al. 2009). As a result, PP has been adopted as the material of choice in several studies (Higgins et al. 2007, Ahrens et al. 2010, Ahrens et al. 2011, Hellsing et al. 2016). However, a number of studies have used materials other than PP for PFAS-related studies. For example, Higgins and Luthy (2006) chose PS tubes over PP or glass because their preliminary, unpublished data provided higher recoveries when using PS tubes for a range of PFASs. Other studies have used polyethylene (PE), polycarbonate (PC) and high-density PE containers (Johnson et al. 2007, Washington et al. 2010), often without any indication as to the suitability of these materials.

One consensus in the published literature is the avoidance of equipment containing fluoropolymer materials like polytetrafluoroethylene (PTFE) in PFAS studies, as their manufacture has historically involved the use of some PFASs as a ‘polymerisation aid’ (Prevedouros et al. 2006). Leaching of remnant PFASs from such products can cause contamination of the dissolved phase (Martin et al. 2004). However, in the case of glass and plastics, there is considerable contradiction and inconsistency in the published literature regarding which materials may be best suited. Losses onto laboratory ware could lead to considerable bias in analytical data. Despite the severe implications of such routine losses due to adsorption onto glass and plastics, it has not been investigated in its own right.

Apart from choice of containers, filtration is another routine consideration in sample handling and preparation. Filtration is often employed as a major clean-up step for most environmental and laboratory samples, during which additional losses can occur (Carlson and Thompson 2000, Ahmad et al. 2001). A study investigating active air-sampling of gaseous PFOA using glass fibre (GF) filters observed that gas-phase PFOA was underestimated due to its sorption onto the GF filters (Johansson et al. 2017). However, an investigation using a variety of PFASs in aqueous phase, testing four different filter membranes, determined GF filters to be suitable for several PFASs, but

recommended specific testing to account for unpredictable effects (Chandramouli et al. 2015). The aim of this study was to examine the sorption losses of PFOA on common glass and plastic materials – specifically, centrifuge tubes and disposable syringe filter membranes – during routine laboratory procedures. Sorption of PFOA from aqueous solutions onto a variety of filter-membranes was tested; the influence of varying concentrations, and two pre-treatments were investigated. Additionally, sorption onto a variety of glass and plastic (PP, PC, PS) tubes was tested. The influence of contact time, pH, ionic strength and PFOA-concentrations were examined to gain insights into the nature of PFOA-binding interactions.

3. Materials and methods

3.1 Materials

Radiolabelled ^{14}C-PFOA with a specific activity of 2.04 GBq/ mmol was purchased from American Radiolabelled Chemicals Incorporation. Optiphase HiSafe 3 scintillation fluid for radio-chemical analysis was purchased from PerkinElmer, Australia. All other chemicals used, including calcium chloride dihydrate ($CaCl_2.2H_2O$), dipotassium hydrogen phosphate (K_2HPO_4), methanol, hydrochloric acid (HCl) and sodium hydroxide (NaOH) were of analytical grade. The specifications of filter-types and tube-types used in this study are listed in Table 1 and Table 2, respectively.

Table 1: Specifications of different filter-types tested for sorption of PFOA.

Filter code	**Membrane type**	**Housing material**	**Pore size (µm)**	**Diameter (mm)**	**Source (product number)**
PP	Polypropylene	Polypropylene	0.45	30	MicroAnalytix (30AP045AN)
GF	Glass fibre	Polyvinyl chloride	20	25	Millipore (SLAP02550)
PVDF	Polyvinylidene fluoride	Polypropylene	0.45	33	Millipore Millex (SLHV033NK)
PES	Polyethersulphone	Polypropylene	0.45	35	MicroAnalytix (MS SF35PS045)
PES+GF[a]	PES with GF pre-filter	Polypropylene	GF 1, PES 0.45	35	MicroAnalytix (MS SF35GPS045)
PTFE	Polytetrafluoroethylene (hydrophobic)	Polypropylene	0.45	25	Sartorius (17576-K)
RC	Regenerated cellulose	Polypropylene	0.45	25	Sartorius (17765-K)
CA	Cellulose acetate	Acrylic resin MBS[b]	0.45	28	Sartorius (16555-K)
CA+GF[a]	CA with GF pre-filter	Acrylic resin MBS	GF 0.7µm^2, CA 0.45	28	Sartorius (17829-K)
NY	Nylon	Polypropylene	0.45	25	ProSciTech (WS1-04525N)

[a]These filter units have two filter membranes in one housing unit, where the GF pre-filter membrane preceded the PES or CA membranes.

[b]MBS – methacrylate butadiene styrene.

Table 2: Specifications of different tubes tested for sorption of PFOA.

Tube code	Material	Lid material	Capacity (mL)	Source (product number)
PP1	Polypropylene	Polyethylene	10	LabServ (LBSCT1202)
PP2	Polypropylene	Polyethylene	10	LabServ (LBSSP1201)
PS	Polystyrene	Polyethylene	10	Rowe Scientific (S10316UU)
PC	Polycarbonate	Polypropylene	10	ThermoFisher (NAL 3118-0010)
G1	Glass	Screw cap, Teflon liner	12	Kimble Kimax (45066A-16100)
G2	Glass	Rubber	10	BD Vacutainer (366430)
PS2	Polystyrene	Polyethylene	10	ThermoFisher (LBSCT1002)

3.2 Filter sorption studies

The sorptive losses through retention of dissolved PFOA onto different filter membrane-types was investigated in triplicate using syringe-filtration through disposable filter units. By means of single-use 10 mL PP syringes, 4 mL of a 14 µg/L PFOA solution was drawn into the syringes, following which filter units were attached to the end of the syringe before plunging the solution through the filter membrane. The initial 2 mL volume of the filtrate was discarded and the subsequent 2 mL was collected, of which 0.5 mL aliquots were used for quantitative analysis. Control samples to account for any sorption occurring on the walls of the syringes were prepared by taking up PFOA solutions in the syringes and dispensing the solutions without attaching any filter units (details in supplementary material). To determine if recovery of PFOA from the filters could be improved, two pre-rinsing treatments, using phosphate solution (100 mM K_2HPO_4) and methanol, were applied to the filters. For the phosphate treatment, 10 mL of a 100 mM K_2HPO_4 solution was plunged through the filter units, followed by 10 mL of Milli-Q water, prior to PFOA filtration. Similarly, for the methanol treatment, 10 mL of methanol was plunged through the filters; membrane-types that were incompatible with methanol were excluded. Finally, the influence of increasing concentrations of PFOA on sorptive losses on three filter membranes (PP, RC and GF) was also tested using an environmentally relevant range of concentrations (0–529 µg/L). The critical micelle concentration (CMC) of PFOA has been reported to be in the range of 1–1.6 $\times$ 10^7 µg/L (i.e., 25–38 mM), at which PFOA molecules can agglomerate to form micelles and hemi-micelles; such phase separation can affect interfacial activity like sorption (Harada et al. 2005, Rattanaoudom et al. 2012). The concentrations used in our studies were around 104 to 106 times lower than the CMC, so the impact of micelle formation on sorption losses is expected to be negligible.

3.3 Tube sorption studies

To measure sorption of PFOA onto different centrifuge tube-types (PP, PS, PC, G1 and G2; Table 2), tests were performed in triplicate under different conditions by varying the contact times, solution pH, ionic strength and PFOA concentrations. When not being varied, the standard test parameters included the use of 8 mL volumes of PFOA solutions of concentrations of 20.5 ± 1 µg/L, prepared in a 10 mM $CaCl_2$ background electrolyte solution or Milli-Q water, and a contact time of 24–48 h. To investigate the influence of contact time, tubes were subjected to shaking times of 1, 2 and 7 days. The influence of pH was examined across a pH range from 4 to 9 where 0.1 M HCl or 0.1 M NaOH was used to adjust solution pH. Background electrolyte solutions of varying concentrations (0–100 mM $CaCl_2$) were used to determine the effect of ionic strength on retention of PFOA. Sorptive losses as a function of concentration were also examined by testing initial PFOA concentrations ranging from 0–415 µg/L. All tubes with test PFOA solutions were placed on an end-over-end shaker for the duration of the test, after which sub-samples (0.5 mL) were taken for quantitative analysis.

3.4 Instrumental analysis

Aliquots (0.5 mL) of all samples, blanks (Milli-Q water) and stock solutions were combined with 4 mL of scintillation fluid in a scintillation vial and analysed radio-chemically using a β-liquid scintillation counter (Perkin Elmer Tri-Carb 3110 RT). Self-normalisation and calibration (SNC) protocol was performed and the ^{14}C counting efficiency was determined to be >90%. The activity of ^{14}C in the samples was measured as disintegrations per minute; each sample was measured for 2 min, three times. Background vials (n = 3) of 0.5 mL of Milli-Q water (instead of sample) were run with each batch of samples to determine the background count and was subtracted from each sample count. Concentrations of PFOA were calculated using the specific activity and the measured ^{14}C activity. The limit of detection for the method calculated using the blanks was determined to be 0.11 µg/L.

3.5 Data and statistical analysis

All experiments were carried out at least in triplicate. The coefficient of variations for the measurement of all stock solutions used in the experiments ranged from 0.35–4.83%. Losses of PFOA through adsorption onto the filters and tubes were calculated using the difference between the amounts of PFOA in the samples before and after the experimental steps (i.e. filtration or shaking). Results are reported as a percentage recovery of PFOA compared to the controls. A mass balance was not attempted as each additional handling, extraction and transfer of every sample would increase the chances for loss of analyte, introducing additional error to the method. Statistical software, IBM SPSS (v. 24), was used to determine if there were significant differences (p <0.05) between treatments. After using analysis of variance test (ANOVA), a Tukey's honestly significant difference test was used to compare treatment means.

4. Results and discussion

4.1 Filter sorption studies

4.1.1 Sorption losses observed on different filter membrane-types

The sorption of dissolved PFOA onto filter membranes was determined using syringe-filtration. As no sorption of PFOA analyte was identified as occurring on the syringe-surfaces (Table S1, supplementary material) likely due to short residence time (<10 s) in the syringes, the sorption losses were calculated using the difference between the amounts of PFOA in the unfiltered and the filtered solutions. Irrespective of the type of membrane tested, recovery of PFOA was <100% in all cases (Figure 1). This implies that at least a certain proportion of PFOA was retained onto the filter membrane or housing material due to adsorption, leading to underestimation of dissolved PFOA concentrations. As it was not possible to make a distinction between the amount of PFOA retained on the membrane and the housing material separately, sorption was considered for the filter unit as a whole. Specifically, recovery ranged from 76.0% at best to 21.2% at worst, depending on the type of membrane used (Figure 1). The highest recoveries were achieved when using PVDF (76.0%), glass-fibre (74.2%), RC (74.0%) and PP (72.3%) membranes. The lowest recovery due to adsorption was displayed by the NY membrane filter (21.2%). Overall, the percentage recoveries after filtration were in the order PVDF≈GF≈RC≈PP>CA>PES≈PTFE>NY.

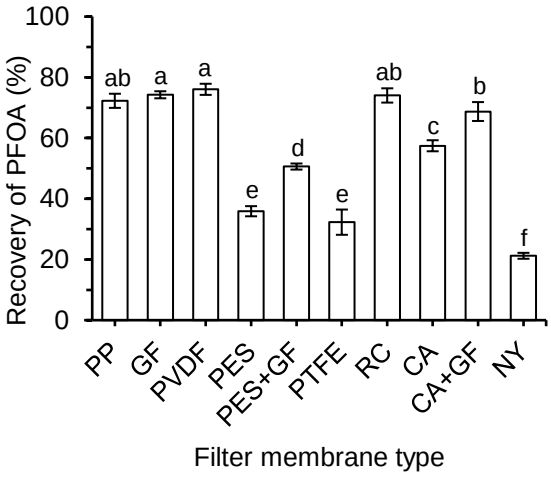

Figure 1: Percentage recovery of ^{14}C-PFOA filtrate solution (13.58 ± 0.33 µg/L) from different syringe filter membranes. Error bars represent standard deviation (n = 4). Different letters denote different statistically significant differences (p <0.05) between groups.

While PVDF showed a high recovery, it is a fluoropolymer, and like PTFE, may cause contamination of analytical blanks, or overestimation of dissolved PFAS concentrations (Martin et al. 2004), so it should generally be avoided in PFAS-based analysis. We did not test for PFAS contamination issues

during filtration as a radiolabelled PFOA solution was used. Interestingly, despite both PVDF and PTFE being fluoropolymers, PFOA-sorption on PTFE was more than two times greater than on PVDF; this may be attributed to the differences in their chemical properties. The carbon-backbone of the polymeric structure in PVDF (chemical formula $[-CH_2\text{-}C\text{-}F_2\text{-}]_n$) is partially fluorinated, whereas that in PTFE (chemical formula $[-CF_2\text{-}CF_2\text{-}]_n$) is fully fluorinated, making PTFE more hydrophobic than PVDF. It is likely that the PFOA tail, being hydrophobic, is able to undergo greater hydrophobic interactions with PTFE, leading to greater PFOA sorption.

When testing a range of filter media with PFAS-spiked water, Chandramouli et al. (2015) reported that the poorest recoveries were observed with PTFE (2–24%), followed by NY (62–80%) filters, while GF filters displayed the best recovery (>85%) overall. For a range of perfluorinated carboxylate and sulphonate compounds, Labadie and Chevreuil (2011) also reported better recoveries using GF (70–98%), as opposed to NY (40–98%); however, specifically in the case of PFOA, GF and NY were reported to perform equally. Like in the case of GF membrane, the recoveries obtained from RC as well as PP membranes in our study were greater compared to other filters, however accounts of the use of these membranes in the published literature are rare. Chain-length of the PFASs were an important factor controlling sorption losses reported in these studies (Labadie and Chevreuil 2011, Chandramouli et al. 2015), where greater sorption occurred as chain-length increased. This has been reported in studies related to sorption in environmental media such as soil and sediments, as well as adsorbents such as activated carbon (Du et al. 2014).

While the literature focussing on PFAS-investigations in water, soil and sediments commonly use GF filters (Lein et al. 2008, Kwadijk et al. 2010, Ahrens et al. 2015), the literature dealing with air-sampling of PFAS is exploring ways to reduce the sorption of PFAS onto GF-filters (Arp and Goss 2008, Johansson et al. 2017). This contrast may be attributed to the differences in sampling and filtration equipment set-up for different environmental media. Moreover, it appears that membrane-types, apart from GF and quartz-fibre filters, have not been tested for PFAS sorption from air. While GF filters have been reported to show the best recoveries for aqueous phases (Labadie and Chevreuil 2011, Chandramouli et al. 2015), it is important to note that glass fibres used in membranes usually have variable structural integrity. As a result, they are often ascribed with a particle retention rating, covering a range of sizes (e.g. 0.8–8 µm in this study), rather than a specific pore-size. The GF membranes used in this study were stated to be of 20 µm pore size, but the manufacturer cannot guarantee an actual pore size. An interesting observation was that the inclusion of a GF membrane as a pre-filter in the case of PES and CA membranes, caused recovery to improve by up to 18% and 11%, respectively, when compared to the PES and CA membranes where no pre-filter was included. Usually, pre-filters are effective at improving recovery in samples with

high particulate load. The solutions used in this study were devoid of any particulate matter, thus it is unclear why an improvement was observed.

One approach to reduce sorption of PFOA onto the filters could be through pre-treatment of the filters to pre-saturate or block the available binding sites for PFOA on the membrane – a strategy that has been demonstrated for other organic compounds (Bin et al. 2000, Hupfeld et al. 2009). However, on pre-treating the membranes with either a phosphate solution (100 mM), or methanol (99% purity), no significant improvements in PFOA-recovery were observed (Figures S1 and S2; supplementary material). In the case of the methanol treatment, in fact, a decrease in recovery of 7–28%, was observed for some membranes (RC, PP and PES; Figure S2). The exact mechanisms controlling the binding of PFOA to the different filter membranes are not known. In the study on active air-sampling of PFOA using GF filters, pre-treatment with a siliconizing reagent led to an appreciable reduction in sorption of gaseous PFOA onto the GF filters (Johansson et al. 2017), particularly when atmospheric concentrations of PFOA were high. While no specific mechanism was identified, it was attributed to deactivation of surface active sites on the GF filter. Given that no benefits in terms of reduction in sorption losses were observed in our study, combined with the added inconvenience, time and expense associated with the process, pre-treatment of disposable filter-units is not recommended for improving recovery from solution. However, pre-rinsing remains a suitable strategy to reduce contamination of the dissolved phase from certain filters (e.g. PTFE) (Labadie and Chevreuil 2011).

4.1.2 Effect of PFOA concentration on PFOA recovery

To test the influence of increasing PFOA concentrations on recovery, three of the filters exhibiting the lowest sorptive losses — PP, RC and GF — were used; PVDF was excluded on account of being a fluoropolymer. In terms of percentage of PFOA recovered (Figure 2), there was no evidence for consistent effect of PFOA concentration on recovery. A similar outcome was reported for PFOA by Chandramouli et al. (2015) when tested on NY filters; PFOA concentrations used ranged from 0.02–1 µg/L, which were 2–3 orders of magnitude lower than the concentrations tested in our study. We used higher concentrations with the expectation that sorption might be saturable, but this was not observed.

As all filter-membranes displayed some losses of PFOA through adsorption, we recommend that it is better to avoid filtration, wherever possible. Other studies have also advised against the use of filtration in sample preparation steps for the same reasons (Schultz et al. 2006, Voogt and Sáez 2006). For instance, Schultz et al. (2006) elected centrifugation as their only viable sample clean-up step when analysing PFAS-contaminated municipal wastewater samples due to such losses. If, however, filtration is considered necessary in any procedures, we advise that specific testing of

analyte-sorption onto filter media is undertaken to account for potential underestimation of dissolved PFAS concentrations due to such losses.

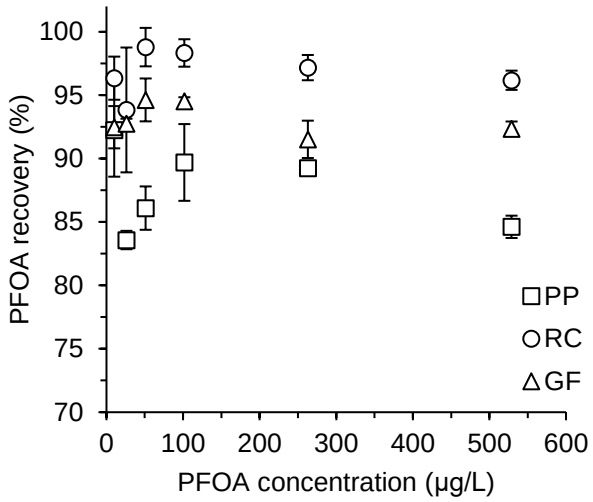

Figure 2: Percentage recovery of ^{14}C-PFOA after filtering through three different filter types (PP, RC, GF) when using a range of ^{14}C-PFOA concentrations (0–528.90 µg/L). Error bars represent standard deviation (n = 3).

4.2 Tube sorption studies

4.2.1 Effect of contact time on recovery of PFOA

Recovery of PFOA decreased in the order G1≈G2>PC>PS>PP (Figure 3), with greater recoveries from glass tubes, compared to the plastic tubes. Specifically, PFOA-recovery observed from glass (G1 and G2) tubes ranged from 77–86%, whereas that in PP tubes ranged from 55–68%, which is contrary to what is widely implicit in the published literature. Amongst the plastics tested, the recoveries from PC (69–78%) and PS tubes (65–73%) were greater than from PP tubes. No significant changes were observed over time (1, 2 and 7 days) in the case of G1, G2 and PC tubes (Figure 3).

In the case of PP and PS tubes, however, some small-time effects were observed. Losses at day 7 were similar to losses observed at day 1. In the case of PP1, PP2 and PS tubes, in fact, losses at day 2 were greater (by 8–13%) than those at days 1 and 7 (Figure 3). Theoretically, at a fixed analyte concentration, recovery was expected to decrease with time and reach equilibrium at a stage where no more PFOA was being sorbed onto the tube walls. As this trend was not observed in our data, it is possible that PFOA sorption onto the glass and plastic surfaces occurred in a much shorter time frame (within hours) than was investigated in this study. In a way, this idea is supported by our observations during syringe-filtration, where despite using polypropylene syringes, no sorption of PFOA was observed on the syringe-surfaces (Table S1, supplementary material). The PFOA solutions

were in contact with the syringes for no longer than 5–10 s, which may have been too short a time for any PFOA analyte to be retained on the surface via sorption. Further studies using shorter timeframes (e.g. <6hrs) would be required to corroborate this.

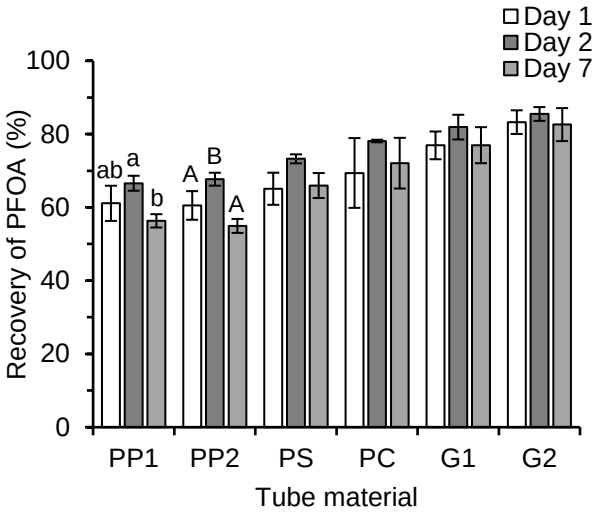

Figure 3: Average concentration of ^{14}C-PFOA remaining in solution after 1, 2 and 7 days when in contact with different centrifuge-tube materials. Error bars represent the standard deviation (n = 3). Concentration of ^{14}C-PFOA used was 21.32 ± 0.07 µg/L. Different letters denote significant differences between days on individual centrifuge tube types.

4.2.2 Effect of solution chemistry on recovery of PFOA

The influence of solution chemistry on sorption of PFOA in different tubes was determined by measuring PFOA-recovery under varying pH (Figure 4a) and ionic strength (Figure 4b) conditions. Both tests corroborated our previous observations that greater recoveries were obtained from the glass tubes, compared to the plastic tubes (G1≈ G2>PC>PS>PP). Specifically, PFOA-recovery observed from glass (G1 and G2) tubes ranged from 93–103%, whereas that in PP tubes ranged from 74–81%. Recoveries from PC and PS tubes were 85–89% and 81–86%, respectively.
On increasing the pH from 4 to 8, the PFOA-recovery from the glass tubes (G1 and G2) remained largely unaffected. In the PC, PS and PP, a slight increase in recovery, by 4.1%, 4.7% and 6.5%, respectively, was apparent. Glass tubes, G1 and G2 displayed the least fluctuations and PP the most. Despite some of these pH effects being statistically significant (p <0.05), on the whole, the sorption losses due to variations in pH (i.e., 1.4–6.5%) were minor when compared to the underlying losses due to the inherent nature of the different materials being tested (i.e., 5–25%).
By using PFOA solutions prepared in background CaCl2 electrolyte solutions of varying concentrations, effects of ionic strength on PFOA recovery were examined. No significant effects of

increasing $CaCl_2$ concentrations were observed on recovery of PFOA in PP, PS and PC tubes (p >0.05). Compared to the control PFOA solution prepared in Milli-Q water, recovery of PFOA from G1 tubes decreased by 5.3% and 6.2%, respectively, in the presence of 25 mM and 100 mM $CaCl_2$ (p 0.043 and 0.015), but no effects were observed for other ionic strength treatments (1 mM, 10 mM and 50 mM $CaCl_2$). In the case of G2 tubes, compared to the control, recovery decreased by 3.5–6.4% (p <0.025) for all ionic strength treatments, except for the 50 mM $CaCl_2$ treatment (p = 0.132).

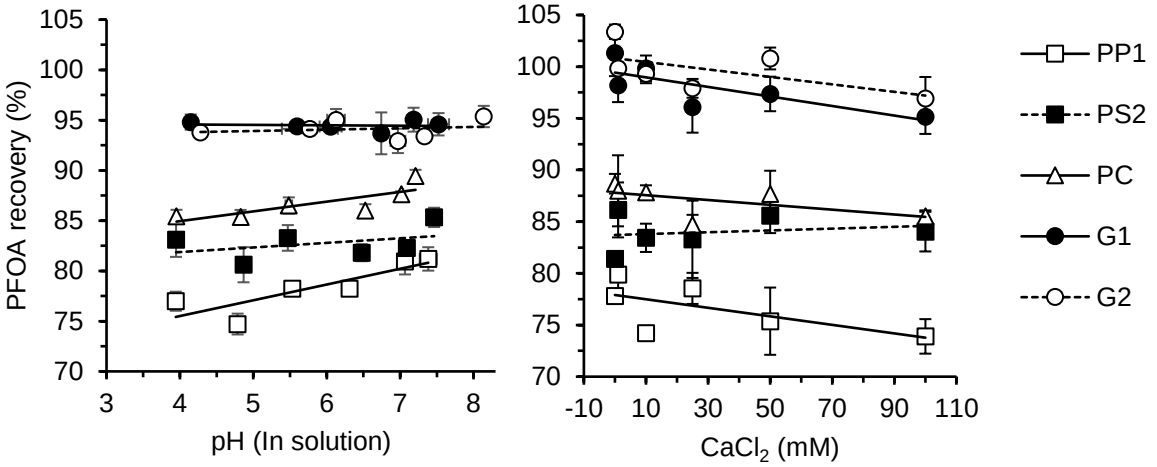

Figure 4. Effect of solution chemistry, including pH (a) and ionic strength (b), on the average percentage recovery of PFOA when in contact with different centrifuge tubes. Test conditions ranged from pH 3 to pH 9 and ionic strength ranged from 0–100 mM $CaCl_2$. Concentration of ^{14}C-PFOA were 20.79 ± 0.07 µg/L and 19.18 ± 0.10 µg/L for pH and ionic strength, respectively. Error bars represent the standard deviation (n = 3). The lines across the data points represent linear regressions.

Ionic strength usually affects the electrostatic nature of a surface as well the solubility of the compound, thus controlling interactions occurring at that surface. Glass is known to have a negative surface charge above pH 2.6 (Gu and Li 2000), whereas a variety of plastics (including PP) have been reported to carry a negative surface charge above pH 3.5–4 (Leininger et al. 1964, Lameiras et al. 2008). In the experimental conditions used in this study (pH 5.6 ± 0.2), all tubes may be expected to carry a slight negative charge. Divalent cations like Ca^{2+} have been found to act as a bridge between the negatively charged functional head groups of PFASs and the negatively charged surfaces of a variety of adsorbents (Higgins and Luthy 2006). It is thus possible that as ionic strength increased, the Ca^{2+}-induced bridging effect caused more PFOA to be retained on the negative surfaces of the glass tubes, thereby slightly decreasing recovery. However, as in the case of solution pH, these variations were relatively minor compared to the considerably greater underlying losses resulting due to the physiochemical nature of the materials themselves.

Glass, which is composed of several polar inorganic components like silica (silicon dioxide), boron trioxide and sodium oxide is known to be hydrophilic in nature (DeRosa et al. 2003). On the other hand, plastic polymers like PP and PS are known to be hydrophobic materials as they are both solid hydrocarbons composed entirely of carbon and hydrogen (Kovalchuk et al. 2014). In comparison, PC may be expected to have a lower hydrophobicity than PP and PS (given the presence of polar oxygen functional groups in its polymeric chemical structure), but greater hydrophobicity than glass. While sorption mechanisms need investigation, greater sorption of PFOA onto the plastics compared to glass may be related to potential hydrophobic interactions of PFOA with the hydrophobic components of the polymeric plastics. Further investigation is required at a molecular level to identify the mechanisms controlling the interactions between PFOA and the different materials it may be in contact with.

4.2.3 Effect of PFOA concentration on recovery of PFOA

On increasing the concentrations of PFOA in the test solutions, the percentage of PFOA recovered from the solutions within each tube-type increased (Figure 5). For instance, as the spiked concentration of PFOA increased from 12–415 µg/L, the recovery of PFOA from PP, PC and G1 tubes improved from 53.7–85.5%, 66.7–95.1% and 75.3–106.3%, respectively. Essentially, the higher the concentration of PFOA in the test solutions, the lower the proportional loss of PFOA onto the container walls, irrespective of the tube-type. This suggests that all plastic and glass tubes tested herein contained a limited number of binding sites on their surface and can only interact with a finite amount of PFOA. Therefore, as the concentration of PFOA increases, the binding sites on the container walls become increasingly saturated. Similar concentration-dependent results for sorption losses have been reported in the case of other organic chemicals such as pesticides (Sharom and Solomon 1981) and polycyclic aromatic hydrocarbons (Chlebowski et al. 2016), as well as inorganic substances such as silver nanoparticles (Malysheva et al. 2016).

Poor recovery, particularly at low concentrations, can present serious implications. One current topic of interest in PFAS-research is the determination of the toxicity profiles of these chemicals. When conducting ecotoxicological testing, if significant sorption losses occur, the test organisms will be exposed to reduced concentrations of the analytes, resulting in inaccurate toxicity thresholds (Sekine et al. 2015). Similarly, when testing drinking water quality, and comparing to guideline values to determine safety, erroneous risk assessments may be made due to such losses. The lowest PFOA concentration tested in this study (12 µg/L) was around 170 times greater than the current USEPA drinking water health advisory limit for PFOA (0.07 µg/L) (USEPA 2016). Consequently, greater levels of losses may be expected to occur in trace monitoring and health-related studies, causing substantial inaccuracies.

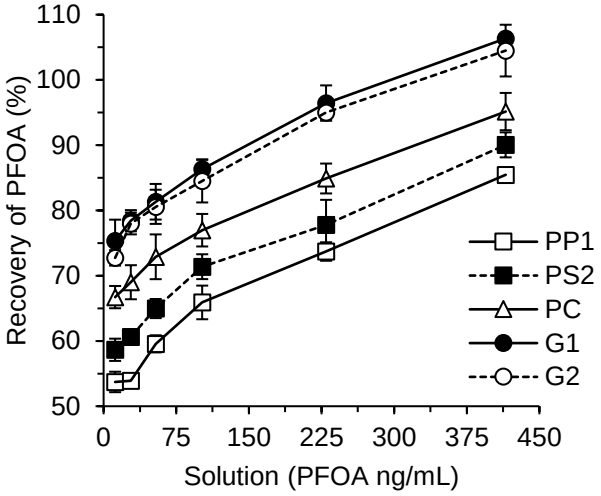

Figure 5: Average percentage recovery of ^{14}C-PFOA in different centrifuge-tube types when in contact with increasing concentrations of ^{14}C-PFOA (0–415.19 µg/L) in solution. Error bars represent standard deviation (n = 3). The lines across the data points represent moving averages.

5. Conclusions and implications

To our knowledge, this is the first study to systematically quantify and report on sorptive losses of dissolved PFOA observed on tubes made from different materials (PP, PC, PS and glass), despite the serious implications of this issue. References to such losses have been made in the published literature but remain largely unsubstantiated. Moreover, contrary to what is implicit in standard protocols (e.g. USEPA and ISO methods) and the published literature, our data emphasise that greater sorption losses of PFOA occurred on PP containers than on glass containers. Irrespective of solution chemistry (pH and ionic strength) or concentration of PFOA tested, sorption of PFOA onto the tube-walls increased in the order glass<PC<PS< PP. Proportional losses decreased when PFOA concentrations of test solutions increased. Due to this concentration-effect, losses can be especially exaggerated when dealing with PFAS solutions of low concentrations, for instance, when reporting on the quality of drinking water samples. Filtration of aqueous PFOA solutions also introduced a major source of error, leading to an underestimation of dissolved concentrations. Our recommendation is therefore to avoid filtration of PFAS solutions where possible, unless it is inevitable. It is possible that even when using tubes or filters made of the same materials, sorption losses may vary widely under different conditions, or with different batches and suppliers – hence it is difficult to ascertain what the 'best' material for PFOA or other PFASs may be. However, if adsorptive losses are monitored using appropriate controls and measured with suitable precision, it would be possible

to minimise errors associated with such losses. Although it is not possible to directly extrapolate from the current dataset for PFOA to apply to other types of PFASs, it is reasonable to suggest that the specific trends may differ depending on the type of PFAS, due to differences in their chain lengths and functional properties. For instance, compared to PFOA, greater losses may occur in the case of perfluorooctanesulphonic acid (PFOS), which binds more strongly than PFOA to most surfaces. Factors such as the co-occurrence of other surfactants and chemicals, as well as the matrix being tested (e.g. freshwater, sea water, soil, sediments, biological fluids and tissues) can also impact sorption dynamics. Consequently, our study highlights the need to account for sorption losses associated with common laboratory ware for each analyte separately as part of sampling and experimental protocols, and carefully consider the choice of suitable materials for use in PFAS-work.

6. Acknowledgements

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8. Supplementary material

Sorption of PFOA onto different laboratory materials: filter membranes and centrifuge tubes

Table S1. Amount of PFOA sorption occurring on syringe-surfaces during syringe-filtration.

While testing the effect of PFOA concentrations on recovery from filters, "unfiltered" PFOA solutions of a range of concentrations (0–529 µg/L) were tested in 2 different ways to determine whether losses on syringes may occur. In the 1st method, the PFOA solutions were taken up in syringes (in the same manner that the filtered solutions were taken up in syringes, but no filter was attached before dispensing), and held for approximately 5 seconds before transferring subsamples into scintillation vials for analysis. These were considered as 'syringe controls'. In the 2nd method, subsamples of the PFOA solutions were directly transferred into scintillation vials for analysis (without the use of a syringe). These were considered as 'direct spikes'. It was determined that the concentration measurements using both methods were not significantly different from each other (p >0.05), demonstrating that no losses of PFOA analyte were observed due to sorption. The relevant data (and accompanying statistics) is shown below:

Nominal PFOA concentration (µg/L)	Measured PFOA concentration; Syringe control (µg/L)	Measured PFOA concentration; Direct spike (µg/L)	ANOVA *p values >0.05*
0	0.0 0.0 0.0	0.0 0.0 0.0	0.519
10	10.5 9.9 10.1	10.2 10.1 10.3	0.972
25	25.1 26.5 25.7	26.6 26.6 25.9	0.237
50	52.3 52.2 52.7	52.2 46.1 51.4	0.261
100	102.7 97.5 103.4	104.1 96.0 106.3	0.818
250	264.6 265.8 266.5	261.5 254.1 264.7	0.159
500	532.5 530.0 529.1	532.2 521.0 528.6	0.402

The syringes were made of polypropylene (PP). In our experiments (Figure 3 of the manuscript), up to ~ 40% sorption losses of PFOA analyte were observed on PP tubes over a 24-hour shaking period. The short residence/contact time (<10 seconds) in the syringe is likely to be the reason why no sorption losses were observed when using the PP syringes.

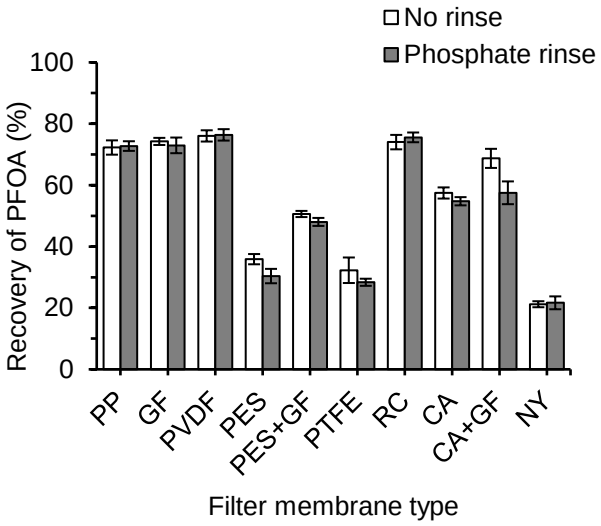

Figure S1. The percentage recovery of PFOA from different syringe filter membranes where the filters were pre-rinsed using a phosphate solution prior to filtering ^{14}C-PFOA solution (13.6 ng/mL). Asterisks denote significant differences between control (no-rinse) and pre-rinsed filters for individual filter types. Error bars represent the standard deviation (n = 4).

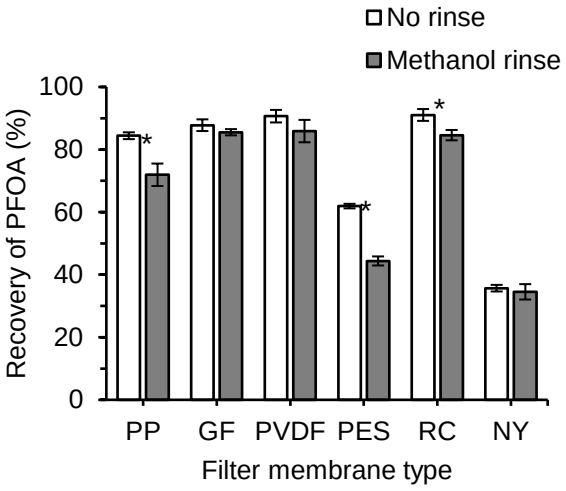

Figure S2. The percentage recovery of PFOA from different syringe filter membranes where the filters were pre-rinsed using a methanol solution prior to filtering ^{14}C-PFOA solution (15.7 ng/mL). Asterisks denote significant differences between control (no-rinse) and pre-rinsed filters for individual filter types. Error bars represent the standard deviation (n = 3).

Chapter 3. Predicting partitioning of radiolabelled ^{14}C-PFOA in a range of soils using diffuse reflectance infrared spectroscopy

Highlights

- Measured data on K_d values for 100 Australian soils for PFOA.
- Key soil properties identified to predict sorption using MLR and DRIFT-PLSR.
- Sorption decreases with increasing depth in soil profile.
- DRIFT-PLSR offers a better model to predict K_d from soil properties than MLR.

Statement of Authorship

Title of Paper	Predicting partitioning of radiolabelled ^{14}C-PFOA in a range of soils using diffuse reflectance infrared spectroscopy.
Publication Status	Published
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Co-Author

Name of Primary Author (Candidate)	Emma R. Knight		
Contribution to the Paper	Experimental development; conducting experiments; data and statistical analysis; modelling of data; critical interpretation; manuscript writing.		
Overall percentage (%)	85%		
Certification:	This paper reports on original research I conducted during the period of my Higher Degree by Research candidature and is not subject to any obligations or contractual agreements with a third party that would constrain its inclusion in this thesis. I am the primary author of this paper.		
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Co-Author Contributions

By signing the Statement of Authorship, each author certifies that: 1) the candidate's stated contribution to the publication is accurate (as detailed above); 2) permission is granted for the candidate in include the publication in the thesis; and 3) the sum of all co-author contributions is equal to 100% less the candidate's stated contribution.

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1. Abstract

The aim of this study was to establish partitioning coefficients (K_d) of perfluorooctanoic acid (PFOA) in a wide range of soils and determine if those values can be predicted from soil properties using multiple linear regression (MLR) and from infrared spectra of soils using partial least squares regression (PLSR). For 100 different soils, the K_d values of spiked radiolabelled ^{14}C-PFOA ranged from 0.6 to 14.8 L/kg and significantly decreased with soil depth (p <0.05) due to soil properties that change with depth. The MLR modelling revealed that PFOA sorption was significantly (p <0.05) influenced, in decreasing order, by organic carbon (OC) content, silt-plus-clay content and soil pH. Soils were partitioned into all soils and surface soils alone. The MLR models using OC, silt-plus-clay content and pH together explained most of the variation in sorption in all soils as well as surface soils alone (0–15cm). However, correlations between soil properties and K_d values in some soils could not be explained by the MLR model. Modelling of K_d prediction in soils with PLSR and diffuse reflectance (mid) infrared Fourier transform spectroscopy (DRIFT) showed comparable success in explaining the predictions of K_d values, including some of the outliers identified in the MLR model. The PLSR loading weights suggested that quartz, and possibly pyrophyllite minerals, were inversely correlated with the K_d values. Given that MLR requires *a-priori* characterisation of a range of soil properties and PLSR-DRIFT is a method based on the direct relationship between spectra and soil components, mid-infrared spectroscopy may be a more economical and rapid technique to predict the solid-liquid partitioning of PFOA in soils.

Keywords; Sorption, Partitioning, Modelling, PFAS, Mid-infrared Spectroscopy, radiolabelled PFOA

2. Introduction

Perfluorooctanoic acid (PFOA), is one of many similar compounds classed as per- and poly-fluoroalkyl substances (PFASs). It has commonly been detected at low concentrations in soils and sediments (ng/g) and in ground and surface waters (ng/L) (Cousins et al. 2016). Perfluorooctanoic acid has been used for many purposes including in aqueous film forming fire-fighting foams, manufacturing of stain and water-resistant carpets, fabrics and textiles as well as non-stick cookware (Richardson and Kimura 2015). Like most PFASs, PFOA has unusually complex properties as it has both hydrophilic (e.g. the COO^- group) and hydrophobic (e.g. fluorocarbon chain) chemical functional groups with surfactant like behaviour and surface activity (SI, Table S1). Contamination by PFASs, such as PFOA, are of concern because of their persistence in the environment due to the stability of the carbon-fluorine (C-F) bonds, their ability to bioaccumulate and their potential toxicity to many terrestrial and aquatic organisms (USEPA 2014). Due to the widespread detection of PFOA in a range

of environmental matrices (surface water, groundwater, soils, sediment), PFOA is prominent among contaminants of emerging concern (Richardson 2009, Cousins et al. 2016). A consideration of the retention of PFOA in soils is therefore important in determining mitigations strategies. However, this requires a thorough understanding of its sorption mechanisms and fate in soils.

Current research has investigated the role of sorption coefficients such as the PFOA soil-water partitioning coefficient (K_d) and the organic normalised K_d value (K_{oc}) in predicting the retention of PFOA in soils. The ranges of K_d and K_{oc} values for PFOA in soils and sediments have been reported to be between 0.12 to 70.79 L/kg and 18.20 to 31622.78 L/kg, respectively (Higgins and Luthy 2006, Kwadijk et al. 2010, Ahrens et al. 2011, Li et al. 2012, Milinovic et al. 2015). These values were usually determined from a very small number of surface soils (<10) (Higgins and Luthy 2006, Ahrens et al. 2011, Li et al. 2012, Milinovic et al. 2015). Small sample sizes can bias the results by co-variation between soil properties due to highly skewed property distributions. These studies have noted a correlation of PFOA sorption with organic carbon (OC) content (Higgins and Luthy 2006, Johnson et al. 2007, Ahrens et al. 2011, Milinovic et al. 2015). However, the partitioning of PFOA in soils is expected to also be affected by a range of soil characteristics including iron oxides, clay content, pH and other soil and solution properties (Li et al. 2012, Du et al. 2014). Metal oxides and oxyhydroxides (e.g. alumina, bohemite, goethite and hematite), could also drive electrostatic interactions between negatively charged PFOA and positively charged mineral surfaces (Wang and Shih 2011, Gao and Chorover 2012, Wang et al. 2012). Recently, Li et al. (2018)) , based on the published sorption data for soils and sediments, concluded that OC alone could only explain <10% of the variability in PFOA K_d values and that both organic and mineral phases must be taken into consideration (along with ambient conditions e.g. pH, salt concentration) when predicting sorption of PFASs in soils.

It would be advantageous to predict K_d values in diverse soil types from common soil properties, assuming that there is a reasonable correlation between the soil properties and K_d. However, such a prediction scheme would involve expensive and time-consuming laboratory analyses, generally involving wet chemistry, so that a more cost effective and rapid method would have considerable advantage.

Diffuse reflectance (mid) infrared Fourier transform spectroscopy (DRIFT) (Nguyen et al. 1991) coupled with partial least squares regression (PLSR) modelling (Martens and Naes 1992, Wold et al. 2001) has been used for many years to determine soil chemical properties. For example, PLSR models have enabled the prediction of characteristics such as soil carbon, particle size distribution, moisture retention, pH, carbonate content and concentrations of exchangeable cations (Ca^{2+}, Mg^{2+}, K^+ and Na^+) as well as concentration of total petroleum hydrocarbons in contaminated soils (Janik

and Skjemstad 1995, Janik et al. 2016b, a). The same technique has also been used to predict soil-water partitioning coefficients of soluble metal cations and oxyanions (e.g. Ag^{2+}, Co^{2+}, MoO_4^{2-}, SeO_4^{2-}) and herbicides (e.g. atrazine and diuron) (Forouzangohar et al. 2008, Kookana et al. 2008, Janik et al. 2015a, b). The DRIFT-PLSR methodology used to predict sorption coefficients for the pesticides atrazine and diuron indicated that organic matter, clays and quartz influenced sorption in surface- and sub-soils (Forouzangohar et al. 2008, Kookana et al. 2008). These studies also highlighted that the DRIFT-PLSR regression coefficients for predicting K_d for pesticides were superior to those based on the K_{oc} approach. In predicting K_d, DRIFT-PLSR has the advantage of providing an inexpensive and rapid method of determining soil properties that may influence sorption of PFOA, compared to expensive and time-consuming laboratory analyses. Considering the complex nature of PFASs, their sorption in soil is expected to depend on several processes and combined soil components (Li et al. 2018). Therefore, we hypothesised that the DRIFT-PLSR approach could be a suitable approach for modelling and predicting K_d values of these compounds across a wide range of soils.

The aim of this study was to investigate the partitioning of PFOA, one of the most commonly detected PFASs, in a wide range of soils using radiolabelled ^{14}C-PFOA, with a view to develop a predictive model based on integrated properties of organic and mineral phases in soils. The partitioning coefficients, K_d and K_{oc} values, were first evaluated by batch sorption experiments in 100 diverse Australian soils (surface soils and subsoils) with varying physico-chemical properties. Multiple linear regression and PLSR analyses, combined with the DRIFT spectra of the different soils, were used to develop models to describe and predict the partitioning of PFOA in soils.

3. Materials and methods

3.1 Materials

Radiolabelled $^{14}C_1$-PFOA in ethanol (2.035 GBq/mmol specific activity; % radiochemical purity) was purchased from American Radiolabelled Chemicals, Incorporated (St Louis, MO, USA). For the sorption experiments, an aqueous solution of ^{14}C-PFOA containing 117.7 Bq/mL (equivalent to 23.9 ng/mL) was prepared in 0.01 M $CaCl_2$. Polycarbonate (PC) 15 mL centrifuge tubes were purchased from VWR Australia. The Optiphase HiSafe 3 scintillation fluid was purchased from PerkinElmer.

3.2 Soils

Soils (100) with widely varying properties were selected from the Australian National Soil Archive (Commonwealth Scientific and Industrial Research Organisation – CSIRO). A summary of soil characteristics for all soils (n = 100) and a subset of surface soils (n = 21) are in Table 1. Individual soil

characteristics and their locations within Australia can be found in the Supplementary Information (SI, Tables S2 and Figure S1).

Table 1: minimum, maximum, median and mean of soil properties for all soils and a subset of all soils (surface soils).

Soil properties	OC (%)	pH ($CaCl_2$)	EC (1:5 dS/m)	CEC ($cmol^+/kg$)	Silt + Clay Content (%)	Cl^- (mg/kg)	ESP (%)	Exchangeable cations ($cmol^+/kg$)		
All soils (n = 100)								**Ca^{2+}**	**Na^+**	**K^+**
Min	0.1	4.9	0.0	1.6	5.0	0.0	0.0	1.2	0.0	0.1
Median	0.3	7.5	0.2	18.3	52.0	31.0	2.8	8.7	0.5	0.8
Max	3.5	8.6	3.4	45.7	88.0	2449.0	43.6	34.2	13.5	3.5
Mean	0.5	7.2	0.4	19.6	49.3	188.6	9.1	11.0	2.2	0.9
Surface soils (n = 21)										
Min	0.3	5.2	0.0	2.3	6.0	0.0	0.0	1.5	0.0	0.1
Median	1.1	6.8	0.2	17.1	37.5	21.0	1.5	10.5	0.2	1.0
Max	3.5	7.3	0.3	45.7	73.0	72.0	11.6	34.2	2.2	3.5
Mean	1.3	6.5	0.2	18.3	36.0	25.4	2.1	13.8	0.4	1.1

3.3 Batch sorption

The sorption experiments were carried out in accordance with the protocol for the adsorption-desorption using a batch equilibrium method by the Organisation for Economic Cooperation and Development (OECD, Method No. 106) (OECD 2000). Each soil was weighed (1 g ± 0.01 g) into 15 mL polycarbonate (PC) centrifuge tubes in triplicate. Preliminary experiments were carried out to assess any losses of PFOA on the materials used during the experiment (centrifuge tubes, caps, filters etc.) and only those that showed minimal losses were used.

To each tube, 9 mL of background electrolyte (0.01 M $CaCl_2$) was added, followed by 1 mL of ^{14}C-PFOA spiking solution, to achieve an initial PFOA concentration equivalent to 2.3 ± 0.1 ng/mL. Once spiked, samples were placed on an end-over-end shaker for 48 hours, for PFOA to reach equilibrium (Wang 2012, Johnson 2017, Zhou 2102), and then centrifuged at 1820 g force for 30 mins. Subsamples (0.5 mL) were taken from approximately 1 cm below the surface of the supernatant liquid for liquid scintillation counting, without filtration. The remaining sample solutions were kept for subsequent pH measurements. For quality control purposes, appropriate controls were also prepared and subjected to the same partitioning procedure and analysis: solution-only controls (spiked samples without soil) were used to determine any losses in activity due to container

sorption. All subsamples (0.5 mL) were combined with 4 mL of scintillation fluid in a scintillation vial then analysed using a liquid scintillation counter (Perkin Elmer (PE) Tri-Carb 3110 TR). Activity was measured as disintegrations per minute (dpm) at 2 min counting. The limit of detection (0.11 ng/mL) for the method was calculated as 3x the standard deviation of the blanks. External standards were used for the instrument which automatically corrected for quenching. Spiking solution was chosen to limit the ^{14}C activity but still allowing appropriate activity measurements at environmentally relevant concentrations. Background dpm values were approximately 10 dpm and raw maximum and minimum sample values were >10 times the background.

Sorption isotherms were not feasible due to the large number of soils used in this study, along with the use of radiolabelled PFOA, for the reasons of radioactive waste and cost considerations. In our study the low concentrations of PFOA used would make it unlikely that saturation of the soil adsorption sites would have occurred and hence sorption should be linear (Delle Site 2001, Ahrens et al. 2011, Schwarzenbach et al. 2016). However, there is also no current literature that investigates PFOA sorption isotherms in soils and this would be highly valuable information for future studies. For reference, in sediments Ahrens et al. (2011) found PFOA isotherms to be linear when using concentrations of 0–150 ng/L, R^2 values of 0.99, 1.00 and 1.00. Similarly, Li et al. (2012) also found PFOA sorption isotherms to be linear for six sediments when using concentrations of 32 to 200 ug/L, with R^2 values of 0.99. Linear relationships were also found for PFOA with granular activated carbon for PFOA concentrations of up to 50 mg/L where Langmuir and Freundlich equations were used and R^2 values were 0.97 and 0.96 respectively (Ochoa-Herrera and Sierra-Alvarez 2008). Due to the observed linearity at low concentrations and lack of other literature on PFOA isotherms in soils the authors have decided to assume that sorption is assumed linear.

3.4 K_d calculation

The K_d values of PFOA were calculated for each soil using the following equation:

$$K_d = \frac{S-C}{C} \times \frac{V}{M} \quad (1)$$

where K_d is the partitioning coefficient (L/kg), S is the initial solution concentration (Bq/L), C is the equilibrium solution concentration (Bq/L) and V/M is the liquid/solid ratio. The equilibrium solution concentrations were corrected to account for activity lost due to container sorption.

3.5 Diffuse reflectance infrared spectroscopy

Analysis of soil samples using DRIFT spectroscopy can be found in Janik et al. (2016b)) Briefly, samples were scanned using a benchtop Fourier transform infrared (FTIR) spectrometer (Frontier, Perkin-Elmer Inc., USA) equipped with a PE auto-focussing DRIFT accessory. Spectra of

approximately 100 mg soil sample were collected in a spectral range 7800 to 450 cm^{-1}, at a spectral resolution of 8 cm^{-1}, and for a 60 sec scan time. The pseudo absorbance units (AU) for the spectra were calculated based on the reflection spectra of the samples (R_s) and the background – a PE silicon carbide disc, which is assumed to have a reflection $R_0 = 1$ – using the following equation: $AU = Log10 (R_0/R_s)$. Spectral data were then imported into The Unscrambler-X™ V10.3 (CAMO, Norway) program for spectral baseline correction and multivariate statistical analysis.

3.6 Statistical analysis

Linear regression analysis was achieved using Microsoft Excel (2013). Statistical analysis for K_d values, with major soil groups and depth, was carried out using IBM SPSS (v. 24). Multiple linear regression analysis and DRIFT-PLSR analysis were conducted using The Unscrambler software. Multiple linear regression analysis was achieved using a cross-correlation matrix to determine which soil characteristics (regression variables) were most highly correlated with K_d values and therefore most likely to be responsible for PFOA sorption (SI, Table S3). Partial least squares regression analysis models were constructed from the soil spectral data (4000 to 450 cm^{-1}) and corresponding K_d values. The coefficient of determination (R^2) values reported for both MLR and PLSR models are those from the "leave one out" cross validation regression method, where each sample is removed in turn from each temporary model in the rotation and then its value predicted from that model. This was completed for all samples. The PLSR models use a number of factors, each contributing to the calibration of the model. The first factor is the most important contributing, often more than half of the total variance. Successive factors improve the model but each becomes less important. A single factor is approximately an MLR model. The factors used in our study are the optimum number of factors that have the lowest error for prediction. The root square mean error (RMSE) and residual predictive deviation (RPD) are also included where RMSE is defined as:

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n}(m_i - p_i)^2}{N}} \quad (2)$$

where *m* are the measured values, *p are* the predicted values, *i* is the sample being tested and *N* is the total number of samples used for the calibration. The RPD is calculated by:

$$RPD = \frac{SD}{RMSE} \quad (3)$$

where SD is the standard deviation of the original data and is a measure of the quality of the model.

4. Results and discussion

4.1 Partitioning coefficients

The K_d values of PFOA ranged from 0.56 to 14.84 L/kg, with a median value of 5.08 L/kg (SI, Figure S2 and Table S2). It is important to note that 12 soils were below the ideal 20% sorption threshold, defined in the OECD protocol, but all soil K_d values were >5% sorption of PFOA (OECD 2000). Hence, these values were appropriate for the inclusion in the regression modelling. These values had a narrower range, compared to a compilation of K_d values reported in the literature: 3.5 to 49 L/kg in soils, but a higher median K_d value (Nakata et al. 2006, Milinovic et al. 2015). Li et al. (2018)) reported median K_d values of 14.13 and 1.48 L/kg (n = 147) for PFOA for laboratory- and field-derived values respectively, based on published data on sorption in soils and sediments.

Simple linear regression analysis showed that the K_d values did not correlate well with any single soil chemical property, suggesting that multiple properties would most likely control the sorption of PFOA in these soils. The R^2 values for single linear regressions were all ≤0.40, with the highest values for OC content (R^2 = 0.36), calcium (R^2 = 0.20) and nitrogen content (R^2 = 0.29) as independent variables (SI, Table S4). Even though OC had the highest R^2 value, it could only explain about one third of the variation in PFOA sorption in these soils. This is in comparison to many other organic contaminants where the soil OC plays a major role in sorption and is why the K_d is often normalised for OC (K_{oc}) (Lüers and Ten Hulscher 1996, Spark and Swift 2002, Chefetz et al. 2008). However, because OC played a minor a role in our study, the use of K_{oc} was considered inappropriate and so the K_d was considered a better measure of PFOA sorption. It is important to note that these results may be different for soils from other regions. For example, in Europe where OC may be more important for modelling because the OC content is much higher (2–6% OC) than in Australian soils (Table 1) (Rusco et al. 2001).

Other soil chemical characteristics, including pH and clay content, were poorly correlated with PFOA sorption, with R^2 values of <0.1. Comparing the K_d values for all surface- (0 to 15 cm stratum) and sub-soils, it is apparent that sorption of PFOA significantly decreased with depth, *p* value <0.05 (Figure 1). This indicates that PFOA has even less affinity to subsoils and may readily leach into groundwater aquifers once it has passed through the surface soil. The reason for the lesser affinity could be contributed to any number of soil properties that change with increased soil depth, including OC, soil texture and pH. The changes in soil properties with depth are likely to be associated with how the soil was originally formed from parent material.

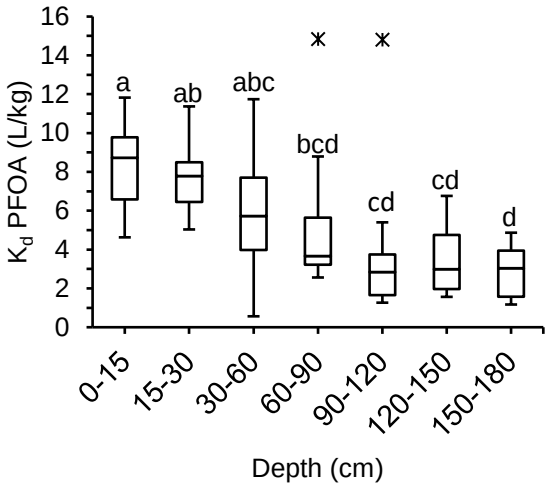

Figure 1: The K_d values of ^{14}C-PFOA in all soils (n = 100). Box plots represent the minimum, median, interquartile range and maximum. Significant differences between depths are denoted with different letters. Samples were considered outliers when they extended more than three box lengths from the edge of the box and are marked with an asterisks.

4.2 Modelling sorption from soil characteristics by MLR

In this study, a simple linear regression analysis, which correlates K_d with a single soil property, did not satisfactorily describe the sorption of PFOA in this wide range of soils. This is in contrast with the work done by Milinovic et al. (2015)) who examined the sorption of three PFAS compounds (including PFOA) in six soils and reported that OC content correlated well with sorption; albeit this was based on a small data set. Examination of their data indicated that this relationship was likely skewed by one peaty soil with high OC content (39% OC). A similar result was reported by Higgins and Luthy (2006), that sorption was predominantly influenced by the sediment OC in five sediments for multiple PFASs (including PFOA). Herein, soil OC, on its own, was found to be a poor predictor of PFOA sorption and additional soil characteristics were needed to more accurately predict PFOA partitioning behaviour across a wide range of soils using MLR. This is consistent with the review of published literature of PFOA sorption in soils and sediments (n = 147) where the OC in soils and sediments could only explain 7% of the total variation in sorption (Li et al. 2018).

Two MLR models, relating K_d to several soil properties, were produced. The first model (MLR1) included all soils (surface- and sub-soils) and the second (MLR2) included only surface soils (0–15cm). For both MLR models silt and clay content were combined as the combination had a positive correlation with K_d compared to that of sand content which had negative correlation. For selection of soil properties see Table S5 (SI).

The first MLR model (MLR1), included several soil properties; OC, pH ($CaCl_2$), silt-plus-clay content, electrical conductivity (EC), Cl^-, cation exchange capacity (CEC), exchangeable Ca^{2+}, Na^+, K^+ and exchangeable sodium percentage (ESP), (Figure 2A and 2B). However, the sorption of PFOA was only significantly influenced (above critical t-value ± 1.98) in MLR1 by a positive relationship with OC and silt-plus-clay content (p <0.05). When modelled without the other soil properties the relationship had an R^2 of 0.61, RMSE of 1.80 and RPD of 1.66 (Figure 2C and 2D). Whereas, soil pH was the only other soil property, in addition to OC and silt-plus-clay content, that appeared to be highly correlated to the sorption of PFOA in these soils (p = 0.06, approaching critical t-value) (Figure 2A). Nevertheless, the strong relationship of pH to the sorption of PFOA has been well documented in the literature (Higgins and Luthy 2006, Wang and Shih 2011, Wang et al. 2012). When pH is included in the model alongside the significant soil properties, OC and silt-plus-clay content, the R^2 value and the quality of the model (RPD) increased slightly compared to only the OC and silt-plus-clay model, 0.61 to 0.63, and 1.66 to 1.73, respectively (RMSE = 1.74) (Figure S3A and S3B).

From the literature, RPD values are a measure of the quality of the model along with R^2 and RMSE, and are grouped as follows: <1.5 is considered poor, 1.5 to 2.0 as acceptable or indicator quality, 2.0 to 3.0 as excellent or good quality and ≥3.0 as analytical quality (Chang et al. 2001, Janik et al. 2016a). The RPD values of 1.83 and 1.73 for Figures 2B and 2D, respectively, indicate the models would be considered as indicator quality.

The second MLR model (MLR2) was developed using data for surface soils only (0 to 15 cm) and included the same soil properties used for MLR1; namely, EC, Cl, CEC, exchangeable Ca^{2+}, Na^+ and K^+, ESP, OC, pH ($CaCl_2$) and silt-plus-clay content (Figure 3A). Of the original 100 soils studied only 21 were surface soils (0 to 15 cm). The MLR2 had a R^2 value of 0.48, RMSE of 1.38 and RPD of 1.43, and the only significant soil property for the model was OC (p ≤0.05) (Figure 3B). However, when OC only was modelled, without the other soil properties, the quality of the model became poor (R^2 = 0.29, RMSE = 1.63 and RPD = 1.21), suggesting that the OC content alone cannot be used to predict the sorption of PFOA in surface soils even though it was found to be the only soil property in MLR2 that was significant. However, when the OC content was modelled along with pH and silt-plus-clay content for surface soils (similar to the MLR1) the R^2 and RPD values increased markedly (R^2 = 0.74, RMSE = 0.98 and RPD = 2.02) compared to those for OC alone (Figure 3C and 3D).

The relationships obtained for the different MLR models (MLR1 and MLR2) are consistent with each other where the relationship is strongest with OC, silt-plus clay content and pH. The positive correlations between K_d and OC were as expected and were consistent with previous reports by other groups (Higgins and Luthy 2006, Ahrens et al. 2011, Milinovic et al. 2015). However, OC was

not the only soil property significantly explaining PFOA sorption, with the positive relationship of silt-plus-clay content in soil and the negative relationship with pH also being important. This suggests that PFOA sorption involves multiple mechanisms. In essence, OC is the main soil component that is capable of interacting with PFOA *via* van der Waals forces between hydrocarbon groups in organic matter and the hydrophobic alkyl chain in PFOA. However, this analysis shows that although clay content in itself is not important the mineral matter, such as exchangeable cations in clays and their characteristics in relation to soil pH, are also important, likely through electrostatic interactions (Pereira et al. 2018). Similarly, Oliver et al. (2019)), found that electrostatic interactions were also very important for variably charged soils for PFAS sorption in soils.

The importance of soil texture in the partitioning of PFOA is also apparent in both MLR models, with K_d showing a positive relationship with silt-plus-clay content (or negative correlation with sand). In this regard, total clay content was found to be poorly correlated, which leaves silt as the main contributor (Table S5). In the literature, clay content has been reported to be positively correlated with the K_d of PFOA in sediments (Li et al. 2012). Perhaps, in their study the types of clay minerals may have been different in terms of their exchange capacity. Other minerals, and particularly metal oxides and oxyhydroxides (e.g. alumina, bohemite, goethite and hematite), could also drive other charge-related adsorptive interactions, through electrostatic interactions between negatively charged PFOA and positively charged mineral sites, and the formation of surface complexes by ligand exchange (Wang and Shih 2011, Gao and Chorover 2012, Wang et al. 2012). Consistent with the relationships derived from the MLR model, these interactions are influenced by pH.

Most soils have a net negative charge and PFOA is expected to remain negatively-charged (pK_a = 2.8 (Moody and Field 2000)) at the relevant pH of most soils. However, the changes in the charge characteristics of minerals in varying soil pH can change the number of binding sites available for sorption of PFOA. For instance, it is reported in the literature that the positively charged sites on alumina and boehmite minerals decrease with increasing pH (Wang and Shih 2011, Wang et al. 2012). The inverse relationship between the increase in pH and decrease in possible binding sites available for sorption is consistent with MLR1 and MLR2 where an increase in pH resulted in a decrease in the K_d value of PFOA (Figures 2 and 3).

Apart from pH and ionic strength, cations (Na^+, K^+, Mg^{2+} and Ca^{2+}) in solution could decrease the adsorption of PFOA if binding is electrostatic, due to electrical double layer compression and bridging between PFOA molecules (Wang and Shih 2011, Wang et al. 2012, Pereira et al. 2018). However, we found no relationship between soil EC and the sorption of PFOA. While in a single soil, increasing the EC of the soil solution could affect sorption of PFOA if binding is electrostatic, this

effect was not dominant across the wide range of soils studied here. While PFOA has surfactant properties that are influenced by dissolved Ca^{2+}, there is no clear evidence that this was the case in this study.

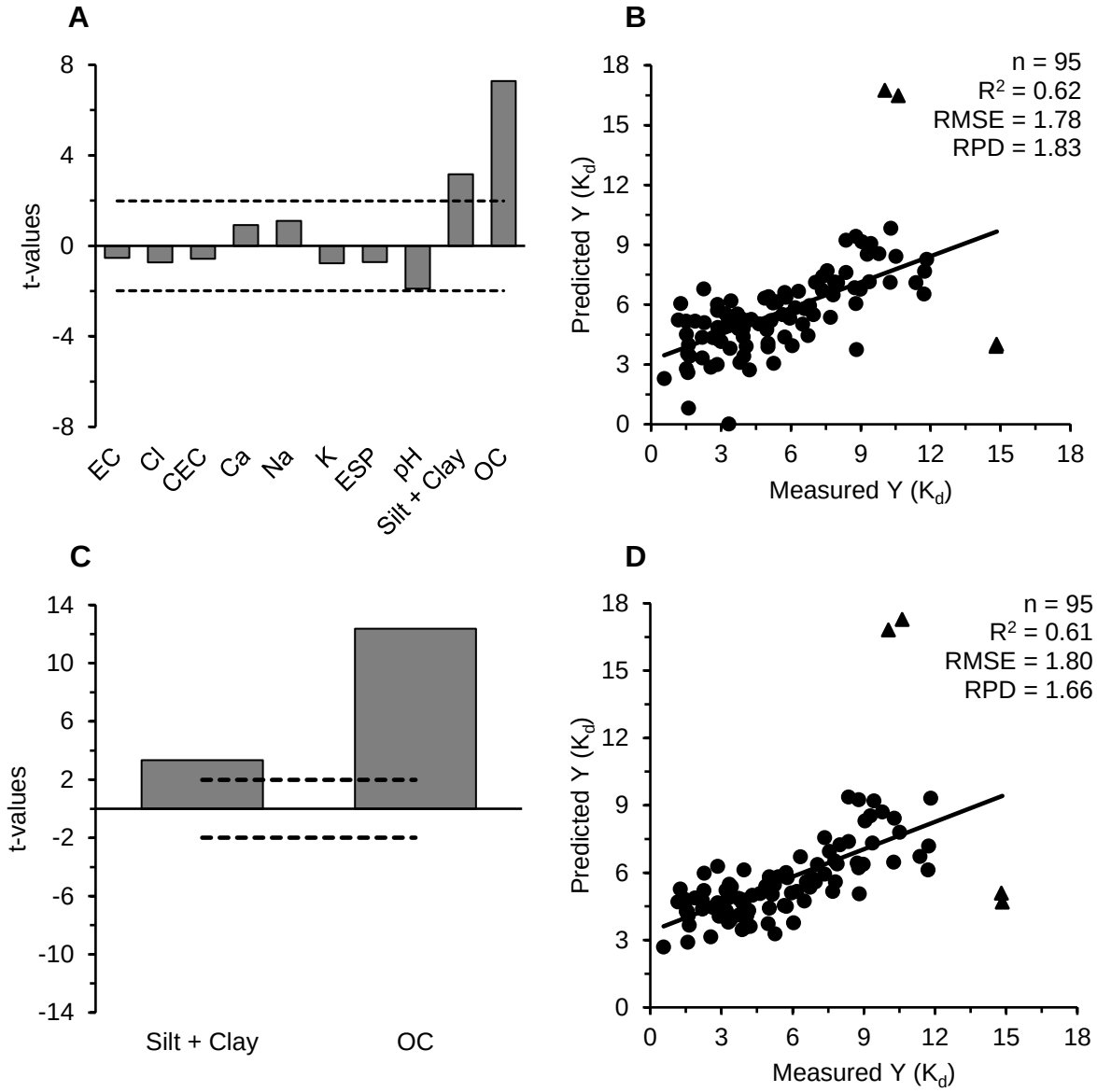

Figure 2: (A) The t-values for soil properties and (C) significant soil properties in relation to the K_d of ^{14}C-PFOA in Australian soils (n = 95) developed using a multiple linear regression model. Regression plots B and D correspond to the number of soil properties displayed in A and C, respectively. The dashed lines in (A and C) above and below represent the critical t value (t = ± 1.99). Note that four samples were considered outliers (▲) as they had high leverage and hence were not included in the model. A fifth sample was unable to be included in analysis due to missing values of soil texture.

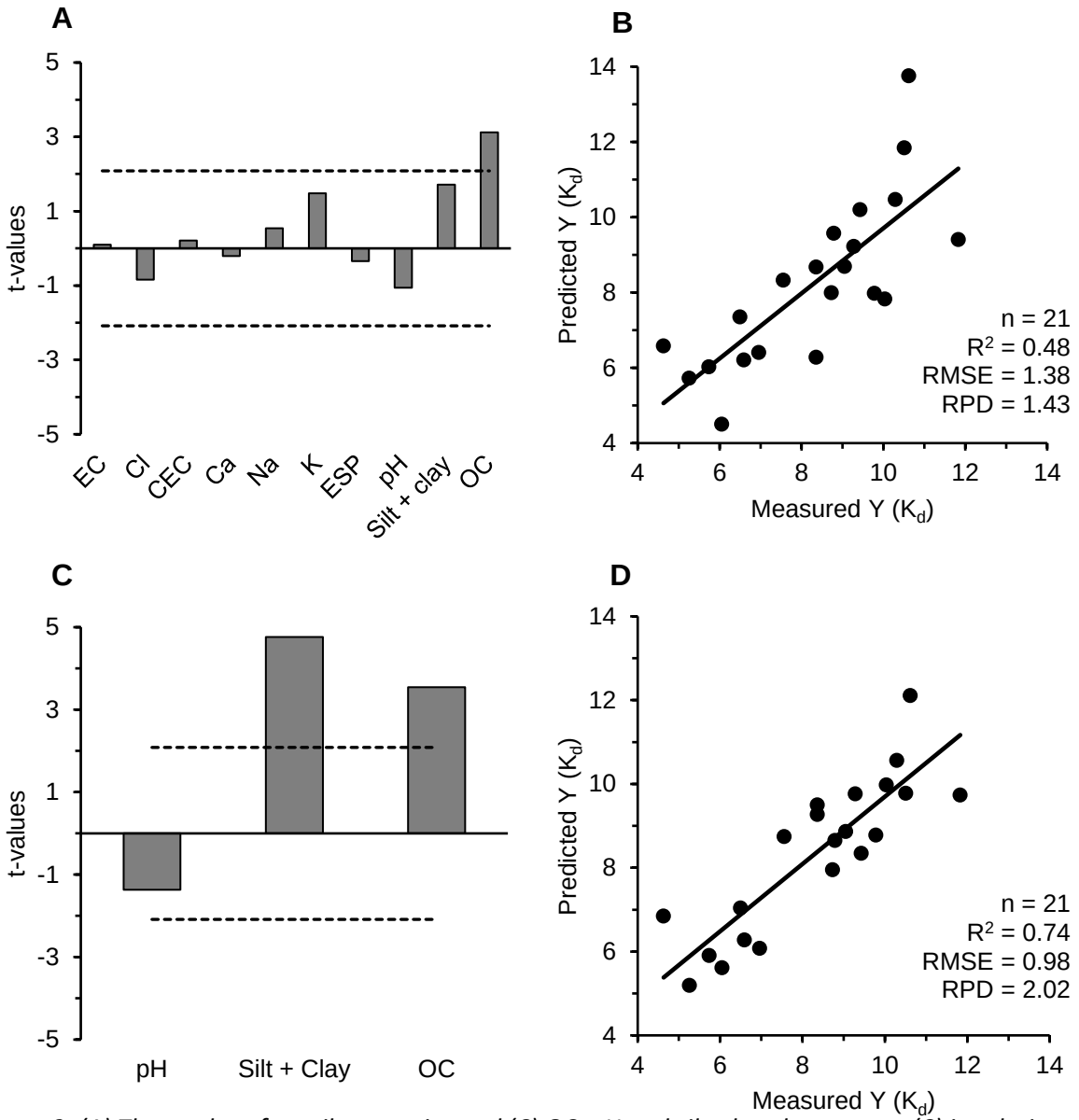

Figure 3: (A) The t-values for soil properties and (C) OC, pH and silt-plus-clay content (C) in relation to the K_d of ^{14}C-PFOA in Australian surface soils, 0–15 cm (n = 21) developed using a multiple linear regression model. Regression plots B and D correspond to the number of soil properties displayed in A and C, respectively. The dashed lines in (A and C) above and below represent the critical t value (t = ± 2.09).

4.3 Modelling sorption by DRIFT-PLSR

The MLR models were based on a relatively small number of defined soil properties assumed to be the most important in defining the relationship with K_d. This assumption limits the scope of the model to only those pre-defined soil properties and does not allow for the possibility that other properties may also have an association with K_d. The use of DRIFT-PLSR may provide additional soil

information for a better understanding of sorption process as there is no subjectivity in the selection of variables for a particular model. Furthermore, the DRIFT method has the advantage that the prediction of Kd is carried out far more rapidly and at a lower cost (Rossel et al. 2006, Zimmermann et al. 2007).

We compared the robustness of the DRIFT model with that from MLR using the same number of soil samples (n = 98). One spectral outlier identified during development of the DRIFT-PLSR model, plus another sample with missing analytical values (for soil texture) in the MLR were not included in the comparison (Figure 4). The MLR model, based on the ten soil properties (OC, pH, silt-plus-clay content, EC, Cl, CEC, exchangeable Ca^{2+}, Na^{+} and K^{+}, and ESP) for all soils, had a low R^2 value of 0.37, high error (RMSE = 2.45) and poor model quality i.e. RPD = 1.30 (Figure 4A). In contrast, the DRIFT-PLSR model (Figure 4B), based on a spectral range of 450 to 4500 cm^{-1}, had a slightly higher cross-validation R^2 value of 0.41, lower error (RMSE = 2.39) and indicator model quality, RPD = 1.77. Between the two modelling types the DRIFT-PLSR model provided a better estimate of K_d.

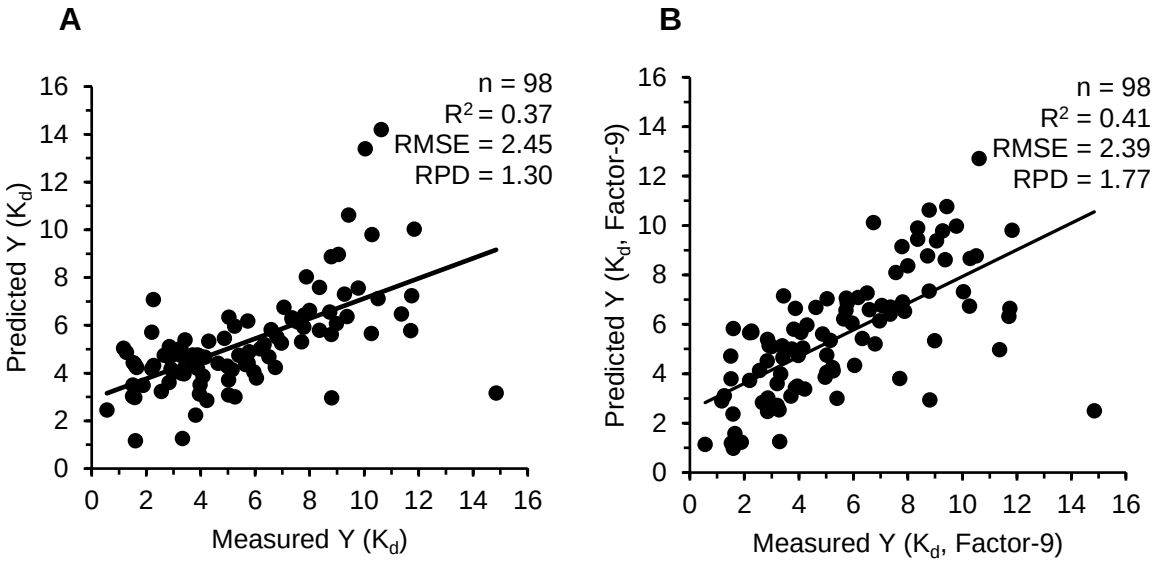

Figure 4: The measured versus predicted K_d values for ^{14}C-PFOA with two different modelling techniques: MLR model using several soil properties (OC, pH, silt-plus-clay content, EC, Cl^{-}, CEC, exchangeable Ca^{2+}, Na^{+}, K^{+} and ESP) (A) and a 9-factor DRIFT-PLSR model (B) for all soils (n = 98). Two samples were omitted from both models, where one sample was a spectral outlier and the other had a missing MLR data values for soil texture.

Similar to the MLR models, two DRIFT-PLSR models relating K_d to soil spectra were produced, the first (PLSR1) included all soils and the second (PLSR2) included only surface soils (0–15cm). For qualitative assessment purposes of DRIFT-PLSR models, the PLSR loading weights indicate the degree of positive or negative correlation with the modelled dependent variable, in this case PFOA K_d. The intensity of the loading weight, at a particular frequency, indicates the degree of correlation with K_d in the calibration model (Figure 5A and S4A, SI). Both inorganic mineral (crystalline and amorphous) and organic components contribute to the loading weights. The DRIFT-PLSR model loading weights, of all soils (PLSR1) (Figure 5A) associated with K_d, were inversely related to pyrophyllite content (a di-octahedral mica-like 2:1 silicate clay; -Al-OH stretching frequency signature at 3700 cm^{-1}) (Van der Marel and Beutelspacher 1976) and carbonates (multiple signatures; calcite at 2592 to 2517 and 1800 cm^{-1}, and dolomite at 2627 to 2522 cm^{-1}) (Nguyen et al. 1991).

The loading weights showed a positive peak for organic matter near 2930 cm^{-1}, but this was overlapped, and minor compared to that of the negative carbonate peaks near 3000 and 2850 cm^{-1} (Figure 5A). These loading weights suggest that carbonate content, possibly a surrogate for certain soil depths, was negatively correlated with the sorption of PFOA in soils (Figure 5A). However, re-analysis of the PLSR model with only the carbonate region range of 2700–2400 cm^{-1} wavenumbers revealed that the association between carbonates and K_d was very weak (R^2 = 0.27). This indicates that there may have been simply a correlation between carbonate and depth through other soil minerals present at depth, rather than a causation, so that the sorption of PFOA could not be accurately predicted in soils rich in carbonate. Similar observations have been made by other workers while predicting sorption of pesticides in Australian soils and when determining soil particle sizes using DRIFT-PLSR models (Forouzangohar et al. 2008, Janik et al. 2016a). From a mechanistic point of view, it is unlikely that the –COO terminal functional group on PFOA would bind to the negative carbonate anion, explaining the poor correlation with carbonate. The regression of measured versus cross-validation predicted PFOA K_d values for the PLSR1 model achieved an R^2 value of 0.54, RMSE of 2.00 and RPD of 1.87 (Figure 5B).

The second DRIFT-PLSR model (PLSR2) based on surface soils only, was carried out to see if there were stronger spectral correlations with PFOA sorption at the surface (Figure 1). The PLSR2 model had loading weights that suggested an inverse relationship with quartz (sand) with multiple negative peaks between 2000 to 1650 cm^{-1} (SI, Figure S4A). The associated loading weights for PLSR1 and PLSR2, in relation to the inverse relationship with quartz (and thus sand content) and thus a positive relationship with silt-plus-clay content, is consistent with both MLR models (Figures 2 and 3). Quartz is known to be a dominant sand in Australian soils which translates to strong spectral peaks in the

2000 to 1800 cm^{-1} region and the 1400 to 500 cm^{-1} region which overlaps with other clay minerals and OC peaks (Nguyen et al. 1991, Janik et al. 1998).

Compared to PLSR1, the inverse relationship with carbonates was not as intense in PLSR2 (SI, Figure S4A), likely due to a lack of carbonates in the surface soils. With this in mind, along with the fact that there is a low turn-over or accumulation of OC in subsoils, it is possible that the high amount of carbonate present in the subsoils outweighed the effect of OC in the PLSR1 model and perhaps is why the inverse relationship with carbonates was not as intense for the PLSR2 surface soil model. The measured versus predicted K_d values of surface soils for PFOA by the PLSR2 model achieved an R^2 value of 0.56, RMSE of 1.34 and RPD of 1.48 (SI, Figure S4B). It was notable that only one PLSR factor was needed to achieve this regression, suggesting a simple and yet robust model.

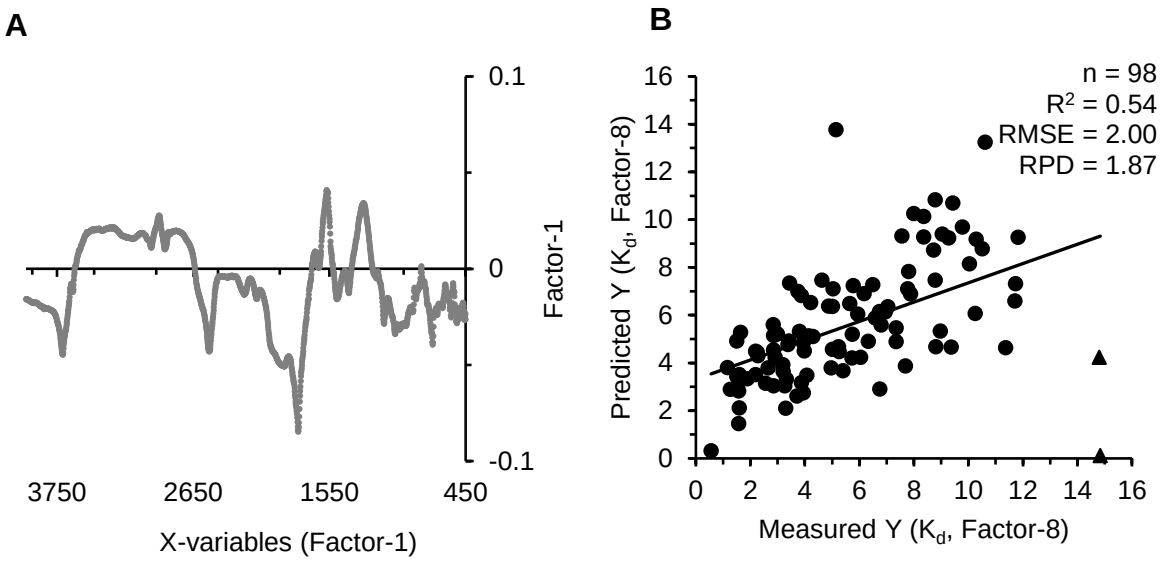

Figure 5: The DRIFT-PLSR loading weights for factor-1 associated with K_d values of PFOA in all soils (A) and the measured versus predicted K_d values for the model (B) (n = 98). Note that two outliers (▲) removed from the model were either spectral or data outliers which significantly influenced and leveraged the model.

5. Conclusions

Given the amphiphilic characteristic of PFASs and their complex sorption properties, their sorption to soil is not likely to be explained by only one or two soil properties. For development and application of MLR models, data from the chemical analysis of a range of soil properties such as OC, silt, clay and pH, is a prerequisite. Mid-infrared spectroscopy has recently developed to such an extent that it is increasingly being used to predict many of the soil properties thought to be

important in the sorption of PFOA, such as soil OC, pH, carbonate content, particle size and exchangeable cations (Ca^{2+}, Mg^{2+}, K^{+} and Na^{+}) (Janik and Skjemstad 1995, Janik et al. 2016b, a). The mid-infrared DRIFT technique explored in this study presents a superior, as well as a time- and cost-effective method, for modelling and estimating K_d of PFOA in soils, especially when compared to simple linear regressions or MLR. To date, the use of spectroscopic techniques to investigate sorption of PFAS compounds have been limited to mechanistic studies with limited application for wide scale quantitative use.

The use of DRIFT-PLSR has been shown in this study to address the growing need for phase partitioning data to effectively model fate and transport of PFOA in the environment. Given the complex nature of PFOA and other PFASs (hydrophobic, hydrophilic and surface active properties), it is crucial that organic carbon content, clay content and pH of soils are taken into consideration (Li et al. 2018). Normalising PFOA K_d values using only OC content of soil is evidently not appropriate given the number of phases in soil that affect sorption. Clearly, mid-infrared analysis and DRIFT-PLSR assessment of spectra allows an integrated assessment of multiple soil properties (in a rapid and cost-effective manner) and therefore maybe particularly suitable to predict sorption of PFASs in a large number of soils. More work is needed to assess the robustness of this approach for other PFASs in diverse range of soils and for different regions of the world.

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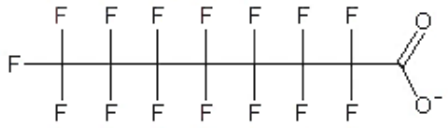
8. Supplementary Information

Predicting partitioning of radiolabelled ^{14}C-PFOA in a range of soils using diffuse reflectance IR spectroscopy

Perfluorooctanoic acid (PFOA) properties

Table S1: Selected physico-chemical properties of perfluorooctanoic acid (PFOA).

Property	PFOA
Molecular structure	
Molecular formula	$C_8HF_{15}O_2$
CAS no.	335-67-1
Molar Mass (g/mol)	414.07
Solubility in water (g/L)	2.3–4.3 (Bhhatarai and Gramatica 2010, Inoue et al. 2012, Rahman et al. 2014)
Acid/Base	Acidic
pKa	0.5,(Goss 2007) 2.8 (Moody and Field 2000)

Soil Characteristics

One hundred soils were selected to give a wide range of physico-chemical properties (Table S2).

Table S2: Selected characteristics of the soils used in the study and the K_d values of PFOA in these soils.

									Exchangeable cations ($cmol^+/kg$)					Particle size (%)			Total (%)			
Soil No.	Depth* (cm)	Soil type texture or other descriptor	Australian soil classification order	State	OC	EC (1:5 dS/m)	Cl (mg/kg)	CEC ($cmol^+/kg$)	Ca	Mg	Na	K	ESP (%)	Sand	Silt	Clay	C	N	K_d ^{14}C-PFOA (L/kg)	pH ($CaCl_2$)
1	0-15	Sandy clay loam	Ferrosol	NSW	1.6	0.1	22.9	17.9	12.6	1.7	0.1	3.5	0.3	47.2	19.2	33.5	1.6	0.1	11.8	5.9
2	90-120	Sandy clay loam	Ferrosol	NSW	0.3	0.0	20.1	14.9	10.3	3.5	0.2	0.8	1.0	27.4	12.4	60.2	0.3	0.1	5.8	6.8
3	150-180	Sandy clay loam	Ferrosol	NSW	0.2	0.0	12.3	16.5	11.4	4.0	0.3	0.9	1.5	29.4	13.9	56.7	0.2	0.0	4.9	6.6
4	90-120	Sandy clay loam	Kandosol	NSW	0.1	0.1	80.2	9.0	3.4	4.5	0.2	0.9	2.3	44.4	12.4	43.3	0.1	0.0	3.9	5.8
5	150-180	Sandy clay loam	Kandosol	NSW	0.1	0.1	39.7	8.0	2.8	4.3	0.2	0.6	3.0	51.4	10.2	38.4	0.1	0.0	4.2	5.5
6	90-120	Sandy clay	Kandosol	NSW	0.1	0.1	11.4	19.7	9.1	7.7	0.6	2.3	2.8	41.6	7.8	50.6	0.1	0.0	1.5	6.9
7	30-60	Sandy clay	Vertosol	NSW	0.6	0.3	14.5	29.1	17.6	6.6	4.3	0.5	15.0	46.5	6.0	47.5	1.0	0.1	7.3	7.5
8	0-15	Loam	Vertosol	NSW	1.3	0.0	22.4	13.6	9.8	2.1	0.2	1.5	1.4	43.8	36.1	20.1	1.7	0.1	9.3	6.3
9	60-90	Loam	Vertosol	NSW	0.2	0.2	39.3	27.2	15.7	9.7	1.5	0.3	5.5	30.8	32.4	36.9	0.3	0.0	5.2	7.4
10	15-30	Sandy clay loam	Ferrosol	NSW	0.8	0.2	25.2	17.4	14.7	1.4	0.0	1.3	0.1	48.9	16.1	35.1	1.0	0.1	7.8	7.3
11	60-90	Sandy clay loam	Ferrosol	NSW	0.1	0.1	17.1	13.5	8.7	3.9	0.0	0.9	0.0	35.5	16.6	47.9	0.1	0.0	3.4	7.4
12	15-30	Sandy clay loam	Chromosol	NSW	0.4	0.0	32.7	10.3	6.8	3.0	0.1	0.4	0.9	50.5	20.9	28.6	0.5	0.1	6.2	6.0
13	150-180	Sandy clay loam	Chromosol	NSW	0.1	0.2	190.1	16.1	9.3	5.8	0.5	0.5	3.2	52.1	19.5	28.4	0.1	0.0	3.2	6.3
14	90-120	Sandy clay	Chromosol	NSW	0.1	2.6	880.0	39.5	10.3	17.8	10.5	0.9	26.6	38.5	8.9	52.6	0.5	0.0	2.2	7.7
15	150-180	Sandy clay	Chromosol	NSW	0.1	1.8	1320.0	28.7	5.3	14.0	9.0	0.5	31.2	36.5	9.3	54.2	0.6	0.0	1.5	7.9
16	120-150	Sandy loam	Calcarosol	NSW	0.1	0.4	99.0	21.8	6.5	8.9	3.5	2.9	16.0	43.2	7.6	49.3	0.3	0.0	2.7	7.7
17	30-60	Sandy loam	Chromosol	NSW	0.2	0.0	9.6	8.7	6.1	2.1	0.0	0.4	0.5	53.0	8.7	38.3	0.2	0.0	5.6	5.7

18	150-180	Sandy clay	Vertosol	NSW	0.1	0.8	668.2	27.4	5.2	13.9	7.5	0.7	27.6	38.7	10.3	51.0	0.1	0.0	1.2	6.2
19	0-15	Sandy loam	Calcarosol	NSW	0.5	0.1	19.0	8.4	5.3	1.8	0.1	1.2	1.5	76.2	3.8	20.0	0.7	0.1	6.5	6.0
20	120-150	Sandy loam	Calcarosol	NSW	0.1	0.6	398.2	18.5	2.3	10.6	3.8	1.8	20.5	48.2	17.7	34.1	2.8	0.0	1.6	7.9
21	90-120	Sandy loam	Kurosol	NSW	0.1	0.0	12.2	12.3	5.6	5.6	0.2	0.8	1.9	53.2	6.8	40.0	0.1	0.0	3.7	6.1
22	0-15	Sandy clay loam	Kandosol	NSW	1.1	0.1	30.9	4.8	3.0	0.7	0.1	0.9	1.2	56.9	21.5	21.6	1.2	0.1	8.4	5.3
23	60-90	Sandy loam	Kurosol	NSW	0.2	0.1	17.4	18.2	11.0	6.1	0.1	1.0	0.6	33.2	1.9	64.9	0.2	0.0	3.2	7.2
24	120-150	Sandy loam	Kurosol	NSW	0.2	0.1	22.8	13.3	7.8	4.7	0.1	0.7	0.9	54.0	18.2	27.7	1.0	0.0	2.2	7.5
25	150-180	Sandy loam	Kurosol	NSW	0.1	0.1	43.0	16.4	8.8	6.4	0.3	1.0	1.7	54.8	25.2	20.0	1.2	0.0	1.6	7.6
26	0-15	Sandy loam	Sodosol	NSW	1.1	0.1	30.9	7.6	6.8	0.5	0.1	0.2	0.7	69.1	22.3	8.6	1.5	0.1	7.6	5.2
27	30-60	Sandy loam	Sodosol	NSW	0.1	0.0	30.9	2.9	2.4	0.3	0.0	0.1	1.6	65.2	23.0	11.8	0.1	0.0	3.3	4.9
28	90-120	Sandy loam	Sodosol	NSW	0.1	0.1	33.7	8.8	4.6	3.8	0.1	0.2	1.4	65.7	12.4	21.9	0.1	0.0	5.0	5.4
29	150-180	Sandy loam	Sodosol	NSW	0.1	0.0	30.9	5.6	2.5	2.7	0.1	0.2	1.5	73.5	9.9	16.6	0.1	0.0	3.9	4.9
30	30-60	Clay	Chromosol	NSW	0.5	0.1	9.0	26.1	15.0	9.1	1.8	0.2	6.7	30.3	19.1	50.6	0.6	0.0	11.7	7.1
31	0-15	Sandy clay loam	Chromosol	NSW	1.1	0.1	17.3	19.0	7.5	8.4	2.2	0.9	11.6	44.5	12.0	43.5	1.2	0.1	10.5	5.2
32	30-60	Sandy clay loam	Chromosol	NSW	0.2	0.1	19.9	23.4	5.9	12.0	3.3	2.2	14.0	38.5	11.2	50.3	0.4	0.0	7.7	6.1
33	150-180	Sandy clay loam	Chromosol	NSW	0.1	0.1	39.0	19.7	6.8	9.0	2.6	1.2	13.3	42.0	14.5	43.6	0.1	0.0	2.9	7.2
34	0-6	Sandy loam	Calcarosol	SA	3.5	0.2	44.0	21.6	20.3	1.1	0.0	0.2	0.0	70.0	11.0	19.0	9.2	0.3	10.0	7.0
35	18-40	Sandy loam	Calcarosol	SA	0.8	0.3	220.0	7.7	6.7	0.9	0.0	0.1	0.0	81.0	5.0	14.0	6.1	0.1	6.7	7.5
36	40-60	Sandy loam	Calcarosol	SA	0.3	0.3	230.0	5.3	4.5	0.7	0.0	0.1	0.0	84.0	4.0	12.0	6.0	0.1	4.2	7.8
37	15-65	Loamy sand	Sodosol	SA	0.1	0.1	0.0	1.6	1.2	0.3	0.0	0.1	0.0	95.0	1.0	4.0	0.4	0.0	0.6	7.6
38	65-100	Loamy sand	Sodosol	SA	0.1	0.1	0.0	9.2	5.7	3.0	0.0	0.4	0.0	78.0	1.0	20.0	0.5	0.0	2.6	7.7
39	0-10	Loamy sand	Tenosol	SA	0.3	0.1	0.0	2.3	1.5	0.6	0.0	0.1	0.0	93.0	1.0	5.0	0.8	0.1	5.3	6.9
40	125-150	Loamy sand	Tenosol	SA	0.1	0.1	0.0	6.0	3.1	2.6	0.0	0.3	0.0	87.0	1.0	12.0	0.3	0.0	1.6	7.4
41	0-15	Sandy clay loam	Chromosol	SA	1.7	0.2	45.0	29.3	23.3	3.3	0.9	1.8	3.1	62.0	8.9	29.1	2.1	0.2	8.8	7.0
42	90-120	Sandy clay loam	Chromosol	SA	0.1	1.8	2340.0	27.4	8.5	6.3	11.9	0.7	43.6	60.3	9.1	30.6	4.8	0.0	1.6	8.1
43	15-30	Sandy loam	Calcarosol	SA	1.0	0.2	36.0	22.1	15.4	5.4	0.5	0.8	2.4	49.2	12.4	38.4	4.1	0.1	8.0	7.6
44	90-120	Sandy loam	Calcarosol	SA	0.2	0.3	46.5	23.5	7.3	10.1	4.5	1.6	21.7	36.7	7.5	55.8	6.9	0.0	14.8	8.6
45	120-150	Sandy loam	Calcarosol	SA	0.2	0.5	112.0	13.7	3.6	4.7	4.3	1.1	31.1	39.8	4.8	55.4	7.0	0.0	5.1	8.6
46	0-15	Loamy sand	Chromosol	SA	0.9	0.1	7.0	9.1	7.2	1.2	0.2	0.5	2.2	90.1	1.0	9.5	1.0	0.1	7.0	6.7
47	60-80	Loamy sand	Chromosol	SA	0.5	0.1	15.0	19.9	15.3	4.1	0.2	0.3	1.0	67.1	5.3	27.6	2.1	0.0	4.3	7.6

48	0-10	Loam	Calcarosol	SA	1.7	0.3	21.0	43.4	29.3	11.4	0.7	2.0	1.6	62.5	12.1	25.4	3.3	0.2	9.4	7.3
49	100-150	Sandy loam	Sodosol	SA	0.2	1.6	843.0	34.2	9.5	13.4	9.8	1.5	28.7	22.6	8.1	69.3	2.7	0.0	5.0	8.1
50	15-30	Clay loam	Calcarosol	SA	0.4	0.2	16.0	29.6	21.3	6.3	0.7	1.3	2.4	39.8	7.7	52.5	1.4	0.1	5.0	7.5
51	0-20	Loamy sand	Sodosol	SA	0.6	0.2	20.0	5.7	4.7	0.7	0.1	0.2	2.3	76.9	1.3	21.8	0.9	0.1	4.6	6.9
52	80-100	Loamy sand	Sodosol	SA	0.2	0.3	33.0	19.4	10.6	4.2	3.6	0.9	18.5	38.5	12.2	49.3	5.4	0.1	1.3	8.0
53	0-10	Loam	Calcarosol	SA	3.4	0.3	40.0	33.3	28.2	2.1	0.0	3.0	0.0	44.0	16.0	40.0	6.8	0.4	10.6	7.0
54	30-50	Loam	Calcarosol	SA	1.0	0.3	73.0	17.4	13.7	2.7	0.3	0.6	1.6	42.0	21.0	37.0	6.1	0.2	7.4	7.5
55	15-30	Loam	Vertosol	SA	0.6	0.4	194.0	33.8	25.7	3.8	3.6	0.7	10.7	34.0	16.0	50.0	2.8	0.2	10.3	7.5
56	80-110	Loam	Vertosol	SA	0.3	0.5	135.0	27.1	12.1	8.2	5.9	0.9	21.8	25.0	20.0	55.0	4.4	0.1	5.4	8.0
57	14-30	Loam	Calcarosol	SA	0.7	0.2	17.0	24.1	19.6	3.0	0.5	1.0	2.1	46.0	15.0	40.0	3.2	0.2	9.0	7.6
58	115-150	Loam	Calcarosol	SA	0.4	0.4	64.0	14.2	5.9	3.8	3.7	0.8	26.2	N/A	N/A	N/A	5.9	0.1	6.8	7.7
59	30-50	Sandy loam	Dermosol	SA	0.5	0.2	20.0	21.0	15.1	5.0	0.4	0.5	1.8	45.6	11.5	42.9	4.0	0.1	6.8	7.7
60	110-150	Sandy loam	Dermosol	SA	0.1	0.8	384.0	26.8	6.8	8.2	10.2	1.6	38.0	45.6	6.1	48.3	2.0	0.1	3.9	8.2
61	110-150	Loam	Calcarosol	SA	0.1	0.9	457.0	27.3	7.3	7.9	10.8	1.3	39.6	39.0	10.0	50.0	3.1	0.1	1.9	8.2
62	0-10	Loam	Dermosol	SA	1.5	0.3	18.0	18.7	14.7	2.2	0.4	1.4	2.0	58.0	10.0	33.0	1.7	0.2	9.8	6.8
63	30-50	Loam	Dermosol	SA	0.6	0.2	44.0	25.3	19.6	4.5	0.7	0.6	2.7	48.0	12.0	40.0	4.9	0.1	5.7	7.5
64	0-20	Loamy sand	Calcarosol	SA	0.9	0.2	18.0	18.0	15.6	1.6	0.2	0.5	1.1	83.0	2.0	15.0	2.0	0.2	6.6	7.2
65	80-100	Loamy sand	Calcarosol	SA	0.2	0.2	21.0	15.9	8.5	6.3	0.8	0.4	5.1	76.0	5.0	19.0	3.5	0.1	1.7	8.1
66	0-20	Loamy sand	Chromosol	SA	0.4	0.1	14.0	4.4	3.1	0.9	0.2	0.3	4.5	89.0	1.0	10.0	0.8	0.1	6.0	6.7
67	60-90	Clay loam	Sodosol	SA	0.2	0.9	589.0	20.1	8.6	6.4	4.3	0.8	21.4	12.0	27.0	61.0	3.9	0.1	2.9	7.9
68	90-130	Clay loam	Sodosol	SA	0.2	1.1	934.0	18.5	7.1	6.7	4.0	0.7	21.6	15.0	35.0	50.0	3.0	0.1	2.3	8.0
69	30-60	Clay	Vertosol	SA	0.7	0.3	15.2	41.4	25.6	10.7	3.0	2.1	7.2	16.9	17.5	65.6	1.2	0.2	11.7	7.5
70	60-105	Clay	Vertosol	SA	0.4	0.5	74.4	39.6	14.9	14.4	8.5	1.8	21.5	13.3	18.8	67.9	2.5	0.2	6.3	7.8
71	10-30	Silt loam	Sodosol	SA	0.3	0.2	14.0	7.1	5.3	1.4	0.0	0.4	0.0	48.9	27.0	24.2	0.6	0.1	6.0	6.7
72	15-30	Clay	Calcarosol	SA	0.6	0.2	25.0	35.3	21.5	9.5	3.5	0.8	9.9	43.1	6.4	50.4	1.0	0.1	7.0	7.3
73	35-55	Clay loam	Calcarosol	SA	0.4	0.2	71.0	22.9	15.7	4.3	2.5	0.4	10.9	49.0	9.0	41.0	5.1	0.1	3.4	7.5
74	0-15	Clay loam	Calcarosol	SA	1.3	0.2	13.0	37.1	30.3	5.0	0.4	1.4	1.1	50.0	10.0	40.0	2.2	0.2	9.0	7.2
75	0-8	Loam	Calcarosol	SA	0.9	0.2	30.0	17.1	10.5	4.9	0.7	1.0	4.1	68.0	9.0	24.0	1.2	0.1	8.7	5.9
76	85-125	Loam	Calcarosol	SA	0.2	0.4	161.0	29.3	14.5	7.9	6.0	0.9	20.5	46.0	13.0	41.0	2.2	0.1	3.7	7.5
77	10-20	Clay loam	Calcarosol	SA	0.5	0.2	10.0	30.4	18.1	8.1	2.9	1.3	9.5	55.0	7.0	38.0	0.9	0.1	7.8	6.5

78	0-15	Clay	Vertosol	SA	1.1	0.3	18.0	45.7	34.2	9.1	0.7	1.7	1.5	27.0	14.0	59.0	1.6	0.2	10.3	6.6
79	60-90	Clay	Vertosol	SA	0.4	0.2	9.0	44.4	27.3	14.7	1.2	1.2	2.7	22.0	14.0	64.0	1.0	0.1	7.9	7.4
80	90-120	Clay loam	Calcarosol	SA	0.2	0.2	8.0	36.5	28.4	6.4	0.3	1.4	0.8	33.0	7.0	60.0	1.5	0.1	2.3	8.1
81	60-90	Loamy sand	Kandosol	SA	0.4	0.1	18.0	18.3	11.6	5.9	0.5	0.3	2.7	61.0	6.0	33.0	2.7	0.1	3.3	7.7
82	90-120	Loamy sand	Kandosol	SA	0.2	0.3	22.0	16.1	8.1	5.4	2.2	0.4	13.7	61.0	6.0	33.0	3.8	0.1	1.5	8.0
83	0-10	N/A	Calcarosol	SA	1.6	0.3	72.0	16.2	14.5	1.1	0.0	0.6	0.0	50.0	30.0	20.0	2.5	0.2	8.4	6.8
84	40-60	N/A	Calcarosol	SA	0.3	0.6	492.0	4.8	2.9	1.5	0.3	0.1	6.3	46.0	37.0	17.0	2.6	0.1	8.8	7.8
85	90-120	Sandy loam	Chromosol	SA	0.2	0.8	853.0	42.4	11.7	15.8	13.5	1.4	31.8	48.0	10.0	42.0	2.3	0.1	3.8	7.8
86	90-120	N/A	Sodosol	SA	0.1	0.9	510.0	26.1	5.7	9.6	9.8	1.0	37.5	48.0	7.0	45.0	2.1	0.0	5.0	8.2
87	90-120	Loamy sand	Calcarosol	SA	0.1	0.4	63.3	10.4	4.1	4.2	1.6	0.5	15.9	60.5	18.2	21.2	1.8	0.1	2.9	7.9
88	25-50	Loamy sand	N/A	SA	0.2	0.1	0.0	9.7	7.6	1.7	0.0	0.4	0.0	80.5	4.7	14.7	0.5	0.1	4.0	7.6
89	50-80	Loamy sand	N/A	SA	0.2	0.2	25.8	13.1	9.0	3.7	0.0	0.4	0.0	67.6	6.8	25.6	0.8	0.1	3.4	7.6
90	80-110	Loamy sand	N/A	SA	0.1	0.2	72.4	13.1	7.5	5.0	0.2	0.4	1.6	53.9	16.5	29.7	1.1	0.1	3.0	7.7
91	40-60	Sandy clay loam	Kandosol	SA	0.6	1.0	910.0	13.3	6.2	4.7	1.9	0.5	14.1	43.6	26.3	30.1	4.4	0.1	3.9	7.7
92	100-125	Sandy clay loam	Kandosol	SA	0.2	1.3	1092.0	7.8	3.0	3.3	1.2	0.3	15.6	48.9	32.6	18.5	4.5	0.1	2.8	8.0
93	10-20	Clay loam	Calcarosol	SA	0.7	0.3	255.0	32.9	23.8	5.6	2.5	1.0	7.7	40.8	12.6	46.6	2.3	0.1	11.4	7.3
94	105-150	Clay loam	Calcarosol	SA	0.2	3.4	2449.0	39.4	15.9	9.9	12.4	1.2	31.5	28.1	12.6	59.3	1.6	0.1	3.3	7.8
95	0-10	Loamy sand	Kandosol	SA	0.5	0.1	31.0	10.3	7.9	1.0	0.3	1.1	3.1	85.4	3.9	10.7	0.9	0.1	5.7	7.2
96	30-50	Loamy sand	Kandosol	SA	0.3	0.1	0.0	9.7	7.3	1.3	0.2	0.9	2.3	77.8	4.9	17.4	1.2	0.1	4.1	7.6
97	25-65	Silty clay loam	Chromosol	SA	0.4	0.3	47.0	22.4	11.2	9.7	0.8	0.7	3.6	24.2	24.4	51.4	0.8	0.1	8.8	7.3
98	70-100	Sandy loam	Dermosol	SA	0.2	0.5	0.0	12.6	3.2	4.6	3.8	1.0	30.3	53.2	13.0	33.8	4.6	0.1	2.9	8.2
99	10-30	Sandy loam	Sodosol	SA	0.7	0.4	65.0	24.2	12.9	7.7	1.8	1.8	7.4	24.6	10.2	65.2	1.8	0.1	9.4	7.3
100	60-90	Sandy loam	Sodosol	SA	0.2	0.4	126.0	10.1	4.1	3.8	2.0	0.2	19.8	45.8	24.4	29.8	1.3	0.1	14.8	7.9

*For statistical analysis, as the ranges of depth varied between samples, a layer number was allocated to each depth of soil (Table S2).

Locations of selected soil samples

Google, My Maps software was used to create a map of locations for the samples selected (Figure S1). Some soils share the same map location but are from different soil depths, in which case only one pin-point is shown on the map for that location (Figure S1).

Figure S1: Locations of samples using Google, My Maps software. The purple pin-pointers indicate the location of the soil samples within regions of southern and eastern Australia.

Layer number and depth of soils

The soils used in this study had a depth range and associated layer number for that depth range. The depth ranges were not always the same throughout the sample set (Table S3). Since the archive layer numbers were not always consistent with the depth range, the layer numbers were reclassified to the depth range that contained the majority of the sample. There were seven layer numbers (1 to 7) assigned for the following depth ranges: 0 to 15 cm, 15 to 30 cm, 30 to 60 cm, 60 to 90 cm, 90 to 120 cm, 120 to 150 cm, and 150 to 180 cm.

Table S3: The number of samples per depth range and the associated layer number, 1 to 7, given to depths of 0 to 15 cm, 15 to 30 cm, 30 to 60 cm, 60 to 90 cm, 90 to 120 cm, 120 to 150 cm and 15 to 180 cm.

Depth range (cm)	Samples per depth range	Layer number for depth range
0 - 6	1	1
0 - 8	1	1
0 - 10	6	1
0 - 15	10	1
0 - 20	3	1
10 - 20	2	2
10 - 30	2	2
14 - 30	1	2
15 - 30	6	2
15 - 65	1	3
18 - 40	1	2
25 - 50	1	3
25 - 65	1	3
30 - 50	4	3
30 - 60	6	3
35 - 55	1	3
40 - 60	3	3
50 - 80	1	4
60 - 105	1	4
60 - 80	1	4
60 - 90	7	4
65 - 100	1	4
70 - 100	1	4
80 - 100	2	5
80 - 110	2	5
85 - 125	1	5
90 - 120	13	5
90 - 130	1	5
100 - 125	1	5
100 - 150	1	6
105 - 150	1	6
110 - 150	2	6
115 - 150	1	6
120 - 150	4	6
125 - 150	1	6
150 - 180	8	7

The K_d of PFOA in relation to the Australian soil classification order

The sorption of PFOA can be observed in Figure S2 in relation to the Australian soil classification order (ASC). Two samples with higher K_d values (8.36 for Kandosol and 14.84 for Sodosol) than those of other soil samples for the same order were considered outliers as they extended more than three box lengths away from the edge of the box (where 50% of the samples lie).

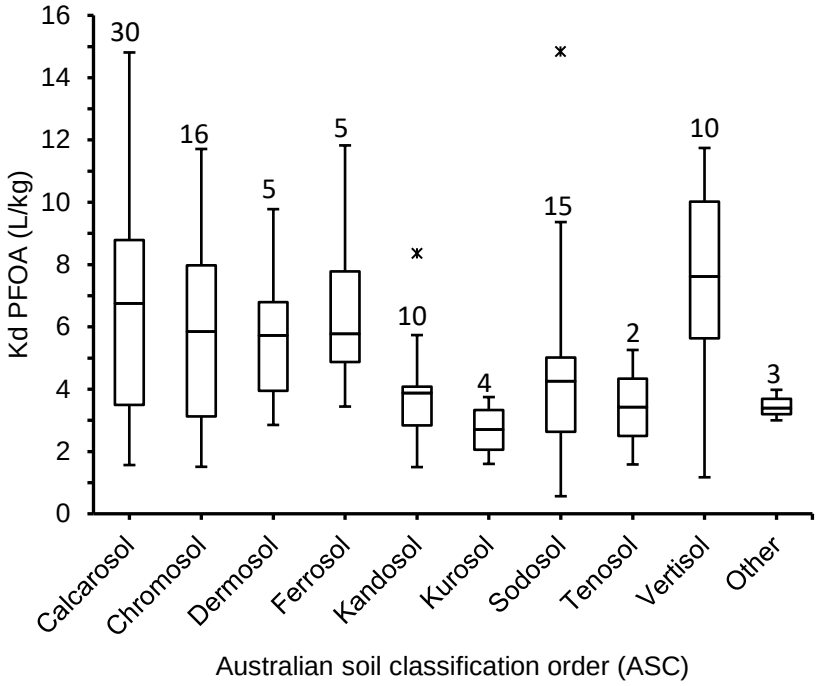


Figure S2: Average K_d values of ^{14}C-PFOA in Australian soils (n = 100). The soils are categorized by the Australian soil classification order (ASC)(Isbell 2016) and numbers above box plots represent the number of samples per soil order. Box plots represent the minimum, median, interquartile range and maximum K_d values and samples that extended more than three box lengths from the edge of the box were considered outliers (*). Individual K_d values are in Table S1.

Linear relationships; soil characteristics and sorption coefficients for PFOA

Table S4: Regression coefficients of determination for linear relationships between individual soil properties and sorption (K_d) values of radiolabelled ^{14}C-PFOA in 100 Australian soils, for all soils (n = 100) and surface soils alone (n = 21).

	K_d PFOA (R^2 value)	
Soil property	**All soils**	**Surface soils**
OC (%)	0.36	0.45
EC (1:5 dS/m)	0.06	0.15
Cl (mg/kg)	0.08	0.07
B (Hot water mg/kg)	0.04	0.25
CEC ($cmol^+/kg$)	0.05	0.41
Ca ($cmol^+/kg$)	0.20	0.35
Mg ($cmol^+/kg$)	0.01	0.22
Na ($cmol^+/kg$)	0.05	0.11
K ($cmol^+/kg$)	0.07	0.49
ESP (%)	0.06	0.00
Sand content (%)	0.01	0.68
Silt + Clay content (%)	0.02	0.68
pH ($CaCl_2$)	0.04	0.05
N (%)	0.29	0.34

Selection of soil properties for MLR; all soils

A cross-correlation matrix was produced to choose which soil properties to use in the MLR analysis (Table S5). Looking solely at the Pearson correlation coefficient (*r*) relating to K_d, those that were >0.1 were chosen for analysis (Table S5). It should also be noted that co-correlations between soil properties were accounted for by selecting only one of the co-correlating properties even if the *r* value was >± 0.1. For this reason, sand content and B were not included in the MLR analysis as they had co-correlations with silt-plus-clay content and Cl, respectively.

The MLR model using all soils and only the surface-soils originally included eleven soil properties; EC, Cl, CEC, Ca^{2+}, Na^{+}, K^{+}, ESP, pH ($CaCl_2$), OC and silt-plus-clay content. The model statistics including *p* value, R^2, RMSE and RPD were determined. One sample was not included in analysis as it had missing values for sand, silt and clay content

References

1. Isbell, R. F. a. 2016. The Australian soil classification. Second edition. edition. CSIRO Publishing.

Table S5: Correlation matrix of soil properties relating to the sorption coefficient, K_d, of PFOA in soils (n = 100). Correlations are represented by Pearson's coefficient, r values and units for the different soil properties are stated in the first and second column from the left.

Soil properties		**EC**	**Cl**	**B**	**CEC**	**Ca^{2+}**	**Mg^{2+}**	**Na^{+}**	**K^{+}**	**ESP**	**Sand content**	**Silt + Clay content**	**K_d**	**pH ($CaCl_2$)**	**OC (%)**
	EC (1:5 dS/m)	1.00	0.90	0.52	0.38	-0.04	0.48	0.77	0.06	0.70	-0.32	0.32	-0.24	0.40	-0.17
	Cl (mg/kg)		1.00	0.37	0.26	-0.11	0.35	0.70	-0.02	0.64	-0.23	0.22	-0.29	0.30	-0.20
	B (Hot water mg/kg)			1.00	0.30	-0.08	0.38	0.71	0.23	0.75	-0.28	0.28	-0.19	0.44	-0.19
	CEC ($cmol^+/kg$)				1.00	0.78	0.75	0.54	0.52	0.36	-0.61	0.61	0.23	0.32	0.20
Exchangeable cations ($cmol^+/kg$)	**Ca^{2+}**					1.00	0.24	-0.03	0.38	-0.19	-0.35	0.35	0.45	0.13	0.52
	Mg^{2+}						1.00	0.68	0.37	0.57	-0.61	0.61	-0.08	0.29	-0.25
	Na^{+}							1.00	0.21	0.92	-0.40	0.39	-0.22	0.42	-0.27
	K^{+}								1.00	0.16	-0.40	0.40	0.26	0.04	0.30
	ESP (%)									1.00	-0.38	0.38	-0.23	0.48	-0.32
	Sand content (%)										1.00	-1.00	-0.16	-0.21	0.08
	Silt + Clay content (%)											1.00	0.16	0.21	-0.08
	K_d (L/kg)												1.00	-0.21	0.60
	pH ($CaCl_2$)													1.00	-0.22
	OC (%)														1.00

MLR all soils with significant soil properties and pH

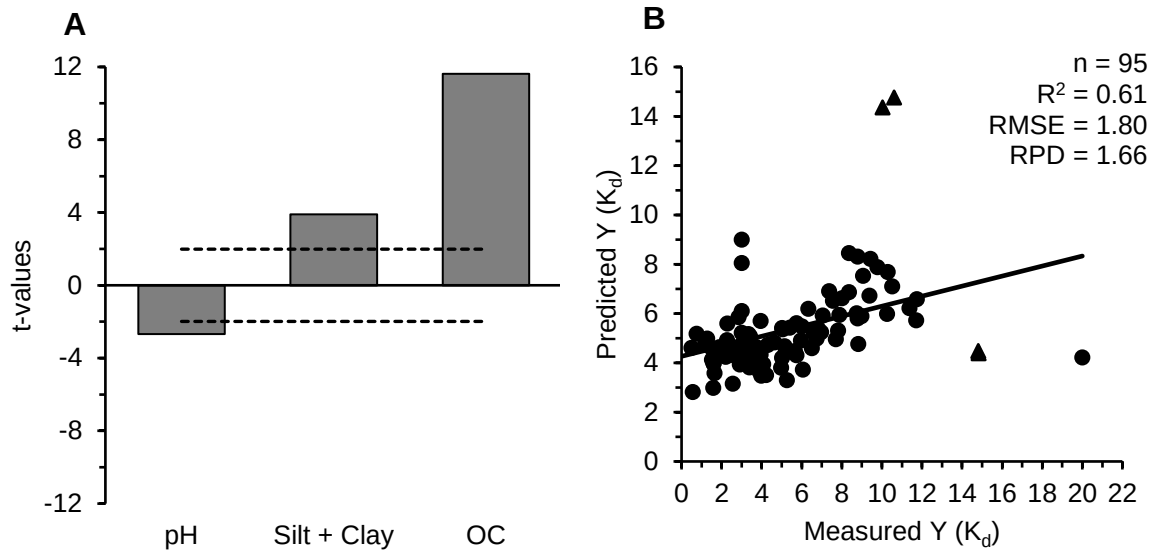


Figure S3: (A) The t-values for significant soil properties and pH in relation to the K_d of ^{14}C-PFOA in Australian soils (n = 95) developed using a multiple linear regression model, and (B) observed versus predicted K_d values. The dashed lines in (A) above and below represent the critical t-value (t = ± 1.99). Note that four samples were considered outliers (▲) as they had high leverage and hence were not included in the model. A fifth sample was unable to be included in analysis due to missing values of soil texture.

DRIFT-PLSR surface soils model

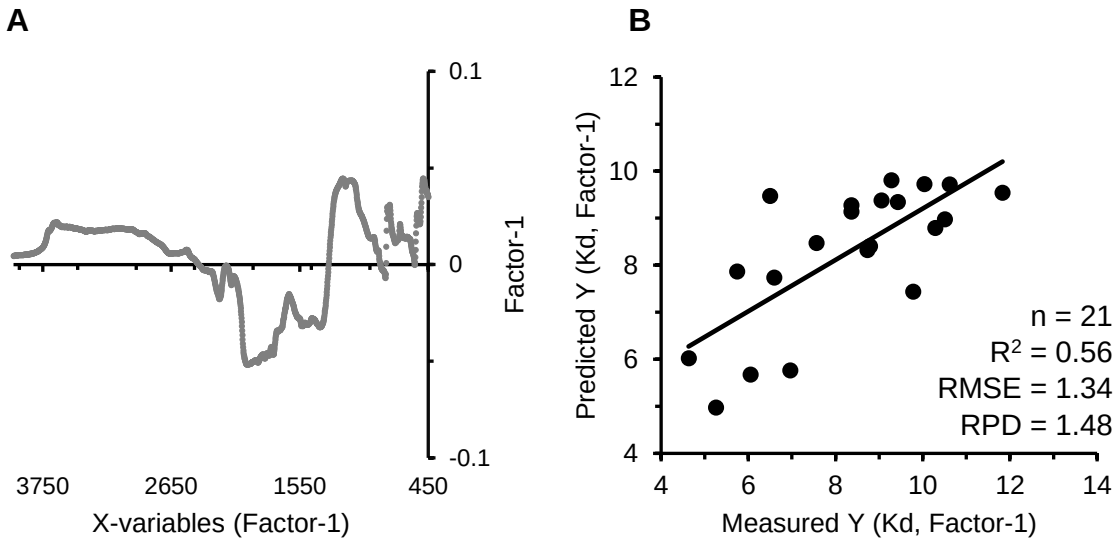


Figure S4: (A) The DRIFT-PLSR loading weights associated with the K_d values of PFOA in surface soils (0–15cm) and (B) measured versus predicted K_d values for the model (n = 21).

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Chapter 4. Partitioning of PFOS and PFHxS in a range of soils.

Statement of Authorship

Title of Paper	Partitioning of PFOS and PFHxS in a range of soils.
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Name of Primary Author (Candidate)	Emma R. Knight		
Contribution to the Paper	Experimental development; conducting experiments; data and statistical analysis; critical interpretation; manuscript writing.		
Overall percentage (%)	80%		
Certification:	This paper reports on original research I conducted during the period of my Higher Degree by Research candidature and is not subject to any obligations or contractual agreements with a third party that would constrain its inclusion in this thesis. I am the primary author of this paper.		
Signature		Date	02/04/2020

Co-Author Contributions

By signing the Statement of Authorship, each author certifies that: 1) the candidate's stated contribution to the publication is accurate (as detailed above); 2) permission is granted for the candidate in include the publication in the thesis; and 3) the sum of all co-author contributions is equal to 100% less the candidate's stated contribution.

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1. Abstract

The aim of this study was to establish partitioning coefficients (K_d) of perfluorooctane sulphonic acid (PFOS) and perfluorohexane sulphonic acid (PFHxS) in a wide range of soils and determine if those values can be predicted from soil properties using multiple linear regression (MLR) and from infrared spectra of soils using partial least squares regression (PLSR). Using the OECD batch method, sorption was measured on 172 different soils. PFOS was more strongly retained in soils than PFHxS – the K_d values ranged from 1.01–27.23 L/kg for PFOS and 1.00–2.00 L/kg for PFHxS, respectively, with average values of 4.37 L/kg, and 1.23 L/kg, respectively. MLR modelling revealed that PFHxS sorption was significantly (p <0.05) influenced, in decreasing order, by exchangeable Mg^{2+} and Ca^{2+}, clay and organic carbon contents. The MLR modelling of PFOS sorption with soil properties was overall unreliable and even transforming K_d values to Log values was unsatisfactory. Modelling of K_d prediction in soils with PLSR and diffuse reflectance (mid)-infrared Fourier transform spectroscopy (DRIFT), for both PFOS and PFHxS was similarly unsuccessful. Log transformation of K_d values only slightly improved the model R^2 value for PFOS sorption (R^2 for MLR 0.10 to 0.18 and 0.06 to 0.10 for DRIFT-PLSR) but not for PFHxS. It is likely that for PFHxS the small number, small value and narrow range of K_d values precluded a good prediction of sorption. However, for PFOS with larger values and a wider range of K_d values, there is only a weak correlation with soil properties in these soils. The reasons for the poor correlation with soil properties are not clear.

2. Introduction

Perfluoroalkyl substances (PFASs), Is a collective term for a large group of similar structured carbon-fluorine (C-F) compounds, of different lengths and functional head groups. Perfluorosulphonic acids (PFSAs), a subgroup of the PFASs, such as perfluorooctane sulphonic acid (PFOS) and perfluorohexane sulphonic acid (PFHxS) are commonly being detected even at low concentrations in soils and sediments (ng/g) and in ground and surface waters (ng/L)(Cousins et al. 2016, Brusseau et al. 2020). Historically, a mix of these compounds have been used in aqueous film forming foams (AFFFs) to extinguish fuel fires at airfields and fire-fighting training grounds due to their surfactant type properties (Moody and Field 2000). These compounds have also been used in the manufacturing of stain and water-resistant carpets, fabrics and textile including non-stick cookware (Richardson and Kimura 2015) leading to low level contamination of these compounds in the environment. Contamination of PFASs in the environment is of concern due to their unusually complex properties. The combination of hydrophobic (C-F chain) and hydrophilic (e.g. SO_3^-) functional groups makes PFASs amphiphilic which means they are able to persist, bioaccumulate and

are potentially toxic to many terrestrial and aquatic organisms (USEPA 2014). The widespread detection of PFASs in different environmental matrices (surface and ground waters, soils and sediments) means that it is important to understand how these contaminants interact with the environment, in particular with soil, so that effective management strategies can be implemented at contaminated sites. However, this requires a thorough understanding of PFASs sorption mechanisms and fate in soils.

Current research has investigated the role of sorption coefficients such as the soil-water partitioning coefficient (K_d) and the organic carbon (OC) normalised K_d value (K_{oc}) in predicting the retention of PFASs, mostly PFOS and perfluorooctanoic acid (PFOA), in soils and sediments. The ranges of K_d values for PFOS and PFHxS have been reported to be between 0–223.87 L/kg and 0–5.1 L/kg, respectively (Higgins and Luthy 2006, Kwadijk et al. 2010, Oliver et al. 2019) and were generally based, in each study, from a very small number of surface soils or sediments (<10) (Higgins and Luthy 2006, Ahrens et al. 2011, Li et al. 2012, Milinovic et al. 2015). Small sample sizes can bias the results by co-variation between soil properties and due to highly skewed (non-normal) property distributions. These studies have noted a correlation of sorption with OC content (Higgins and Luthy 2006, Johnson et al. 2007, Ahrens et al. 2011, Milinovic et al. 2015).

However, in a recent study compiling published sorption data for soils and sediments, <10% of the variability in K_d values for PFOS was explained by the OC content alone. Mineral phases were also suggested to be important when predicting sorption of PFASs in soils (Li et al. 2018). The partitioning of PFASs in soils is expected to also be affected by other soil properties, including pH and concentrations and type of cations in the soil solution (Li et al. 2012, Du et al. 2014). Metal oxides and oxyhydroxides (e.g. alumina, bohemite, gibbsite, goethite and hematite) could also drive electrostatic interactions between the negatively charged PFASs and positively charged mineral surfaces (Wang and Shih 2011, Gao and Chorover 2012, Wang et al. 2012).

It would be valuable to be able to predict K_d values in all soil types, assuming there is a good relationship between K_d values and some soil properties. However, these types of predictions would be costly and time-consuming as laboratory analysis of soils involves several different wet chemistry methods. The use of diffuse reflectance (mid)-infrared spectroscopy coupled with partial least square regression analysis (DRIFT-PLSR) (Janik et al. 1998) could provide a cost-effective and more efficient alternative. DRIFT-PLSR modelling has been used previously for the prediction of several soil chemical characteristics, including soil carbon content, particle size distribution, moisture retention, pH, carbonate content and concentrations of exchangeable cations (Ca^{2+}, Mg^{2+}, K^+, and Na^+) as well as concentrations of total petroleum hydrocarbons in contaminated soils (Janik and Skjemstad 1995,

Janik et al. 2016b, a). The prediction of K_d values for inorganic ions and the pesticides diuron and atrazine in a wide range of soils has previously been successful using DRIFT-PLSR (Forouzangohar et al. 2008, Kookana et al. 2008, Janik et al. 2015a, b). The DRIFT-PLSR x-loading weights suggested that the sorption of diuron and atrazine in surface- and sub-soils was influenced by organic matter, quartz and clays (Forouzangohar et al. 2008, Kookana et al. 2008). Comparing the DRIFT-PLSR approach and the K_{oc} approach, these authors found that the regression coefficients for the DRIFT-PLSR methodology were greater than the K_{oc} approach. This type of prediction in regards to PFASs has only recently been investigated in our previous work (Chapter 3) with radiolabelled ^{14}C-PFOA (Knight et al. 2019), where the DRIFT-PLSR modelling indicated the sorption of PFOA in 98 soils was influenced by negative correlations with quartz (sand) and pyrophyllite minerals. It is likely that the sorption of PFASs will be affected by multiple soil properties (Li et al. 2018, Knight et al. 2019) and that the DRIFT-PLSR modelling could provide a possible prediction for many more PFASs, in a range of soils.

The aim of this study was to investigate the partitioning of PFOS and PFHxS, in a wide range of soils, with the view to develop a predictive model for both PFSAs, based on integrated properties of organic and mineral phases in soils. The sorption coefficients were first evaluated by batch sorption experiments in 172 diverse Australian surface and subsurface soils, with varying physico-chemical properties. Multiple linear regression and DRIFT-PLSR analysis were then used to create models to describe the partitioning of PFOS and PFHxS in soils.

3. Materials and methods

3.1 Materials

Unlike PFOA (as reported in Chapter 3), ^{14}C radiolabelled materials were not available for PFOS and PFHxS during these studies and hence non-radiolabelled materials had to be used. Powdered forms of perfluorohexane sulphonic acid (PFHxS, ≥98% purity) and perfluorooctane sulphonate potassium salt (PFOS, ≥98% purity) were purchased from Sigma-Aldrich. Mass-labelled standards of $^{13}C_8$-PFOS and $^{18}O_2$-PFHxS were purchased from Wellington Laboratories (Canada).

3.2 Soils

There was a total of 172 soils with widely varying properties used in this study. One hundred of the soils were selected from the Australian National Soil Archive (Commonwealth Scientific and Industrial Research Organisation – CSIRO). The remaining 72 soils were provided by the New South

Wales (NSW) Office of Environment and Heritage (OEH). A summary of the soil characteristics for all soils can be found in Table 1 and supplementary information (SI) Table S1.

Table 1: Minimum, maximum, median and mean (± standard error) soil properties for the test soils (n = 172).

Soil properties	OC (%)	pH ($CaCl_2$)	EC (1:5 dS/m)	CEC ($cmol^+/kg$)	Clay (%)
Min	0.1	3.3	0.0	0.0	0.0
Max	9.0	8.6	3.4	55.9	69.3
Median	0.4	6.6	0.1	14.9	31.5
Mean	0.9 ± 0.1	6.2 ± 0.1	0.3 ± 0.0	17.1 ± 0.9	32.2 ± 1.4

3.3 Batch sorption

The sorption experiments were conducted in accordance with Organisation for Economic Cooperation and Development (OECD) Protocol 106 (OECD 2000). For each soil, 1.5 g soil was weighed into a 10 mL polypropylene (PP) tube (selected based on methods from Shoemaker et al. (2009)) in triplicate, with 6.5 mL of 0.5 mM $CaCl_2$. While sorption of PFOA to PP tubes may be greater than to glass and polycarbonate (Chapter 2), it is unknown if this is the case for PFSAs. Thus, PP tubes were found easier to use in the laboratory and sorption could be corrected for by using appropriate controls. The soils were equilibrated for 24 hours on an end-over-end shaker and then 1 mL of 375 ng/mL PFAS mix (PFOS and PFHxS) was added to each tube, vortexed and placed on the end-over-end shaker for a further 24 hours. The total nominal concentration of PFAS in each tube was 50 ng/mL, which is within the environmentally relevant range of PFOS and PFOA concentrations from soil survey data collated in a recent review (Brusseau et al. 2020). The samples were centrifuged at 2200 *g* force for 15 mins before an aliquot was taken and mixed with an equal amount of methanol. In each sample, 10 ng/mL of internal standards ($^{13}C_8$-PFOS and $^{18}O_2$-PFHxS) was added before samples were refrigerated at 4°C until analysis.

The remaining sample solutions were measured for pH and electrical conductivity (EC) (µS/cm) before being filtered through a cellulose acetate syringe filter. Sample solutions were then diluted 5 times before concentrations of Al, Ca, Fe, K, Mg, Mn, Na, P and S were determined using a PerkinElmer® Avio™ 200 inductively coupled plasma optical emissions spectrometer.

A single spiking protocol was chosen due to the large number of soils used in this study. It was considered that the concentrations used in this study were not high enough to cause saturation of soil adsorption sites and therefore sorption should be linear (Delle Site 2001). For PFOS, linear

isotherms were found in soils using concentrations of 5–1000 µg/L, resulting in R^2 values of ≥0.9 (Milinovic et al. 2015). Another study investigating concentrations between 0.02 and 1.00 µg/L, lower than those used in this current study, found a near linear isotherm for PFOS with an R^2 value of 0.85 (Enevoldsen and Juhler 2010). Isotherm studies for PFHxS in soils currently have not been reported. For reference, PFHxS and PFOS sorption using concentrations of 0.5–100 µg/L was found to be linear in sediments, with linear R^2 values of 0.83 and 0.99, respectively (Chen et al. 2016). Linear relationships were also found for PFHxS and PFOS with soil extracted humic substances at PFSA concentrations of 50–5000 µg/L, where R^2 values were >0.99 for both PFHxS and PFOS (Zhao et al. 2014). These observations indicate that the spiking concentration used in this study (50 µg/L) should fall within the range of sorption linearity for both PFOS and PFHxS.

3.3.1 K_d calculation

The K_d values of PFOS and PFHxS were calculated for each soil using the following equation:

$$K_d = \frac{S-C}{C} \times \frac{V}{M} \quad (1)$$

where K_d is the partitioning coefficient (L/kg), S is the initial solution concentration (µg/L), C is the equilibrium solution concentration (µg/L) and V/M is the liquid/solid ratio. Due to complications described in the SI, the nominal concentration (50 µg/L) was used as the initial concentration.

3.4 Diffuse reflectance infrared spectroscopy

The analysis of soil (collection of spectra) was achieved using the methods described by Janik et al. (2016b). Briefly, a benchtop Fourier transform infrared (FTIR) spectrometer (Frontier, Perkin-Elmer Inc., USA) and equipped with a Perkin-Elmer (PE) auto-focusing DRIFT accessory, was used to scan the samples of approximately 100 mg. Soil spectra in the spectral range of 7800–450 cm^{-1} were collected at a spectral range of 8 cm^{-1} and scanned for 60 s. Pseudo-absorbance units (AU) were calculated for the spectra based on the reflection spectra of the samples (R_s) and the background – a PE silicon carbide disc, which is assumed to have a reflection of $R_0 = 1$ when using the following equation: $AU = \text{Log10}(R_0/R_s)$. The analysis of spectral data was then conducted through The Unscrambler-X™ (CAMO, Norway) program after baseline correction.

3.5 Instrumental analysis

Concentrations of PFOS and PFHxS were determined by liquid chromatography triple quadrupole time of flight mass spectroscopy (LC-QTOF) using an Exion LC ™ (Sciex) and a TripleTOF ™ 5600+ mass spectrometer (Sciex) equipped with a DuoSpray ion source. The mass spectrometer was operated in negative mode set for high sensitivity using product ion scans (Table S4). Chromatographic separation was performed using a Luna® C18 30 x 2 mm (5 µm), 100 Å

(Penomenex) pre-column and a Hypersil GOLD™ pentafluorophenyl (PFP) 100 x 1 mm (3 µm) HPLC column (Thermo Scientific), maintained at a constant temperature of 40 °C. The mobile phase was comprised of two eluents, 5 mM ammonium acetate (A) and 100% methanol (B) using a binary gradient system totalling 12 min and a flow rate of 0.45mL/min. The gradient of (A) was 95% for 2 min, 55% by 5 min, 5% by 7 min and held for 1 min before returning to 95% by 8.10 min for the remaining time. The mass spectroscopy ion source temperature was maintained at 550 °C, with a spray voltage of 4000 and collision energy of -10 V.

3.6 Quality assurance and quality control

Three sets of blanks were run in conjunction with the soil samples for quality assurance and quality control purposes. Tube blanks (contained no soil and no spike), spike blanks (contained spike and no soil) and soil blanks (containing soil and no spike). The spike blanks determined the initial or highest concentration that should be possible without sorption from the soil, but in some instances, this was not the case when compared with measured samples concentrations. These cases were investigated further in the supplementary information and concluded that potentially a combination of soil matrix effects from several different soil properties may have been the cause. Due to the issues with the spike blanks in the K_d calculation the expected nominal concentration, 50 µg/L, was used as the initial solution concentration. As per the OECD protocol (OECD 2000), only soils with >20% sorption are reported in this study, which significantly limited the total number of K_d values presented (see supplementary information for more details).

Instrument detection limits, limit of detection (LOD) and quantification (LOQ), were calculated as three times and ten times the standard deviation, respectively, of the lowest standard (Table S5). Measured concentrations in the soil blanks were all below the LOQ.

3.7 Statistical analysis

Linear regression analysis was conducted using Microsoft Excel (2013). Statistical analysis for sorption coefficients with soil depth was achieved using IBM SPSS (v. 24). Multiple linear regression analysis and DRIFT-PLSR analysis were carried out using The Unscrambler software. The MLR modelling was achieved by first considering which soil characteristics were highly correlated with K_d values, for both PFOS and PFHxS, using a cross correlation matrix with Pearson r values (Table S6). The DRIFT-PLSR models were constructed from the soil spectral data (4000–450 cm^{-1}) and the corresponding sorption coefficients (K_d values and Log K_d values). Note that for both MLR and DRIFT-PLSR, models were constructed using soils with K_d values >20% sorption threshold (Table S1), n = 111 for PFOS and n = 42 for PFHxS. The coefficient of determination (R^2) values observed for both the MLR and DRIFT-PLSR models are those from the “leave four out” cross validation regression method,

whereby a set of four randomly selected samples are removed, repeated 20 times, from each temporary model and then their values predicted from that model.

The PLSR models use several factors, each contributing to the calibration of the model, often more than half of the total variance. Successive factors improve the model, but each becomes less important and a single factor is approximately equivalent to an MLR model. The factors used in our study are the optimum number of factors that have the lowest error for prediction where possible. The root mean square error (RMSE) is also included as a measure of the model variation and is defined as:

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n}(m_i - p_i)^2}{N}} \quad (2)$$

where *m* are the measured values, *p* are the predicted values, *i* is the sample being tested and *N* is the total number of samples used for the calibration. In our previous work, Knight et al. (2019), the inclusion of the residual predictive deviation (RPD) statistic was included as a measure of the quality of the model. However, since publishing the study it has come to our attention that the RPD is not a good measure of model quality and hence is not used in the current study (Minasny and McBratney 2013).

4. Results and discussion

4.1 Sorption

Based on the median and average K_d values, the sorption affinity of PFOS was greater than PFHxS. This sorption affinity has been suggested to be related to the C-chain length of the molecules, where an increase in chain length (from C6–C8) increases the observed K_d values (Ahrens et al. 2010, Pereira et al. 2018, Oliver et al. 2019). Across all soils, the K_d values of PFOS and PFHxS ranged from 1.01–27.23 L/kg and 1.00–2.00 L/kg, respectively, with average values of 4.37 L/kg, and 1.23 L/kg, respectively (Table 2 and Table S1). The range of K_d values for PFOS in this study were in the range, even if slightly on the lower end, of those reported for Australian soils by Oliver et al. (2019); 0–38.4 L/kg and Milinovic et al. (2015); 9–444 L/kg. Very few studies to date have reported sorption coefficients for PFHxS but the range of PFHxS K_d values in our study are very simliar to those reported for a smaller set of Australian soils by Oliver et al. (2019); 0–5.1 L/kg.

A recent analysis of global sorption data of PFASs in soils and sediments found that the median laboratory-derived K_d value for PFOS was 15.49 L/kg (Li et al. 2018), which is higher than the median K_d value found in this study for PFOS (Table 2). This is likely due to many international soils and

sediments with higher carbon contents being included in the study of Li et al. (2018) compared to Australian soils.

Table 2: Minimum, maximum, median, mean (± standard error) and skewness of the K_d values for PFOS and PFHxS.

	PFOS (L/kg)	PFHxS (L/kg)
Number of soils	111	42
Min	1.01	1.00
Max	27.23	2.00
Median	2.66	1.15
Mean	4.37 ± 0.45	1.23 ± 0.03
Skewness	2.63	1.50

4.2 Simple linear regression

Linear regressions of PFOS and PFHxS sorption coefficients and OC resulted in R^2 values of 0.19 and 0.12, respectively (Figure 1). Despite the low R^2 values for both PFOS and PFHxS, both the relationships were significant (p <0.05) for the number of soils in the model. The R^2 value improved for the PFHxS model, to 0.46, when 11 soils from the NSW soils set were removed from the model (Figure 1C). The 11 soils removed did not appear to have any common characteristics that could explain why they contributed poorly to the model. The same did not occur for the regression of OC and K_d values for PFOS. Other soil chemical properties, such as pH, EC and clay content did not correlate well with the sorption of PFOS and PFHxS, with R^2 values of <0.1. Removing the 11 NSW soils from the modelling of other soil characteristics and PFHxS K_d values did not improve their modelling, unlike with OC content.

The K_d values of PFOS and PFHxS did not appear to change (p >0.05) with an increase in soil depth, R^2 = 0.00 for PFOS and R^2 = 0.09 for PFHxS. However, like OC content, the removal of the 11 NSW soils increased the R^2 of the linear model to 0.21 for PFHxS only and this relationship became significant (p <0.05). However, further investigation of the linear relationship between PFHxS K_d values and soil depth did not show any significant differences (p >0.05) for K_d values at different depths. These results are in contrast to Knight et al. (2019) (Chapter 3), who found a significant relationship, of decreasing K_d values with increasing soil depth using the same 100 soils set (R^2 value = 0.48).

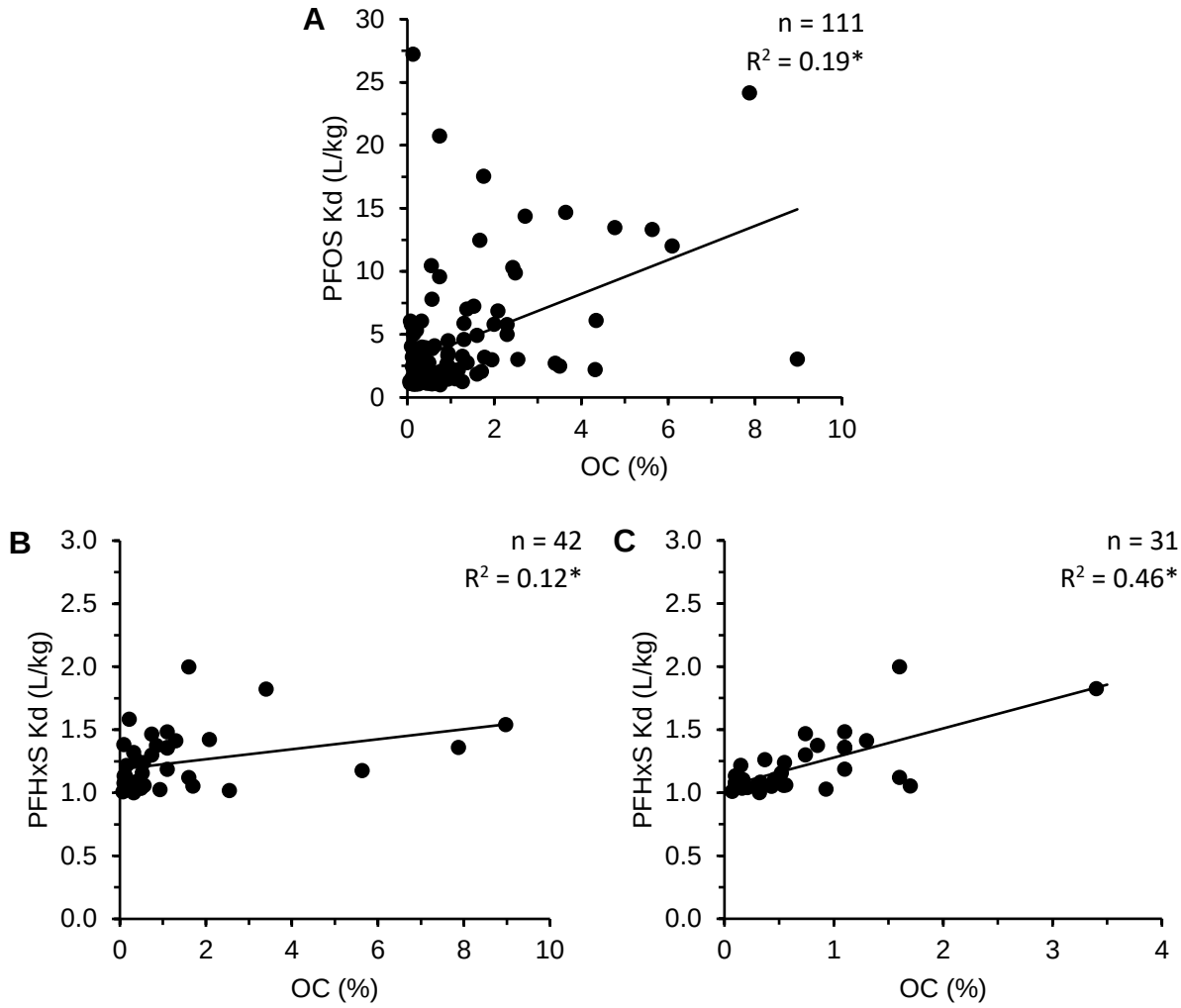

Figure 1: The K_d values of (A) PFOS and (B and C) PFHxS in relation to soil organic carbon content, with varying numbers of soils. Asterisks (*) indicate the significance of the models (p <0.05).

4.3 Modelling sorption from soil characteristics by MLR

In this study, no single soil property correlated well with K_d values for PFOS and PFHxS in soils. This result is supported by a review based on published literature which found that sorption behaviour of a number of PFASs could not be described by one soil property (Li et al. 2018). Multiple linear regression modelling of PFOS and PFHxS K_d values in relation to several soil properties was conducted to establish which sol properties might be having the greatest influence on the sorption.

The MLR modelling of PFOS initially also had nine soil properties, the same as the PFHxS MLR model: OC, cation exchange capacity (CEC), clay content, pH, EC and exchangeable Ca^{2+}, Mg^{2+}, Na^{+} and K^{+} (Figure 2). However, the initial model was unreliable with an extremely low R^2 value of 0.05 and high RMSE of 4.66 (Figure 2). Only one soil property, OC, significantly influenced the sorption of PFOS to

these soils. However, the positive relationship with OC was still relatively weak, with an R^2 = 0.10 and high model variation, RMSE = 4.54. Due to the low R^2 values and the high RMSE in the PFOS models, these models are highly unreliable. Thus, no soil property significantly affected sorption of PFOS in these soils.

Attempts were made to improve the MLR modelling of PFOS K_d values by Log transformation. While this improved the initial model, R^2 = 0.13 and RMSE = 0.33, after removing three of the least significant soil properties the modelling was unable to continue due to a rank deficiency (Figure 2E and F). The observed rank deficiency indicates that there is not enough information from the data to estimate the model. Prior to this point in the modelling process, the R^2 = 0.18 and the RMSE = 0.31, where only a positive relationship with OC and negative relationship with pH significantly influenced the model (p <0.05), even though clay content, CEC, EC and exchangeable Mg^{2+} were still included in the model (Figure 2E and F). The Log transformation of PFOS K_d values initially improved the MLR model, the rank deficiency indicates further unreliability.

The MLR modelling for PFHxS K_d values initially included the same nine soil properties as the PFOS MLR: OC, cation exchange capacity (CEC), clay content, pH, EC and exchangeable Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}, R^2 = 0.26 and RMSE = 0.19 (Figure 3). After removing the soil properties that were having the least influence, the sorption of PFHxS was significantly influenced (above critical t-value ± 2.02) by positive relationships with OC, clay content and exchangeable Ca^{2+} and negatively influenced by exchangeable Mg^{2+} (p <0.05), R^2 = 0.32 and RMSE = 0.18 (Figure 3).

While the MLR models for PFOS K_d values and soil properties were unreliable, there are still some similarities with results in the literature. For instance, Milinovic et al. (2015) also found a strong relationship between PFOS K_d values and OC content, R^2 = 0.99. Pereira et al. (2018) also found an inverse relationship for PFOS K_d values and pH – as pH increased, the sorption decreased – in a soil with a high amount of OC (45%). However, the same relationship between pH and K_d values for PFHxS was not observed. In contrast, to the significant relationship with OC observed in this study, Oliver et al. (2019) found no significant relationship between PFOS and PFHxS K_d values and OC in seven tropical Australian soils. The results in Oliver et al. (2019) also indicated that sorption of PFOS and PFHxS occurring at different pH values was not consistent with the concentrations of multi-valent cations (e.g. Ca^{2+}, Mg^{2+}) in solution. This is also in contrast to the MLR model of PFHxS K_d values and soil properties. The reason for the contrasting results could be due to the smaller and lower range of K_d values for PFHxS than those reported by Oliver et al. (2019).

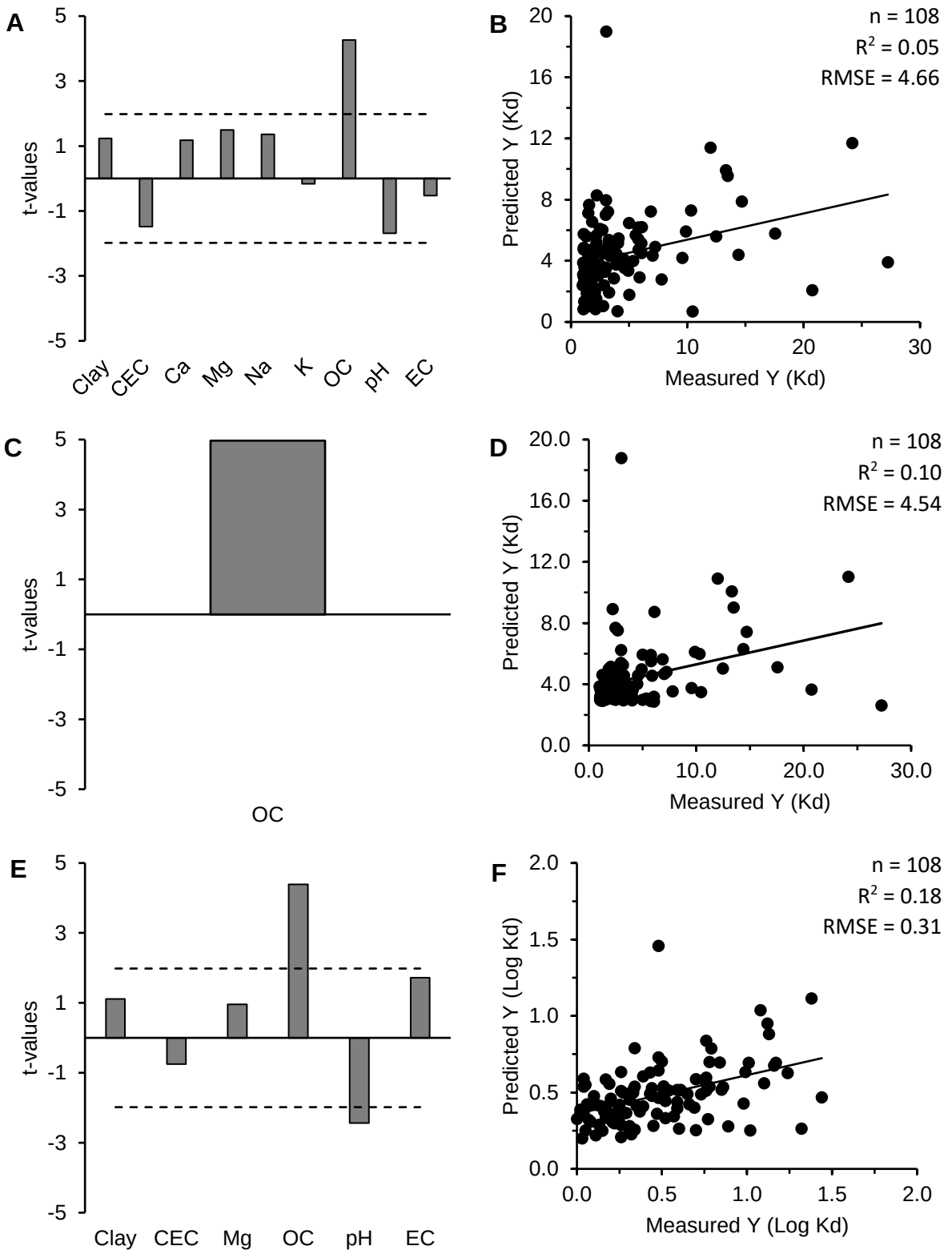

Figure 2: (A) The t-values for soil properties, (C) significant soil properties in relation the K_d of PFOS in Australian soils showing >20% sorption (n = 108) developed using a multiple linear regression model. (E) The t-values of the Log K_d values. Regression plots B, D and F correspond to the number of soil properties displayed in A, C and E respectively. The dashed lines in (A and E) above and below represent the critical t-value (t = ± 1.98). Three samples were unable to be included in analysis due to missing values for many soil properties.

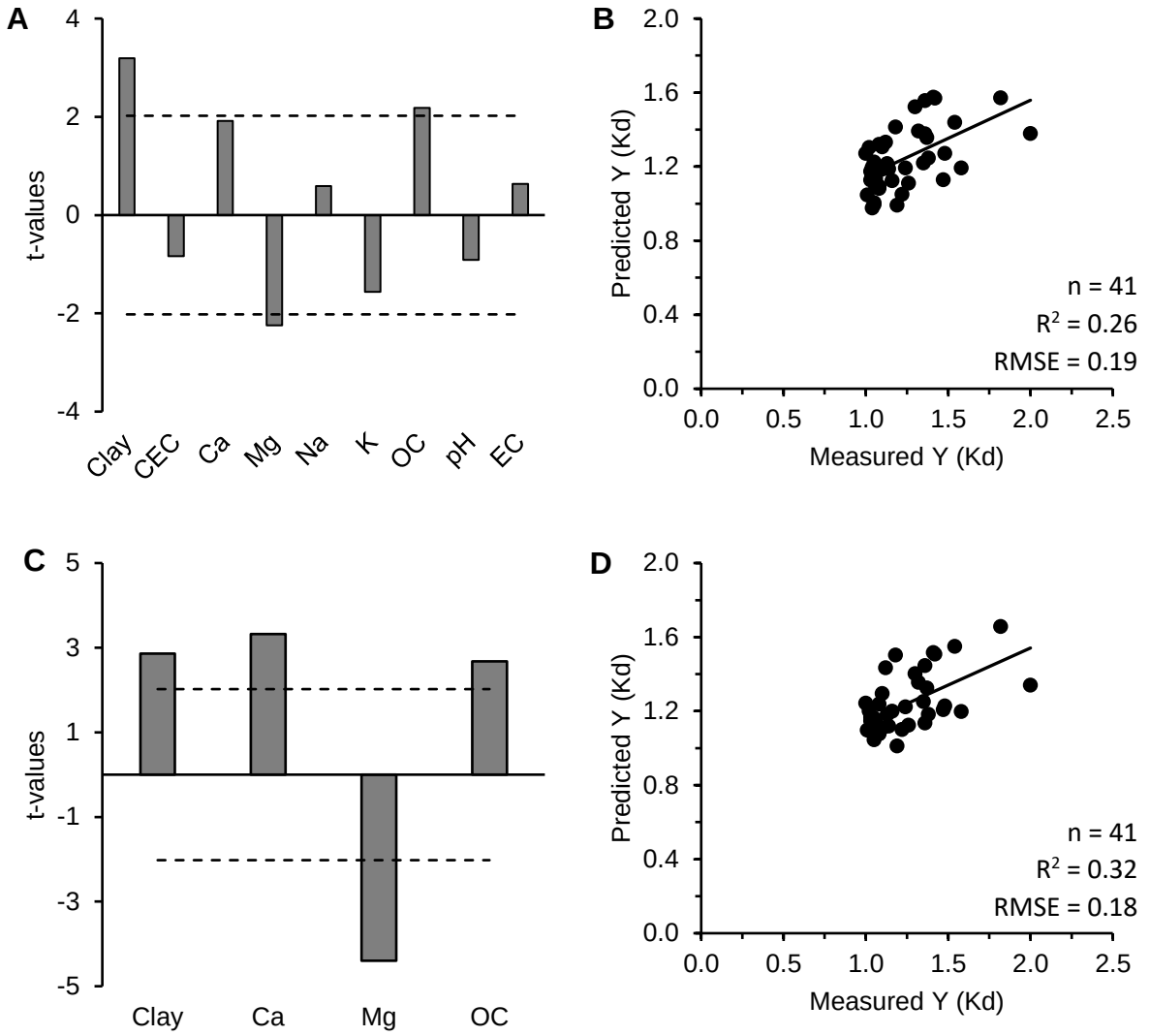

Figure 3: (A) The t-values for soil properties and (C) significant soil properties in relation to the K_d of PFHxS in Australian soils showing >20% sorption (n = 41) developed using a multiple linear regression model. Regression plots B and D correspond to the number of soil properties displayed in A and C, respectively. The dashed lines in (A and C) above and below represent the critical t-value (t = ± 2.02). One sample was unable to be included in analysis due to missing values for many soil properties.

4.3 Modelling sorption by DRIFT-PLSR

The MLR models were based on a chosen set of soil properties that were assumed to be the most important for the sorption of PFOS and PFHxS. This limits the scope of the models to only those pre-defined soil properties and does not allow the possibility of other non-measured soil properties influencing the sorption of PFOS and PFHxS in those soils. Therefore, the use of DRIFT-PLSR may expand the understanding of the sorption process as all data points (from soil spectra) are included, not just the subjectively selected soil properties.

No spectral outliers were identified, using principal component analysis (PCA), prior to conducting DRIFT-PLSR for either the PFOS or PFHxS data sets. The DRIFT-PLSR models relating soil spectra to PFOS and PFHxS K_d values were also unreliable with $R^2 = 0.06$ and RMSE = 4.64 for PFOS and no viable cross-validation model was produced for PFHxS (Figure 4). Similar to the MLR models, attempts to improve the DRIFT-PLSR models by transforming the data produced only slight increases for the PFOS model, $R^2 = 0.10$ and RMSE = 0.33. The DRIFT-PLSR model for PFHxS remained unchanged and is likely due to the already small range of PFHxS K_d values compared to PFOS (Table 1). Due to the unreliability of the models, discussion of the x-loadings weights and soil characteristics influencing sorption would be questionable.

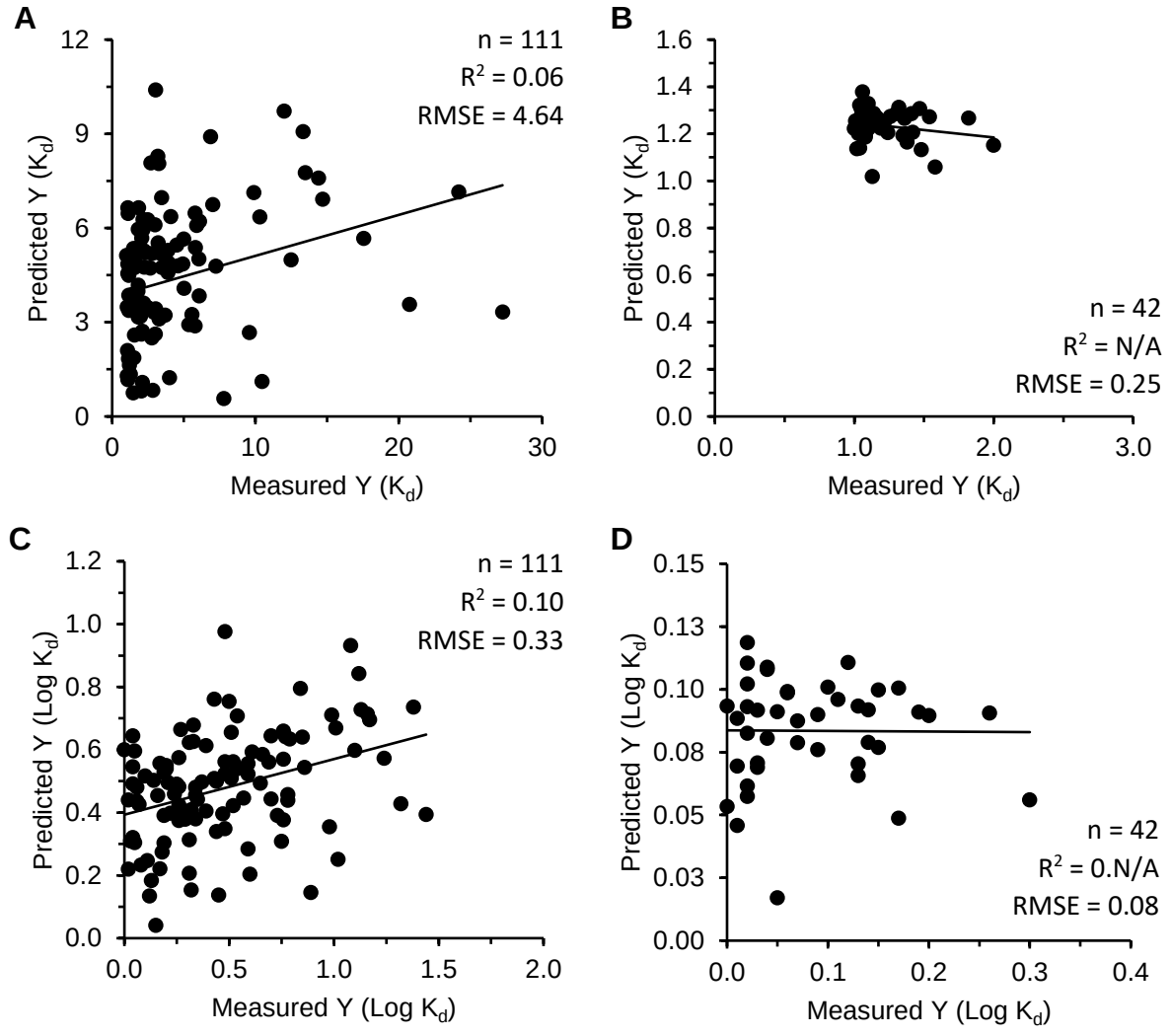

Figure 4: The DRIFT-PLSR measured versus predicted K_d values (A and B) and Log K_d values (C and D) for PFOS and PFHxS, respectively.

5. Conclusions

This study investigated the sorption of PFOS and PFHxS on 172 soils of varying properties. The range and median K_d values of both PFOS and PFHxS were within those reported in the literature and consistent with the sorption affinities (PFOS>PFHxS) also reported in other studies. Linear regressions and MLR modelling indicated that K_d values for PFOS were highly influenced by the soil OC content, whereas PFHxS K_d values were highly influenced by OC content, clay content and exchangeable Ca^{2+} and Mg^{2+}. However, the MLR and DRIFT-PLSR approaches were unable to provide a reliable prediction of K_d values from the properties in these soils. This could be due to sorption of both PFASs being low (<20%) in many of the soils that precluded inclusion in the regression analyses. However, these results confirm the high mobility of these compounds in most Australian soils. Australian soils have lower C contents than many other countries and this set of soils reflects this – the median OC content was 0.4%. There was a very low and narrow range of K_d values for PFHxS indicating this compound will be very mobile in all Australian soils, much more so than PFOS. The reasons for the weak correlation between PFOS K_d values and soil properties is unclear.

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8. Supplementary information

Partitioning of PFOS, PFHxS and PFOA in a range of soils

Soil Characteristics

One hundred and seventy-two soils were selected to give a wide range of physico-chemical properties (Table S1). The measured K_d values with >20% sorption are included and where there is no value, sorption was <20%.

Table S1: Soil properties for all soils tested in this study and the calculated K_d values for PFOS and PFHxS.

								Exchangeable cations ($cmol^+/kg$)						
no.	PFOS K_d* (L/kg)	PFHxS K_d* (L/kg)	Depth (cm)	Clay (%)	Silt (%)	Sand (%)	CEC ($cmol^+/kg$)	Ca	Mg	Na	K	OC (%)	pH ($CaCl_2$)	EC (µS/cm)
1	1.85	1.12	0-15	33.5	19.2	47.2	17.9	12.6	1.7	0.1	3.5	1.60	6.6	304.0
2			90-120	60.2	12.4	27.4	14.9	10.3	3.5	0.2	0.8	0.29	7.1	111.2
3			150-180	56.7	13.9	29.4	16.5	11.4	4.0	0.3	0.9	0.19	7.2	81.8
4	1.15		90-120	43.3	12.4	44.4	9.0	3.4	4.5	0.2	0.9	0.14	7.0	96.3
5	2.47		150-180	38.4	10.2	51.4	8.0	2.8	4.3	0.2	0.6	0.11	6.5	84.2
6			90-120	50.6	7.8	41.6	19.7	9.1	7.7	0.6	2.3	0.11	8.0	97.3
7			30-60	47.5	6.0	46.5	29.1	17.6	6.6	4.3	0.5	0.55	8.5	227.6
8	4.59		0-15	20.1	36.1	43.8	13.6	9.8	2.1	0.2	1.5	1.30	6.7	176.3
9			60-90	36.9	32.4	30.8	27.2	15.7	9.7	1.5	0.3	0.23	8.0	154.3
10	1.01		15-30	35.1	16.1	48.9	17.4	14.7	1.4	0.0	1.3	0.75	7.8	165.7
11			60-90	47.9	16.6	35.5	13.5	8.7	3.9	0.0	0.9	0.12	7.9	126.5
12	1.73		15-30	28.6	20.9	50.5	10.3	6.8	3.0	0.1	0.4	0.36	6.6	80.7
13			150-180	28.4	19.5	52.1	16.1	9.3	5.8	0.5	0.5	0.11	7.0	141.0
14	5.78		90-120	52.6	8.9	38.5	39.5	10.3	17.8	10.5	0.9	0.09	7.3	2899.7

15	6.07		150-180	54.2	9.3	36.5	28.7	5.3	14.0	9.0	0.5	0.07	7.8	2509.0
16			120-150	49.3	7.6	43.2	21.8	6.5	8.9	3.5	2.9	0.05	8.7	363.9
17	1.80		30-60	38.3	8.7	53.0	8.7	6.1	2.1	0.0	0.4	0.20	7.2	81.0
18			150-180	51.0	10.3	38.7	27.4	5.2	13.9	7.5	0.7	0.07	7.3	794.3
19	1.54	1.16	0-15	20.0	3.8	76.2	8.4	5.3	1.8	0.1	1.2	0.52	6.7	105.0
20			120-150	34.1	17.7	48.2	18.5	2.3	10.6	3.8	1.8	0.05	9.0	303.0
21		1.01	90-120	40.0	6.8	53.2	12.3	5.6	5.6	0.2	0.8	0.07	7.2	73.7
22	1.59	1.35	0-15	21.6	21.5	56.9	4.8	3.0	0.7	0.1	0.9	1.10	6.1	90.3
23	1.77	1.10	60-90	64.9	1.9	33.2	18.2	11.0	6.1	0.1	1.0	0.17	7.5	129.4
24	1.66	1.22	120-150	27.7	18.2	54.0	13.3	7.8	4.7	0.1	0.7	0.15	7.8	166.8
25	1.13		150-180	20.0	25.2	54.8	16.4	8.8	6.4	0.3	1.0	0.06	8.3	130.2
26	1.58	1.48	0-15	8.6	22.3	69.1	7.6	6.8	0.5	0.1	0.2	1.10	5.7	91.6
27		1.13	30-60	11.8	23.0	65.2	2.9	2.4	0.3	0.0	0.1	0.10	6.1	58.0
28	1.52	1.08	90-120	21.9	12.4	65.7	8.8	4.6	3.8	0.1	0.2	0.10	6.3	72.4
29	1.10	1.08	150-180	16.6	9.9	73.5	5.6	2.5	2.7	0.1	0.2	0.10	6.3	58.5
30	1.39	1.10	30-60	50.6	19.1	30.3	26.1	15.0	9.1	1.8	0.2	0.46	7.7	179.8
31	1.49	1.19	0-15	43.5	12.0	44.5	19.0	7.5	8.4	2.2	0.9	1.10	5.9	87.6
32			30-60	50.3	11.2	38.5	23.4	5.9	12.0	3.3	2.2	0.24	6.9	178.5
33			150-180	43.6	14.5	42.0	19.7	6.8	9.0	2.6	1.2	0.05	8.4	148.2
34	2.48		0-6	19.0	11.0	70.0	21.6	20.3	1.1	0.0	0.2	3.50	7.57	541.73
35	2.05		18-40	14.0	5.0	81.0	7.7	6.7	0.9	0.0	0.1	0.76	8.01	187.70
36	1.07		40-60	12.0	4.0	84.0	5.3	4.5	0.7	0.0	0.1	0.26	8.57	129.07
37			15-65	4.0	1.0	95.0	1.6	1.2	0.3	0.0	0.1	0.05	8.62	97.37
38	1.28		65-100	20.0	1.0	78.0	9.2	5.7	3.0	0.0	0.4	0.05	8.47	150.87
39	1.41		0-10	5.0	1.0	93.0	2.3	1.5	0.6	0.0	0.1	0.30	7.62	109.20
40			125-150	12.0	1.0	87.0	6.0	3.1	2.6	0.0	0.3	0.05	8.09	91.17
41			0-15	29.1	8.9	62.0	29.3	23.3	3.3	0.9	1.8	1.70	7.58	292.87
42	1.31		90-120	30.6	9.1	60.3	27.4	8.5	6.3	11.9	0.7	0.13	9.21	1732.00
43	2.33		15-30	38.4	12.4	49.2	22.1	15.4	5.4	0.5	0.8	0.97	8.22	350.10

44			90-120	55.8	7.5	36.7	23.5	7.3	10.1	4.5	1.6	0.23	9.87	383.73
45			120-150	55.4	4.8	39.8	13.7	3.6	4.7	4.3	1.1	0.20	9.99	470.03
46	1.46		0-15	9.5	1.0	90.1	9.1	7.2	1.2	0.2	0.5	0.93	7.41	236.93
47	1.21		60-80	27.6	5.3	67.1	19.9	15.3	4.1	0.2	0.3	0.48	7.68	185.13
48	2.06	1.05	0-10	25.4	12.1	62.5	43.4	29.3	11.4	0.7	2.0	1.70	7.80	354.77
49	1.56		100-150	69.3	8.1	22.6	34.2	9.5	13.4	9.8	1.5	0.24	8.99	1316.67
50			15-30	52.5	7.7	39.8	29.6	21.3	6.3	0.7	1.3	0.40	7.99	206.70
51			0-20	21.8	1.3	76.9	5.7	4.7	0.7	0.1	0.2	0.61	7.52	211.23
52			80-100	49.3	12.2	38.5	19.4	10.6	4.2	3.6	0.9	0.24	9.64	288.27
53	2.70	1.82	0-10	40.0	16.0	44.0	33.3	28.2	2.1	0.0	3.0	3.40	7.35	454.47
54	1.97		30-50	37.0	21.0	42.0	17.4	13.7	2.7	0.3	0.6	0.98	7.83	217.30
55	1.64		15-30	50.0	16.0	34.0	33.8	25.7	3.8	3.6	0.7	0.59	8.24	332.97
56			80-110	55.0	20.0	25.0	27.1	12.1	8.2	5.9	0.9	0.27	9.27	399.20
57	1.82		14-30	40.0	15.0	46.0	24.1	19.6	3.0	0.5	1.0	0.67	8.23	171.60
58			115-150	N/A	N/A	N/A	14.2	5.9	3.8	3.7	0.8	0.38	9.06	239.03
59	1.16		30-50	42.9	11.5	45.6	21.0	15.1	5.0	0.4	0.5	0.49	8.29	179.13
60			110-150	48.3	6.1	45.6	26.8	6.8	8.2	10.2	1.6	0.12	9.47	863.00
61			110-150	50.0	10.0	39.0	27.3	7.3	7.9	10.8	1.3	0.14	9.49	928.00
62			0-10	33.0	10.0	58.0	18.7	14.7	2.2	0.4	1.4	1.50	7.31	255.33
63	1.57		30-50	40.0	12.0	48.0	25.3	19.6	4.5	0.7	0.6	0.58	7.85	223.80
64	2.04	1.37	0-20	15.0	2.0	83.0	18.0	15.6	1.6	0.2	0.5	0.85	8.22	251.97
65			80-100	19.0	5.0	76.0	15.9	8.5	6.3	0.8	0.4	0.16	8.57	152.73
66	1.36		0-20	10.0	1.0	89.0	4.4	3.1	0.9	0.2	0.3	0.39	7.47	180.23
67			60-90	61.0	27.0	12.0	20.1	8.6	6.4	4.3	0.8	0.22	8.98	949.00
68			90-130	50.0	35.0	15.0	18.5	7.1	6.7	4.0	0.7	0.16	9.02	1095.67
69			30-60	65.6	17.5	16.9	41.4	25.6	10.7	3.0	2.1	0.66	8.10	198.40
70			60-105	67.9	18.8	13.3	39.6	14.9	14.4	8.5	1.8	0.41	9.00	281.37
71	3.69	1.00	10-30	24.2	27.0	48.9	7.1	5.3	1.4	0.0	0.4	0.32	6.69	108.60
72	1.10		15-30	50.4	6.4	43.1	35.3	21.5	9.5	3.5	0.8	0.64	8.23	337.00

73			35-55	41.0	9.0	49.0	22.9	15.7	4.3	2.5	0.4	0.41	8.68	182.20
74	5.89	1.41	0-15	40.0	10.0	50.0	37.1	30.3	5.0	0.4	1.4	1.30	7.68	234.03
75	3.34	1.03	0-8	24.0	9.0	68.0	17.1	10.5	4.9	0.7	1.0	0.93	6.24	114.47
76			85-125	41.0	13.0	46.0	29.3	14.5	7.9	6.0	0.9	0.21	9.19	291.60
77	1.46	1.06	10-20	38.0	7.0	55.0	30.4	18.1	8.1	2.9	1.3	0.54	7.37	184.77
78	2.14	1.36	0-15	59.0	14.0	27.0	45.7	34.2	9.1	0.7	1.7	1.10	6.90	321.67
79	2.23	1.05	60-90	64.0	14.0	22.0	44.4	27.3	14.7	1.2	1.2	0.43	8.06	143.13
80			90-120	60.0	7.0	33.0	36.5	28.4	6.4	0.3	1.4	0.16	9.30	961.67
81	2.84	1.26	60-90	33.0	6.0	61.0	18.3	11.6	5.9	0.5	0.3	0.37	8.37	146.43
82			90-120	33.0	6.0	61.0	16.1	8.1	5.4	2.2	0.4	0.19	9.62	168.20
83	4.92	2.00	0-10	20.0	30.0	50.0	16.2	14.5	1.1	0.0	0.6	1.60	7.27	285.00
84	2.11	1.05	40-60	17.0	37.0	46.0	4.8	2.9	1.5	0.3	0.1	0.29	8.77	344.40
85			90-120	42.0	10.0	48.0	42.4	11.7	15.8	13.5	1.4	0.22	9.05	1079.33
86			90-120	45.0	7.0	48.0	26.1	5.7	9.6	9.8	1.0	0.11	9.40	660.33
87			90-120	21.2	18.2	60.5	10.4	4.1	4.2	1.6	0.5	0.13	8.94	197.47
88	1.82		25-50	14.7	4.7	80.5	9.7	7.6	1.7	0.0	0.4	0.20	8.16	108.67
89	2.18	1.03	50-80	25.6	6.8	67.6	13.1	9.0	3.7	0.0	0.4	0.16	8.15	195.63
90	5.02		80-110	29.7	16.5	53.9	13.1	7.5	5.0	0.2	0.4	0.14	8.25	141.00
91	7.79	1.06	40-60	30.1	26.3	43.6	13.3	6.2	4.7	1.9	0.5	0.56	8.35	145.50
92			100-125	18.5	32.6	48.9	7.8	3.0	3.3	1.2	0.3	0.18	9.42	185.33
93	20.74	1.30	10-20	46.6	12.6	40.8	32.9	23.8	5.6	2.5	1.0	0.74	8.12	241.40
94	5.57		105-150	59.3	12.6	28.1	39.4	15.9	9.9	12.4	1.2	0.19	8.02	2422.33
95	10.46	1.24	0-10	10.7	3.9	85.4	10.3	7.9	1.0	0.3	1.1	0.55	7.78	355.90
96	4.00	1.08	30-50	17.4	4.9	77.8	9.7	7.3	1.3	0.2	0.9	0.33	8.08	466.43
97	3.93		25-65	51.4	24.4	24.2	22.4	11.2	9.7	0.8	0.7	0.41	7.93	187.83
98		1.04	70-100	33.8	13.0	53.2	12.6	3.2	4.6	3.8	1.0	0.21	9.85	265.47
99	9.57	1.47	10-30	65.2	10.2	24.6	24.2	12.9	7.7	1.8	1.8	0.74	7.82	291.33
100			60-90	29.8	24.4	45.8	10.1	4.1	3.8	2.0	0.2	0.20	9.22	216.83
101			15	17.0	6.0	51.0	14.2	9.3	3.7	1.0	0.5	0.3	7.00	94.0

102	5.80		24	11.0	18.0	69.0	10.6	4.9	1.5	1.0	1.3	2.0	6.04	160.0
103	9.88		415	32.0	29.0	34.0	32.4	15.3	10.6	0.7	0.3	2.5	6.04	146.6
104	5.00		5	23.0	19.0	46.0	19.4	14.3	5.4	0.2	1.2	2.3	6.03	106.1
105			5	8.0	6.0	86.0	4.0	2.0	2.7	0.4	0.5	0.1	6.30	92.7
106			3	41.0	44.0	15.0	21.5	8.2	11.2	0.7	0.7	0.5	6.27	120.6
107			5	25.0	12.0	60.0	21.4	8.3	9.9	3.2	0.2	0.8	6.46	138.5
108	7.02		10	14.0	18.0	25.0	7.2	0.2	2.3	0.6	0.7	1.4	5.50	166.7
109			51	9.0	8.0	47.0	7.6	6.3	1.1	1.0	0.5	0.3	5.54	61.8
110			542	9.0	10.0	81.0	6.8	1.2	2.1	0.2	0.6	0.2	5.53	67.3
111	1.12		42	53.0	33.0	14.0	21.0	0.6	2.7	0.6	0.5	0.4	4.89	79.5
112	7.24		35	9.0	21.0	61.0	6.2	1.2	1.4	0.5	0.6	1.5	4.89	103.3
113			100	39.0	24.0	37.0	45.0	30.4	22.1	0.9	0.3	0.4	6.83	157.3
114			20	14.0	10.0	76.0	3.0	1.2	0.5	0.3	0.3	0.3	6.75	68.4
115	12.00		15	37.0	34.0	29.0	26.2	10.1	9.6	0.2	0.8	6.1	5.83	100.2
116	3.27		25	14.0	27.0	42.0	8.4	2.9	0.8	0.2	0.7	0.2	5.98	62.5
117	14.69		285	21.0	33.0	24.0	25.1	18.6	7.0	0.5	0.6	3.6	6.08	153.9
118	2.16		15	52.0	24.0	22.0	19.4	11.6	8.0	0.3	1.0	0.5	6.12	71.6
119	14.39		4	50.0	19.0	28.0	41.9	24.2	14.3	0.0	3.7	2.7	6.39	210.7
120	4.50		185	12.0	11.0	64.0	5.8	0.2	1.6	0.3	0.4	0.9	4.90	81.0
121	10.31		448	59.0	17.0	24.0	52.2	26.5	20.0	1.5	1.9	2.4	6.45	285.9
122	2.11		5	5.0	1.0	93.8	1.2	0.4	0.3	0.2	N/A	0.3	5.78	64.2
123	3.88		275	12.0	13.0	50.0	3.6	0.3	0.5	0.3	0.1	0.6	5.14	70.5
124	3.03		5	39.0	27.0	34.0	13.9	3.7	3.2	0.4	0.3	0.3	5.30	58.4
125	5.34		5	27.0	31.0	42.0	8.5	1.1	3.7	0.6	0.3	0.2	4.95	227.6
126	6.86	1.42	15	61.0	27.0	12.0	7.7	1.1	0.6	0.3	0.5	2.1	5.00	86.9
127			509	50.0	14.0	36.0	31.6	16.3	11.3	3.8	0.5	0.5	7.05	238.3
128	2.93		115	27.0	10.0	48.0	6.9	4.2	0.9	0.7	0.8	0.4	6.57	80.9
129	6.05	1.32	313	65.0	20.0	15.0	7.1	0.1	2.0	0.3	0.6	0.3	4.97	60.1
130	1.83		215	46.0	5.0	49.0	21.0	2.2	4.2	2.1	2.3	0.5	5.21	92.6

131	27.23	1.14	85	37.0	19.0	43.0	7.2	0.1	3.4	1.8	0.3	0.1	4.73	75.6
132	13.47		1	27.0	35.0	36.0	9.2	3.2	2.6	0.2	1.4	4.8	5.24	108.0
133	12.48		175	11.0	36.0	53.0	3.3	1.6	0.9	0.3	0.3	1.7	4.87	103.5
134	17.55		5	55.0	31.0	14.0	5.7	1.6	0.3	0.2	0.2	1.8	4.71	89.1
135	4.09		423	29.0	31.0	39.0	4.1	3.1	0.9	0.3	0.4	0.6	4.69	64.9
136	1.16		335	10.0	13.0	37.0	4.5	2.8	0.8	0.4	0.8	0.6	5.56	78.4
137	3.26		5	4.9	1.0	93.9	3.0	0.5	0.6	0.4	0.1	1.3	4.50	70.8
138	5.78		1	10.0	15.0	62.0	8.8	4.0	3.5	0.5	0.8	2.3	5.64	140.0
139			5	25.0	12.0	62.0	7.5	3.0	1.6	0.2	0.7	0.6	5.77	67.1
140	13.31	1.18	1	35.0	25.0	39.0	13.9	5.6	2.8	0.3	1.7	5.6	5.66	198.7
141	1.05		85	32.0	26.0	42.0	12.1	8.8	3.7	0.4	0.7	0.2	6.41	77.0
142	6.10		1	9.0	26.0	54.0	20.0	3.7	2.4	0.2	1.3	4.3	4.88	141.1
143	3.18		284	60.0	21.0	19.0	55.9	30.4	20.3	0.5	1.8	1.8	6.64	212.6
144			5	29.0	6.0	13.0	36.0	13.9	16.9	0.6	5.0	0.6	7.13	236.9
145				N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A		5.67	84.9
146	24.17	1.36	95	5.0	12.0	83.0	21.0	13.4	7.5	2.7	0.4	7.9	5.81	402.0
147			15	0.0	0.0	99.7	3.1	0.8	0.4	0.2	N/A	0.8	4.64	69.6
148			75	42.0	20.0	37.0	9.7	0.1	1.2	1.8	0.5	0.1	5.22	114.3
149	2.21		5	8.0	6.0	71.0	10.1	3.2	1.6	0.3	0.7	4.3	5.50	76.3
150			255	10.0	12.0	53.0	7.4	2.4	1.4	0.3	0.9	0.9	5.83	72.6
151	1.10		80	36.0	18.0	46.0	17.5	1.6	7.3	0.9	0.4	0.6	4.81	101.9
152	3.01	1.02	1	4.0	4.0	92.0	2.3	0.5	0.8	0.2	0.4	2.5	3.74	95.6
153	2.99		235	17.0	9.0	74.0	2.1	0.6	0.7	0.2	0.2	1.9	4.43	61.8
154	1.09		313	62.0	25.0	13.0	24.0	14.0	7.6	0.5	0.3	0.6	6.23	70.7
155	4.04	1.38	15	44.0	18.0	38.0	6.1	0.9	2.8	0.6	0.3	0.1	4.80	93.5
156	1.05		245	7.0	3.0	90.0	0.0	0.0	0.5	0.1	0.2	0.1	5.81	52.8
157	3.48		45	18.0	39.0	43.0	4.4	0.6	1.0	0.6	0.2	0.9	4.78	72.1
158	3.21		91	34.0	32.0	34.0	9.2	0.4	5.8	0.7	0.2	0.1	4.87	97.8
159	2.19		5	19.0	40.0	37.0	5.9	1.3	2.3	0.5	0.5	1.2	5.23	111.0

160	3.46	1.09	421	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A		6.19	190.8
161	2.77		1	13.0	19.0	57.0	13.0	0.7	0.8	0.4	0.4	1.4	4.64	65.8
162	3.88	1.58	15	45.0	3.0	43.0	7.7	0.0	2.1	0.3	0.3	0.2	4.66	46.4
163	1.82			N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A		5.51	75.2
164	2.66		5	17.0	17.0	23.0	5.3	1.1	1.9	0.4	0.6	0.9	5.28	87.8
165	2.77	1.04	205	3.0	6.0	91.0	15.1	1.1	0.5	0.4	0.3	0.5	3.90	289.5
166	1.26		90	12.0	14.0	68.0	5.6	0.4	1.4	0.4	0.4	1.3	6.04	151.6
167			45	14.0	11.0	56.0	6.5	3.3	2.9	0.7	1.1	0.9	5.94	79.8
168	1.81		205	56.0	14.0	30.0	4.8	0.5	2.1	0.3	0.7	0.4	4.43	81.1
169			65	31.0	7.0	32.0	22.4	10.3	8.2	4.4	0.6	0.3	7.94	493.6
170			215	4.0	5.0	48.0	2.0	0.5	0.5	0.2	0.3	0.2	4.93	52.5
171			25	29.0	24.0	47.0	10.9	1.2	4.4	3.9	0.5	0.2	5.85	108.0
172	3.04	1.54	240	11.0	34.0	40.0	19.3	15.1	3.3	0.1	1.5	9.0	6.10	134.7

*K_d values were calculated as described in section 3.3.1. Troubleshooting of measured concentrations used in the K_d calculation are further described in the section that follows.

N/A – indicates values which were not available or not measured.

Analytical determination of PFAS concentrations in spiking and sample solutions

In the process of calculating K_d values from the measured solution concentrations, it was apparent that the spiked blank sample concentrations (stock spiking solutions) were, in many cases, less than the measured sample concentrations, which led to negative K_d values. Several potential analytical errors for the stock spiking solutions were scrutinised in order to try and understand why this was occurring and these are listed below.

1) Was the stock concentration (containing PFOS and PFHxS) correct or did it change over time?
    a. The stock concentration was measured before the experiment to check it was correct and the experiment would not have proceeded without this step. The concentration of both PFOS and PFHxS was approximately 375 µg/L in the stock solution.
    b. The stock solution was diluted (nominally) to 10 µg/L in triplicate in each batch of samples and the average concentrations across all batches were 8.4 µg/L for PFOS and 11.1 µg/L for PFHxS.
    c. The stock concentration of PFOS was also measured 6 months later and a concentration of 383.5 µg/L of PFOS was observed.

Conclusion: It is unlikely that the stock concentrations of PFOS and PFHxS were incorrect. This is based on the measured stock concentrations before, during and long after the experiment was completed.

2) Was the stock concentration not transferred into the samples or spike blanks correctly?
    a. Triplicate replicates were used, and a high proportion of replicates had a coefficient of variation of <20%.

Conclusion: The reproducibility of the replicates indicates that the spike solution was spiked correctly into the samples and quality controls, or if there was an error in transferring the solution into samples it was at least consistent throughout the experiment.

3) Was there contamination from the laboratory in the sorption samples?
    a. If there was contamination of the samples, it would be expected to influence the concentrations measured in the samples and quality controls. However, most of the replicates were close in measured concentrations (see point 2).
    b. The soil blanks were all below the limits of detection (LOD).
    c. The $CaCl_2$ was also below LODs for concentrations of PFASs.

Conclusion: It is unlikely that a large number of samples were contaminated without also affecting the quality control samples. The soil blanks and $CaCl_2$ solution was shown not to contribute to any potential measurable contamination in the samples. Other sources of contamination, not tested, could have also included pipette tips, vial inserts and centrifuge tube lids but these would appear unlikely sources for elevated (over initial) concentrations of PFASs, as observed in some sorption samples.

4) Were there matrix effects from $CaCl_2$, pH or salinity of the stock or sample solutions that affected mass spectrometric analysis? The term "matrix effects" refers to the difference in the response of an analyte in the standard solution versus the response of the same analyte in the samples. Matrix effects could result in either suppression or enhancement of analyte response.
    a. A small test was initially conducted on the stock concentration to see if dilution with water or $CaCl_2$ affected the measured concentrations. This initial test indicated that this could potentially be the case, as averages stock concentrations diluted in 0.5mM $CaCl_2$ were 25.7 µg/L and 28.9 µg/L for PFOS and PFHxS, respectively and average stock concentrations diluted in water were 52.8 µg/L for PFOS and 43.4 µg/L for PFHxS.
    b. A small-scale experiment was undertaken, using the same methods as in the main manuscript (section 3.3) to investigate the concentrations of $CaCl_2$ on measured PFASs concentrations. The $CaCl_2$ concentrations used were 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.75 and 1 mM. The results from this test found no significant (p >0.05) differences in measured concentrations for PFHxS in the tested range of $CaCl_2$ treatments. However, significant increases in measured concentrations for PFOS were observed between 0 to 0.4 mM $CaCl_2$ but not observed between 0.4 to 1 mM $CaCl_2$ (Table S2).
    c. Other aspects such as EC and pH were also considered. The sample measured concentrations were regressed against both pH and EC and found there was no correlation between measured concentrations for both PFSAs and EC. However, there was a significant correlation (p <0.05) between pH values and measured PFOS concentrations with and a r value of 0.38 for 172 soils (Table S3). The same correlation was not observed for PFHxS.

Table S2: Measured concentrations of PFOS, PFOA and PFHxS in different $CaCl_2$ concentrations. Different letters denote significant differences between each concentration of PFASs in regards to the $CaCl_2$ molarity used.

$CaCl_2$ conc. (mM)	PFHxS (µg/L)	PFOS (µg/L)
0.0	42.8 [a]	25.6 [a]
0.1	43.7 [a]	30.2 [b]
0.2	44.2 [a]	34.7 [cd]
0.3	43.9 [a]	34.2 [cd]
0.4	44.8 [a]	37.1 [d]
0.5	43.3 [a]	32.9 [bc]
0.75	44.1 [a]	33.8 [bcd]
1.0	44.5 [a]	33.9 [cd]

Table S3: Correlations between concentrations of PFOS and PFHxS and soil properties EC and pH (n = 171). The correlations are represented by Pearson's coefficient, r values. Asterisks (*) indicate significant (p <0.05) correlations between variables.

	pH ($CaCl_2$)	EC (µS/cm)
PFOS (µg/L)	0.38*	0.00
PFHxS (µg/L)	-0.09	0.01

Conclusion: It is likely that the measured concentrations of PFOS were affected by the positive relationship with soil pH, which indicates that a matrix effect of pH on PFOS concentrations could explain why the PFOS measured concentrations in soil samples were higher than those in the spiked blank samples (no soil). However, the same relationship was not observed between PFHxS concentrations and pH, which does not resolve why the sample concentrations were higher than spiked blank controls for PFHxS. Concentrations of $CaCl_2$ did not appear to consistently influence measured concentrations of PFOS or PFHxS.

Overall conclusions and resolution

Despite the investigations undertaken above to determine the cause of the apparent higher than expected concentrations in the sample solutions, there did not appear to be an obvious reason why

the high concentrations in the samples occurred. Matrix effects from the soils that could not be corrected for by the response of the internal standards are thought to have the most likely influence on the differences in measured samples concentrations to those of the spiked blank samples. However, there was no consistent influence from concentrations of $CaCl_2$ in solution or EC on the measured sample concentrations. The soil pH was positively correlated with PFOS solution concentrations in samples but the same was not observed for PFHxS concentrations. This result suggests that there may be different matrix affects affecting both PFSAs in varying ways and perhaps even multiple soil properties contributing to the matrix effect.

Matrix effects, if observed in the future, could be overcome by performing clean up procedures, like liquid-liquid extraction, on the aqueous samples prior to analyses by LC-QTOF. An example of liquid-liquid extraction can be found in Backe et al. (2013).

As there were significant issues arising from using the spiked blank concentrations in the K_d calculation, the expected nominal concentration (50 µg/L) was used as the initial solution concentration.

Multiple reaction monitoring transitions

Table S4: Analyte name, abbreviation, and the multiple reaction monitoring (MRM) transitions (parent, quantifiers and qualifiers) for LC-QTOF. Unavailable transitions are written as N/A.

	MRM transitions		
PFAA	Parent	Quantifier	Qualifier
PFOS	499	99	80
$^{13}C_8$-PFOS	507	99	N/A
PFHxS	399	99	80
$^{18}O_2$-PFHxS	403	103	N/A

Limits of detection and quantification

Table S5: The limits of detection (LODs) and quantification (LOQs) of PFOA, PFOA and PFHxS in soil solution. The LODs and LOQs were calculated as 3x and 10x the standard deviation of the lowest standard.

	LOD (µg/L)	LOQ (µg/L)
PFOS	2.34	2.59
PFOA	1.42	2.11
PFHxS	1.08	1.41

References

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Correlation matrix

Table S6: Cross correlation matrix of soil properties and K_d values of PFOS and PFHxS. Correlations are represented by Pearson's coefficient, r values and units for the different soil properties are stated in the first column from the left.

Soil Properties	PFOS K_d	PFOS Log K_d	PFHxS K_d	PFHxS Log K_d	Clay	Silt	Silt+Clay	Sand	CEC	Ca	Mg	Na	K	OC	pH	EC
PFOS K_d (L/kg)	1.0															
PFOS Log K_d (L/kg)	0.9	1.0														
PFHxS K_d (L/kg)	0.1	0.2	1.0													
PFHxS Log K_d (L/kg)	0.1	0.2	1.0	1.0												
Clay (%)	0.1	0.1	0.1	0.1	1.0											
Silt (%)	0.3	0.3	0.2	0.2	0.1	1.0										
Silt+Clay (%)	0.2	0.2	0.2	0.2	0.9	0.5	1.0									
Sand (%)	-0.2	-0.3	-0.2	-0.3	-0.8	-0.6	-0.9	1.0								
CEC ($cmol^+/kg$)	0.1	0.1	0.1	0.1	0.6	0.0	0.5	-0.4	1.0							
Ca ($cmol^+/kg$)	0.0	0.0	0.3	0.2	0.4	-0.1	0.3	-0.3	0.9	1.0						
Mg ($cmol^+/kg$)	0.1	0.1	-0.2	-0.2	0.6	0.0	0.5	-0.5	0.8	0.6	1.0					
Na ($cmol^+/kg$)	0.1	0.1	-0.2	-0.2	0.4	-0.1	0.2	-0.2	0.4	0.1	0.5	1.0				
K ($cmol^+/kg$)	0.1	0.1	0.2	0.2	0.3	0.0	0.3	-0.3	0.6	0.5	0.4	0.1	1.0			
OC (%)	0.4	0.4	0.3	0.4	-0.2	0.3	0.0	0.0	0.2	0.2	0.1	-0.1	0.3	1.0		
pH ($CaCl_2$)	-0.2	-0.3	-0.1	-0.1	0.2	-0.3	0.0	0.1	0.4	0.5	0.3	0.3	0.1	-0.3	1.0	
EC (µS/cm)	0.0	0.1	0.2	0.2	0.3	-0.2	0.2	-0.1	0.4	0.2	0.5	0.9	0.1	-0.1	0.3	1.0

Chapter 5. An investigation into the long-term binding and uptake of PFOS, PFOA and PFHxS in soil – plant systems

Highlights

- PFOS, PFOA and PFHxS appear to retain bioavailability in soil over time.
- PFHxS was the most, and PFOS the least, bioaccumulative PFAA across a range of soils.
- PFAA bioaccumulation in plant shoots was mainly dependent on organic carbon content.
- Across soils, bioaccumulation was inversely related to PFAA partitioning.

Statement of Authorship

Title of Paper	An investigation into the long-term binding and uptake of PFOS, PFOA and PFHxS in soil – plant systems.
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Name of Primary Author (Candidate)	Emma R. Knight		
Contribution to the Paper	Experimental development; conducting experiments; data and statistical analysis; modelling of data; critical interpretation; manuscript writing.		
Overall percentage (%)	85%		
Certification:	This paper reports on original research I conducted during the period of my Higher Degree by Research candidature and is not subject to any obligations or contractual agreements with a third party that would constrain its inclusion in this thesis. I am the primary author of this paper.		
Signature		Date	04/09/2020

Co-Author Contributions

By signing the Statement of Authorship, each author certifies that: 1) the candidate's stated contribution to the publication is accurate (as detailed above); 2) permission is granted for the candidate in include the publication in the thesis; and 3) the sum of all co-author contributions is equal to 100% less the candidate's stated contribution.

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1. Abstract

This study investigated the potential aging and plant bioaccumulation of three perfluoroalkyl acids (PFAAs), perfluorosulphonic acid (PFOS), perfluorooctanoic acid (PFOA) and perfluorohexanesulphonic acid (PFHxS) in 20 soils over a six-month period. Sorption coefficients (Log K_d) ranged from 0.13–1.28 for PFHxS, 0.17–1.06 for PFOA and 0.98–2.03 for PFOS, respectively, and bioaccumulation factors (Log BAFs) ranged from 0.29–1.24, 0.22–1.46 and 0.05–0.65 for PFHxS, PFOA and PFOS, respectively. Over the six-month period, K_d values significantly increased for PFHxS and PFOA but the magnitude of the increase was very small and did not translate into differences in plant PFAA-concentrations between aged and freshly spiked treatments. The K_d and BAF values were modelled by multiple linear regression (MLR) to soil physico-chemical properties and by partial least squares regression to soil spectra acquired by diffuse reflectance mid-infrared Fourier transform spectroscopy (DRIFT-PLSR). Modelling of each PFAA was influenced by different soil properties, including organic carbon, pH, CEC, exchangeable cations (Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}) and oxalate extractable Al. BAF values were not strongly correlated to any soil property but were inversely correlated to K_d values. Our results indicate that limited aging occurred in these soils over the six-month period.

Key words: Bioaccumulation factors; Mid-infrared spectroscopy; Modelling, Organic contaminants; PFAAs; Soil properties.

2. Introduction

Perfluoroalkyl acids (PFAAs) have been commonly detected in many environmental matrices across the world due to their widespread use and persistence, including in soil, sediments, biosolids, waterways and in animals. In Australia, for example, there are several sites where the use of PFAAs, a key ingredient in aqueous film forming foams, at fire-fighting training grounds and air-fields for preventative measures against fuel fires has led to widespread contamination surrounding those sites (AECOM 2015, Bräunig et al. 2017). Other sources of PFAAs in the environment are contaminated groundwater or re-claimed water used for irrigation and also the use of biosolids as fertiliser. However, measured concentrations of PFAAs in the environment vary widely depending on the source of contamination, where maximum concentrations of PFOA and PFOS range between 0.01–123 µg/kg and 0.003–162 µg/kg, respectively, in soil survey data and 2–50000 µg/kg and 0.4–460000 µg/kg, respectively, from primary source contamination (Brusseau et al. 2020). Therefore,

understanding how these chemicals behave in the environment is important as it affects the way management and remediation strategies are implemented.

There is currently limited understanding of the soil-chemical interactions of PFAAs in the environment, particularly their aging in soil. For many organic contaminants aging in the soil can be a significant process and is important in determining the exposure and bioavailability of the chemicals to the surrounding environment over time (Alexander 2000). For instance, many organic contaminants, including naphthalene, anthracene, phenanthrene, fluoranthene, pyrene, atrazine and 4-nitrophenol (Hatzinger and Alexander 1995, Kelsey and Alexander 1997, Chung and Alexander 1998, Tang et al. 1998) are known to become less bioavailable to organisms over time (Alexander 2000). Whether or not the same is true for PFAAs has not been determined. Theoretically, the longer the contaminant resides in soil the more chance it has to move deeper into the soil matrix sites that are not easily accessed, even by some microorganisms (Alexander 2000). Two methods to examine aging of contaminants in soils have previously been assessed i.e. changes in the concentration of contaminants in the soil pore-water over time (expressed as sorption coefficients i.e. K_d values) and by plant uptake (expressed as bioaccumulation factors, BAFs). The mechanisms of aging can be influenced by different soil properties and type of contaminant present. While studies on aging are limited, different soil properties, in particular organic carbon (OC) content, are already known to be a major influence on the short-term retention, i.e. sorption, of PFAAs in soils (Higgins and Luthy 2006, Li et al. 2012, Pereira et al. 2018). However, OC is unlikely to be the only soil property influencing the sorption of PFAAs to soils or sediments (Li et al. 2018, Knight et al. 2019). In the review by Li et al. (2018) the authors found that while OC is important, <10% of sorption of PFAAs to soils could be explained by the OC content alone (n = 147 for PFOA and n = 178 for PFOS).
Several studies have already investigated the uptake of PFAAs by plants in both biosolid-amended soils and hydroponic systems. BAFs ranging from 0.07–3.19 for perfluorooctanoic acid (PFOA), 0.10–3.12 for perfluorooctanesulphonic acid (PFOS) and 0.15–7.56 for perfluorohexane sulphonic acid (PFHxS) have been reported in these studies (Lechner and Knapp 2011, Blaine et al. 2013, Zhao et al. 2014b, Bizkarguenaga et al. 2016). For a given PFAA, the concentrations taken up by plant roots will also depend on the soil properties and the plant species (and its protein content) (Wen et al. 2016). However, there is also no current literature describing the relationship between soil properties and bioaccumulation of PFAAs into plants, nor the potential for bioavailability of PFAAs to change over time (aging). It is expected that the uptake of PFAAs in plants would be influenced by several soil properties and inversely related to soil sorption (K_d).
Considering the likelihood that soil properties influence both sorption and uptake of PFAAs into plants, being able to predict these processes from the soil properties would be advantageous. The

modelling of soil properties (from wet chemistry and soil spectra) with PFAAs has been investigated previously using two different modelling strategies: multiple linear regression (MLR) and diffuse reflectance mid-infrared Fourier transform spectroscopy coupled with partial least squares regression analysis (DRIFT-PLSR) (Knight et al. 2019). However, the modelling of soil properties and BAF values has not previously been investigated for PFAAs.

This study therefore aimed to investigate how soil properties may affect sorption (K_d values) and bioaccumulation (BAF values) for PFOA, PFOS and PFHxS and to evaluate, through MLR and DRIFT-PLSR modelling, whether aging of these PFAAs affects either process, sorption or bioaccumulation.

3. Materials and methods

3.1 Chemicals

Powdered forms, of PFOA (95% purity), PFHxS (≥98% purity), PFOS-K salt (≥98% purity) and Hoagland's No. 2 basal salt mixture were obtained from Sigma-Aldrich (Australia). Powdered PFAAs contained both linear and branched isomers. Mass labelled standards of $^{13}C_4$-PFOA, $^{13}C_8$-PFOA, $^{13}C_8$-PFOS and $^{18}O_2$-PFHxS were purchased from Wellington Laboratories (Canada). Bond Elut carbon cartridges were purchased from Agilent (Australia).

3.2 Soil incubation and bioaccumulation

Twenty air-dried and sieved (<2 mm) soils were chosen based on a range of soil properties. These soils were collected from different locations in Australia. A summary of main soil characteristics is provided in Table 1, and all characteristics can be found in the supplementary information, Table S1.

Table 1: Summary of the soil characteristics from the 20 test soils.

Soil properties	**OC (%)**	**pH ($CaCl_2$)**	**Clay (%)**	**CEC (NH_4)**	**Exchangeable cations**			
					(cmol+/kg)			
					Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}
Minimum	0.3	4.5	1.6	2.1	1.3	0.2	0.3	0.0
Median	1.6	5.7	8.6	9.5	5.6	1.9	0.7	0.6
Maximum	11.0	8.0	60.0	41.6	38.4	9.9	1.3	2.0
Mean	2.3	6.0	13.9	12.8	7.5	2.4	0.7	0.8

Soils were weighed (2.35 kg) into plastic polypropylene zip-lock bags before being spiked with a mixture of PFOA, PFHxS and PFOS in water. The spike was added to the soil using a spray bottle and routinely mixed until the spray bottle was empty. Any remaining volume of water was added, based on weight to reach 60% field capacity where the soils had a final nominal concentration of 500 µg/kg of PFOA, PFOS and PFHxS. This concentration was chosen to represent an environmentally relevant concentration for contaminated sites (Wen et al. 2016, Bräunig et al. 2019). The soils were then thoroughly mixed until homogeneous. The spiked soils were then split and transferred into closed-bottom pots, with four 500 g replicates and one 350 g replicate. This same procedure was carried out for the non-spiked soils. For dose confirmation, subsamples of 10 g were taken from each of the spiked 500 g pots. All pots were then placed in a constant temperature room at 20°C for six months (to age) where they were watered once a week and randomised fortnightly.

After 6 months, all soils were dried in a glasshouse before the non-spiked soils were spiked using the same concentration and methodology as the soils already spiked. The pots of soils were placed in a constant environment room set at 25°C day/ 18°C night (± 3°C) 12 h light: 12 h dark, 60% relative humidity, for two days to equilibrate before planting. Five pre-germinated *Phaseolus vulgaris* seeds (Dwarf Bean Tendegreen; Mr Fothergills) were planted into each of the 500 g replicates (4 replicates per soil treatment) and later thinned to two plants per pot when plants had grown >5 cm in height. The time of thinning and harvesting was affected by soil type as the same plants in some soils grew faster than in other soils – all plants were thinned and harvested at the same phenological stage of growth in an effort to target similar dry matter yields across soils, in contrast to harvesting all plants at one time – hence the plants should have transpired the same amount of water to produce the same amount of dry matter (transpiration efficiency) (de Wit 1958, Tanner and Sinclair 1983). *Phaseolus vulgaris* was chosen for this study based on research showing that PFOA and PFOS tend to accumulate greater in beans versus other species due to their higher protein contents (Wen et al. 2016).

Plants were watered daily and randomised every three days. Rhizobia strain, CC511, was added to the soil one week after planting to assist in nodulation and nitrogen-fixation of *P. vulgaris*. Full strength Hoagland's nutrient solution (20 mL of 1.6 g/L) was added 16 days after planting and again at 38 days (5 mL). Plant shoots were harvested, where the shoot met the soil, when the plant had reached the stage of flowering, and after producing small beans (Feller 2001). As noted above, these stages were reached at different times for different soils, but for the same soil, for aged and freshly spiked soil treatments, plants were harvested at the same time. Shoots were rinsed in Milli-Q water after harvest, patted dry with clean paper towel and measured for total biomass (wet weight) before being freeze dried for extraction.

3.3 Sample extraction and analysis

3.3.1 Soil porewater extraction

Porewater (PW) samples were taken from the 350 g pots at time zero, two, four and six months. No plants were grown in the 350 g pots. Methods for porewater extraction can be found in Thibault and Sheppard (1992). Briefly, 2 x 25 g or 3 x 20 g portions of soil were taken and transferred inside a disposable plastic syringe with a glass wool insert, then placed in a plastic tube. The tubes were then centrifuged at 3569 *g* for 45 min to obtain the porewater after which the syringe was removed and the tube centrifuged again at 30940 *g* for 30 min before collecting the porewater into glass autosampler vials and stored at 4°C until analysis. Control solutions of 20 µg/L and 100 µg/L of PFOS, PFOA and PFHxS mix in water were used in triplicate with each porewater sampling event to ensure contamination from the process was negligible and to correct for any sorption to laboratory ware (Lath et al. 2019). For analysis, porewater samples and calibration standards were made using 0.25 mL of sample and 0.25 mL of methanol.

3.3.2 Soil and plant extraction

Soil and plant extractions of PFAAs were carried out following methods produced by Bräunig et al. (2019), with some changes. For soil, 0.5 g freeze dried soil was weighed into a 15 mL polypropylene (PP) tube and spiked with 20 µL of an internal standard mixture (200 µg/L in methanol) containing $^{13}C_4$-PFOA, $^{13}C_8$-PFOS and $^{18}O_2$-PFHxS. After 30 mins, 5 mL of methanol: ammonia (99:1%) was added and sonicated for 20 mins and centrifuged at 2095 g force for 10 min before collecting the supernatant in a fresh tube and repeating with 3 mL of methanol: ammonia. Samples were reduced to 1 mL under nitrogen gas (N_2) and heat (40°C) before acidification with 10 µL of acetic acid. Samples were then plunged through, using a disposable syringe, a methanol conditioned (1 mL) Bond Elut carbon cartridge (100 mg) and collected into a 1.5 mL PP vial. The tube was rinsed with a further 1 mL of methanol and passed through the cartridge before being reduced to 0.4 mL under N_2 and heat and then reconstituted to 1 mL with 8 mM ammonium acetate in water and 4 ng (20 µL of 200 µg/L in methanol) of $^{13}C_8$-PFOA was added.

For plant extractions, 0.1 g of freeze-dried plant material was weighed into a 15 mL PP tube with 4 ng of internal standards ($^{13}C_4$-PFOA, $^{13}C_8$-PFOS and $^{18}O_2$-PFHxS) and after 30 min, 1.5 mL of 200 mM sodium hydroxide and 3.5 mL of methanol were added, vortexed and placed in a fridge (4°C) overnight. The samples were then sonicated for 20 min, acidified with 75 µL of 4 M hydrochloric acid, centrifuged for 20 min at 3724 g force and then repeated with 1 mL of methanol minus the acidification step. Collected supernatants were evaporated to 1 mL by N_2 and heat (40°C) before being plunged through a methanol conditioned (3 mL) Bond Elut carbon cartridge (250 mg). The

cartridge was washed with a further 0.3 mL of methanol and collected into a 1.5 mL PP vial before the samples were reduced to 0.4 mL under heat and nitrogen gas before being reconstituted to 1 mL using 8 mM ammonium acetate in water and 4 ng of $^{13}C_8$-PFOA was added. Extracts in some cases were diluted to ensure concentrations were within the instrumental calibration range.

3.3.3 Instrumental analysis

Concentrations of PFOA, PFOS and PFHxS in the porewater samples were determined by liquid chromatography triple quadrupole time of flight mass spectroscopy (LC-QTOF) using an Exion LC ™ (Sciex) and a TripleTOF ™ 5600$^+$ mass spectrometer (Sciex) equipped with a DuoSpray ion source. The mass spectrometer was operated in negative mode set for high sensitivity using product ion scans (Table S2). Chromatographic separation was performed using a Luna® C18 30 x 2 mm (5 µm), 100 Å (Phenomenex) pre-column and a Hypersil GOLD™ pentafluorophenyl (PFP) 100 x 1 mm (3 µm) HPLC column (Thermo Scientific), maintained at a constant temperature of 40 °C. The mobile phase was comprised of two eluents, which were (A) 5 mM ammonium acetate and (B) 100% methanol using a binary gradient system totaling 12 min and a flow rate of 0.45mL/min. The gradient of (A) was 95% for 2 min, 55% by 5 min, 5% by 7 min and held for 1 min before returning to 95% by 8.10 min for the remaining time. The ion source temperature was maintained at 550 °C, with a spray voltage of 4000 V and collision energy of -10 V.

Soil and plant extracts were analysed using methods published by Bräunig et al. (2019), with some alterations. Briefly, concentrations of PFAAs in soil and plant extracts was determined by high performance liquid chromatography (Nexera HPLC, Shimadzu Corp., Kyoto Japan) coupled with a tandem mass spectrometer (6500+ QQQ Sciex, Concord, Ontario, Canada) utilising multiple reaction monitoring (MRM) in negative electrospray ionisation mode (Table S2). Chromatographic separation, 5 µL of sample, was achieved by a gradient elution using a Gemini NX C18 (50 x 2 mm, 3 µm particle size, 110 Å pore size, Phenomenex, Lane Cove, Australia) column maintained at a constant temperature (50 °C) and flow rate (0.3 mL/min). The mobile phase composition consisted of (A) methanol:water (1:99, v:v) and (B) methanol:water (95:5, v:v), each with 8 mM ammonium acetate. A pre-column (C18 50 x 4.6 mm, 5 µm particle size, Phenomenex, Lane Cove, Australia) was fitted between the mobile phases and the injector-to-trap to delay any background PFAAs stemming from the HPLC system. Retention time and a comparison of the ratios of MRM transition area among the samples and the calibration standards in the same sample run was conducted to verify the peaks and concentrations measured. Analysis and quantification was based on isotopic dilution methods using mass-labelled standards that were spiked prior to sample extraction. Calibration standards were made to match the sample matrix, with methanol: ammonium acetate in water (40:60), totaling 1 mL with a range of 0.1 to 100 µg/L (0.1, 0.4, 1, 4, 10, 20, 40, 100 µg/L).

3.3.4 Analytical quality assurance and quality control (QA/QC)

All glassware prior to use was acid washed and then methanol rinsed and dried, before use, to prevent contamination. In each batch of soil and plant samples, multiple quality control measures were implemented including quality control standards, blanks (Milli-Q water), duplicate samples and native spikes. Calibration standards were injected multiple times during each batch and only regression coefficients (R^2) >0.975 were considered acceptable. The three PFAAs were quantified by calculating the ratio between the sample area and the internal standard area relative to the calibration curve. Dilutions of some samples were required to achieve measured concentrations within the calibration range. The average recoveries can be found in Table S3.

Analytical limits of detection (LODs) and quantification (LOQs) for the HPLC-MS and QTOF methods were calculated as three times and ten times the standard deviation, respectively, of the lowest standard (Table S3). No PFAAs were detectable in the procedural blanks for soil, plant and porewater samples. Low level contamination was present in soil blanks (using non-spiked soils) but this was negligible, <1%, compared to spiked PFAA concentrations.

3.4 Diffuse reflectance infrared spectroscopy

The methodology for analysis of soil samples using DRIFT spectroscopy can be found in Janik et al. (2016). In short, samples were scanned using a benchtop Fourier transform infrared (FTIR) spectrometer (Frontier, Perkin-Elmer Inc., USA) equipped with a Perkin-Elmer (PE) auto-focussing DRIFT accessory. Spectra were collected from soil samples, 100 mg, over a 60 s scan time in the spectral range 7800 to 450 cm^{-1} and a resolution of 8 cm^{-1}. Pseudo absorbance units were calculated for the spectra based on the reflection spectra of the samples (R_s) and the background (A PE silicon carbide disc, which is assumed to have a reflection $R_0 = 1$) using the following equation: $AU = \log10 (R_0/R_s)$. This data then underwent spectral baseline correction and multivariate statistical analysis using The Unscrambler-X™ V10.3 (CAMO Analytics, Norway) software.

3.5 Data and statistical analysis

Statistical factorial analysis was achieved using IBM SPSS (v. 24) for differences between plant, porewater and bioaccumulation factors (BAFs) with different soil types at different time points. Multiple linear regression analysis and DRIFT-PLSR analysis were carried out using The Unscrambler software, and in a similar method to Knight et al. (2019). The PLSR models were created using soil spectral (4000 to 450 cm^{-1}) and the respective BAF values for each soil. For both the MLR and PLSR models, the coefficient of determination (R^2) values are from the “leave one out” cross validation regression model, where each sample in turn is removed from that model and carried out for all samples selected for the model. Several factors are used for the PLSR models, with each supporting

the calibration of the model. The first PLSR factor is the most valuable and the first factor is equivalent to an MLR model using spectral data. The optimum number of factors was used in our study to obtain the lowest error for prediction. The root square mean error (RMSE) and the residual predictive deviation (RPD) are included where the RMSE is defined as:

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n}(m_i - p_i)^2}{N}} \quad (1)$$

where *m* are the measured values, *p are* the predicted values, *i* is the sample being tested and *N* is the total number of samples used for the calibration. Bioaccumulation factors (BAFs) for each of the PFAAs for *P. vulgaris* shoots using the concentration in the plant shoots (C_p µg/kg, dry weight) divided by the initial soil concentration (C_s µg/kg, dry weight – at time zero) calculated on a per replicate basis, Equation 2.

$$BAF = 1 + Log(\frac{C_p}{C_s}) \quad (2)$$

In situ sorption coefficients, K_d (L/kg) were calculated using the average initial measured soil concentration (at time zero), C_{AS} (µg/kg), divided by the porewater concentrations, C_{PW} (µg/L), from 0, 2, 4, and 6 months (Equation 3). The K_d values were log transformed to normalise variances.

$$K_d = 1 + Log\ (\frac{C_{AS}}{C_{PW}}) \quad (3)$$

4. Results and discussion

4.1 Soil porewater and sorption

The Log K_d values for the 20 soils ranged from 0.1–0.7 for PFHxS, 0.1–1.1 for PFOA and 0.6–2.1 for PFOS (Table 2 and Table S5). The average Log K_d values for all three PFAAs, in all soils, increased in the following order: PFHxS<PFOA<PFOS with the Log K_d values for PFOS being approximately three times higher than those for PFOA and PFHxS (Table 2), consistent with other studies (Ahrens et al. 2010, Oliver et al. 2019). Other studies have also reported an increase in sorption with increasing chain length for both perfluorosulphonic acids (PFSAs) and perfluorocarboxylic acids (PFCAs) and greater sorption of PFSAs than their corresponding PFCAs (Ahrens et al. 2010, Ahrens et al. 2011, Pereira et al. 2018).

The Log K_d for PFOA and PFHxS significantly (p <0.05) increased over the six-month period for the 20 soils, but the overall magnitude of any increase was small and inconsistent (Table 3). The Log K_d of PFOS did not significantly change over the six-month period.

There is consensus through the literature that while OC has an important role in influencing the sorption of PFAAs in soils, due to the complex nature of soil-PFAA interaction, other soil properties could also influence the sorption, including pH, cation concentration, surface charge and mineral composition (Ahrens et al. 2011, Li et al. 2012, Li et al. 2018).

Table 2: Summary of sorption coefficients, Log K_d and bioaccumulation (Log BAF) for PFHxS, PFOA and PFOS for 20 different soils. The averages, n = 4 for Log BAF values and n = 2 for Log K_d values (at 0 month time interval), are plus or minus the standard error.

	PFHxS		PFOA		PFOS	
	Log K_d	Log BAF	Log K_d	Log BAF	Log K_d	Log BAF
Minimum	0.13	0.29	0.17	0.22	0.98	0.05
Median	0.27	0.67	0.41	0.51	1.60	0.11
Maximum	1.28	1.24	1.06	1.46	2.03	0.65
Average	0.37 ± 0.05	0.70 ± 0.03	0.47 ± 0.03	0.58 ± 0.02	1.56 ± 0.06	0.16 ± 0.01
Skewness	2.17	0.37	1.13	1.41	-0.25	2.21

Table 3: Average Log K_d values (n = 20 soils) at 0, 2, 4 and 6 months for PFOS, PFOA and PFHxS ± the standard error of the mean (n = 2–3). For each compound significant differences ($p < 0.05$) are denoted with different letters.

	Log K_d		
Incubation period (months)	PFHxS	PFOA	PFOS
0	0.37 ± 0.05^{a}	0.47 ± 0.03^{a}	1.56 ± 0.06^{a}
2	0.35 ± 0.04^{a}	0.54 ± 0.05^{b}	1.55 ± 0.06^{a}
4	0.46 ± 0.03^{c}	0.69 ± 0.04^{d}	1.72 ± 0.04^{b}
6	0.41 ± 0.03^{b}	0.58 ± 0.03^{c}	1.58 ± 0.04^{a}

4.1.1 Sorption – Simple and multiple linear regressions

Simple linear regression of Log K_d values and soil properties was investigated using a cross correlation matrix and are represented by the Pearson's coefficient r values. The r values ≥± 0.5 are discussed. The Log K_d values for PFOA were highly correlated with OC (r = 0.9), exchangeable cations Ca^{2+} Mg^{2+} and K^+ (r = 0.7, 0.6 and 0.5, respectively) and oxalate-extractable Al (r = 0.5) and Fe (r = 0.6). The Log K_d values for PFOS were highly correlated with OC (0.5) and exchangeable cations Ca^{2+}, Mg^{2+}, Na^+, K^+ (r = 0.5, 0.5, 0.6 and 0.7, respectively). The Log K_d values for PFHxS were positively correlated with OC, (r = 0.7) oxalate-extractable Fe (r = 0.5) and exchangeable cations Ca^{2+} and Mg^{2+} (r = 0.5 and 0.7, respectively) (Table S5).

To further understand the different roles that soil properties play in the soil-PFAA interactions, multiple linear regression modelling was employed. All multiple linear regression models initially included 10 soil properties (OC, pH, clay, exchangeable cations Ca^{2+}, Mg^{2+}, Na^+, K^+ and oxalate extractable Al, Fe, Mn,). The least significant soil property was sequentially removed from the model which gradually increased the R^2 of the models, until a point where removing too many decreased the R^2 value or the soil properties remaining were all significant (p <0.05). The models reported are those that have the highest R^2 values with significant soil properties. One soil, Karri Loam, had to be removed from the PFHxS Log K_d model as it was significantly adversely influencing the MLR model.

The MLR modelling of PFOA Log K_d values in relation to soil properties resulted in an R^2 of 0.82, with significant (p <0.05) positive correlations with OC and pH and a negative correlation with exchangeable Ca^{2+} (Figure 1A and B). The best MLR model for PFHxS Log K_d values (R^2 = 0.63) had significant positive correlations with OC, pH and exchangeable Mg^{2+} and a negative correlation with oxalate-extractable Al (Figure 1C and D). The best MLR model for PFOS Log K_d values (R^2 = 0.49) had significant positive correlations with exchangeable Mg^{2+} and Na^+ and a negative correlation with oxalate-extractable Al (Figure 1E and F). PFOS sorption did not have a significant relationship with OC in the MLR modelling. While the R^2 value of the PFOS MLR model was the lowest, it is likely the small number of samples (n = 20) and the narrow range of K_d values for all three PFAAs restricted the capability and certainty (RMSE) of the models to predict which soil properties were affecting sorption.

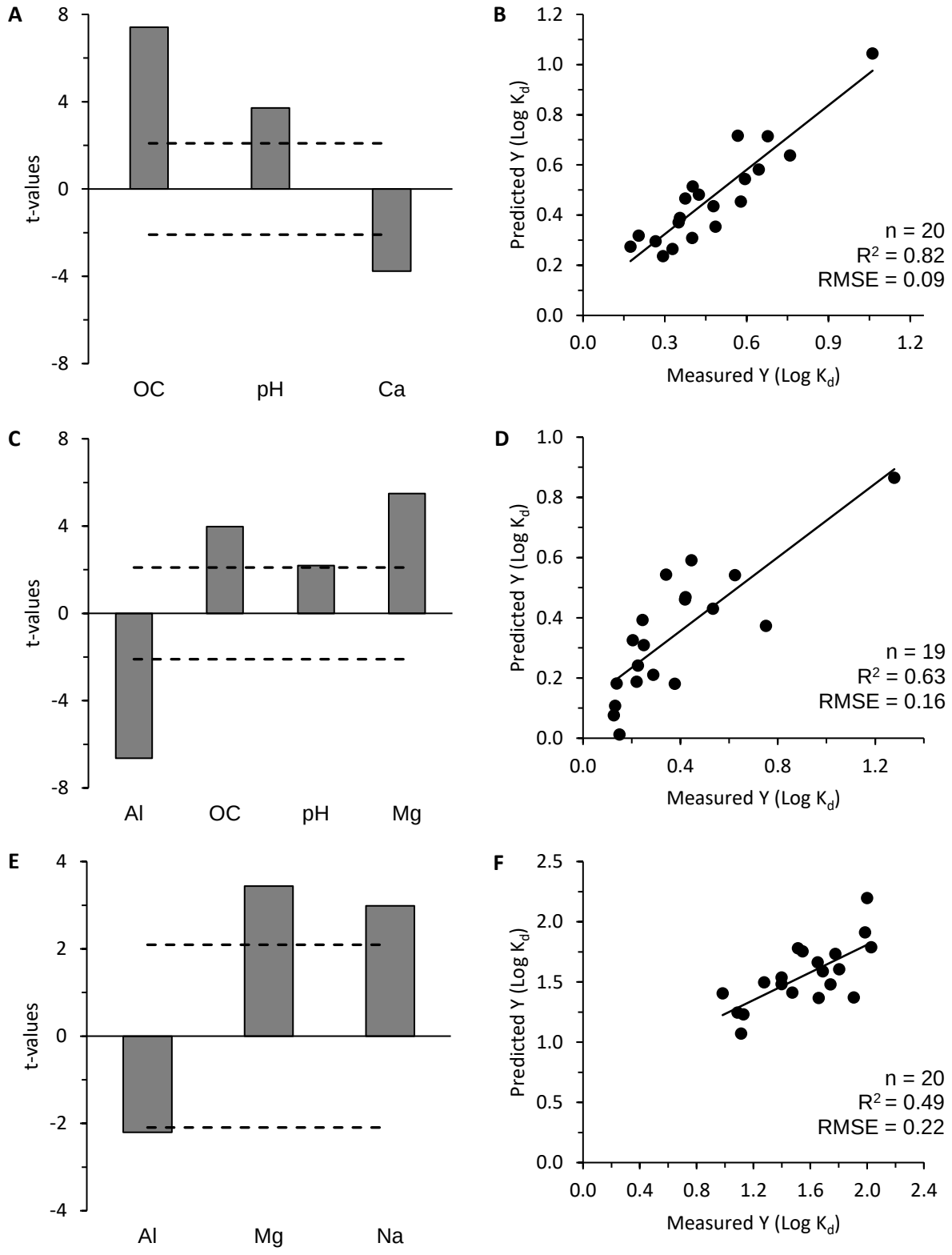

Figure 1: The t-values for significant soil properties in relations to the Log K_d of (A, B) PFOA, (C, D) PFHxS and (E, F) PFOS in soils. (A), (C) and (E) were developed using multiple linear regression model. The dashed lines in (A), (C) and (E) above and below the x-axis represent the critical t-value for the number of soils. Regression plots (B), (D) and (F) correspond to models developed with the soil properties displayed in (A), (C) and (E).

For PFOA, the MLR results in this study are similar to Knight et al. (2019), in relation to the positive correlation between PFOA K_d values and OC. However, soil texture did not explain a significant amount of the variation in K_d values in our smaller set of 20 soils compared to the larger set of soils in Knight et al. (2019). This is likely due to the low overall variance in K_d values and range of soil properties as well as the difference in soil properties used in the initial models.

The increase in sorption of PFAAs, and in this study PFOA and PFHxS, with increases in OC has been reported in several studies (Higgins and Luthy 2006, Li et al. 2012, Milinovic et al. 2015). However, a review article using published data from the literature found that the OC content of soils and sediments could only explain approximately 7% of the total variation in sorption of PFASs (n = 147) (Li et al. 2018). The correlations reported here support the hypothesis that OC alone cannot predict the sorption of PFAAs in soils. Similar to other organic contaminants, the positive relationship between OC and sorption could be due to hydrophobic interactions, where the C-F chain interacts with the alkyl/aromatic groups of OC and/or due to electrostatic interactions *via* cations bridging between negatively charged sites on organic matter and the charged terminal head groups of PFAAs (e.g. SO_3^-, CO_2^-). For PFOS, the MLR results indicated that there was no significant correlation between OC and Log K_d in these soils.

Other studies have found both negative (Higgins and Luthy 2006, Wang and Shih 2011, Zhao et al. 2014a) or no relationship of soil pH with sorption of PFAAs (Oliver et al. 2019). Multivalent cations have also been shown to influence the sorption of PFAAs (Higgins and Luthy 2006, Pereira et al. 2018) where different concentrations of these cations in the soil solution at different pH values may interact with retention of PFAAs on soil surfaces (e.g. cation bridging).

4.1.2 Sorption – DRIFT-partial least squares regression

The x-loading weights can be used for qualitative analysis of the DRIFT-PLSR and are indicative of the level of positive and negative correlations with the K_d values of PFOA, PFHxS and PFOS. At an individual IR frequency the intensity of the loading weight highlights the degree of correlation in the calibration model with K_d. It is important to note that mineral (amorphous and crystalline) and organic components can be represented in the loading weights.

The DRIFT-PLSR model loading weights for all soils in relation to the Log K_d of the three PFAAs, PFOA, PFOS and PFHxS had relatively similar correlations, with three main correlations of interest, slightly varying intensity for each compound (Figure 2). The x-loading weights were inversely related to pyrophyllite (a di-octahedral mica-like 2:1 silicate clay: - Al-OH stretching frequency signature at 3700 cm^{-1}) (Van der Marel and Beutelspacher 1976) and weakly overlapped (positively) with kaolinite minerals at 3628–3622 cm^{-1} (Van der Marel and Beutelspacher 1976). For all three

compounds, weak, positive loading weights for gibbsite could be observed at 3530–3450 cm^{-1}. Strong broad banded, negative correlations with quartz (sand) were observed at 2000–1800 cm^{-1} and 2000–1850 cm^{-1} (Nguyen et al. 1991, Janik and Skjemstad 1995) for all three PFAAs. Much weaker, positively correlated alkyl -CH_2 peaks, a main component of soil organic matter, resulted in two easily discernible loading weights in the 2930–2850cm^{-1} region. These peaks are common for organic matter in most Australian soils, together with a broad band envelope at 3400 and sharper, overlapped peaks near 1680–1400 cm^{-1} (Nguyen et al. 1991). The visible intensity of the peaks decreased in the following order PFOA>PFHxS>PFOS, as does the R^2 value of each model, R^2 = 0.64, 0.41 and 0.16, respectively (Figure 2). The relatively low R^2 values for PFOS, compared to PFOA and PFHxS is likely from the highly clustered set of K_d values. Stronger positive correlations were observed at 1226–1210 cm^{-1}, 1190 cm^{-1}, 1135 cm^{-1} (Si-O) and 1080-1060 cm^{-1} (Si-O-Si stretching vibrations) and are difficult to identify due to the many overlapping or inverted frequencies in this region, including from silicate clay minerals (kaolinite, illite and smectite) and quartz (Van der Marel and Beutelspacher 1976, Nguyen et al. 1991). The MLR and DRIFT-PLSR modelling results were thus comparable, with similar soil properties highlighted as influencing the sorption of PFOA, PFOS and PFHxS, and including positive correlations with OC and negative correlations with oxalate Al (or pyrophyllite/kaolinite, which can be both crystalline or amorphous).

4.2 Plant uptake and bioaccumulation factors

4.2.1 Plant uptake

Concentrations of PFOA, PFOS and PFHxS were detected in all plant shoots and is most likely the result of root uptake and translocation to shoots, rather than *via* a volatilisation pathway to leaves (due to the low vapour pressure of the three PFAAs) (Öberg and Liu 2011). In another study investigating uptake of PFASs in wheat, found no detectable concentrations of PFOA, PFHxS or PFOS were measured in their control plants, which provides further evidence that the volatilisation pathway is unlikely to contribute to the concentrations of PFAAs in the plants from contaminated soil (Zhao et al. 2014b). The concentrations of the different PFAAs in the plant shoots varied from soil to soil but concentrations generally increased, with some exceptions, in the following order: PFHxS>PFOA>PFOS (Figure 3). There were limited differences (p <0.05) in concentrations of PFAAs in plant shoots for aged and non-aged soils. Some significant differences were observed, but these were small in magnitude and inconsistent (Figure 3). For example, if aging had occurred, consistently lower concentrations in the plants growing in aged *versus* freshly spiked soils could be expected, but this was not observed. There was a significant increase in Log K_d values for PFHxS and PFOA between 0 and 6 months (Table 3), but the magnitude of these increases were very small, 0.04 to 0.1 log units. Hence there was little aging of all PFAAs in these soils.

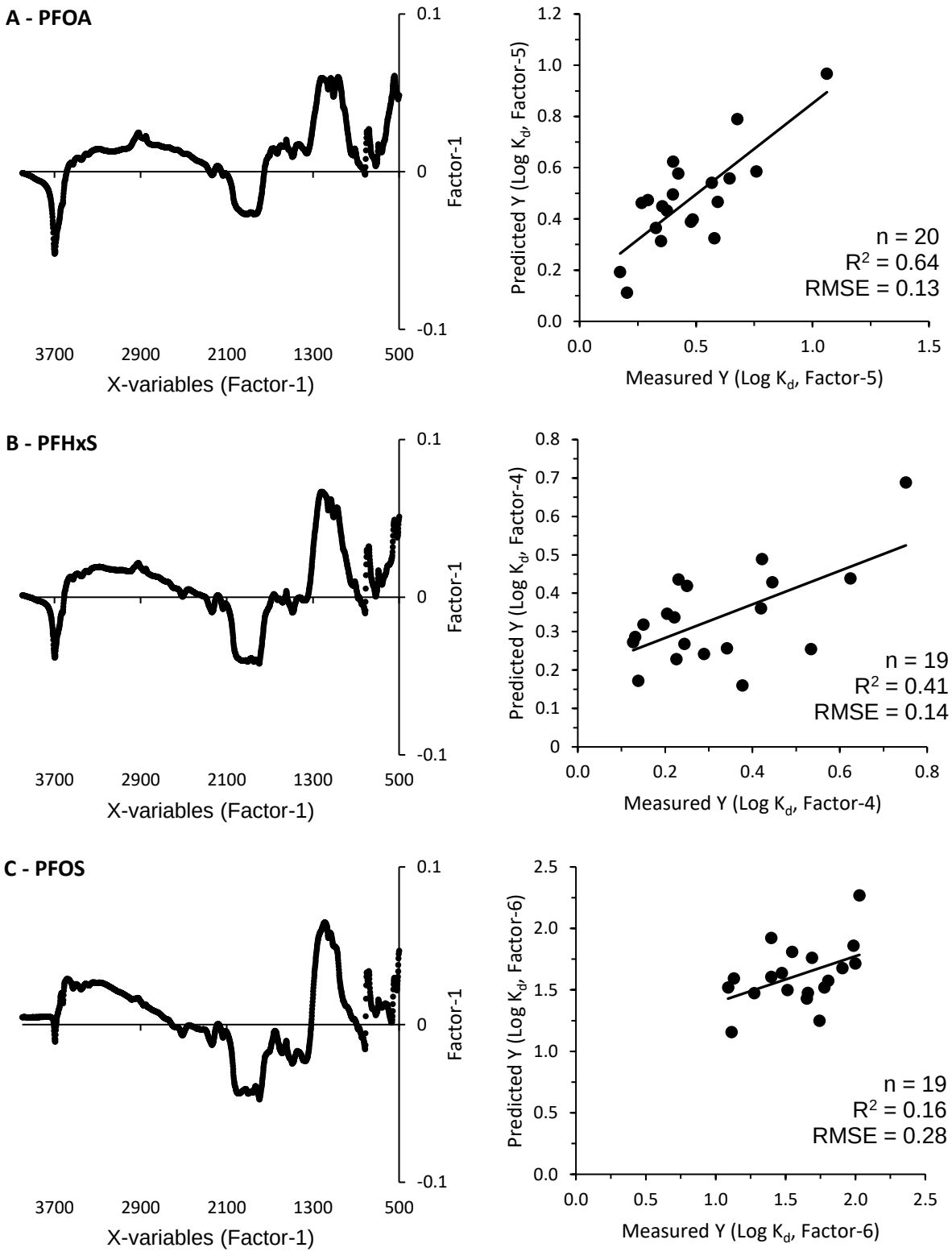

Figure 2: DRIFT-PLSR of soil spectra in relation to Log K_d values for (A) PFOA, (B) PFHxS and (C) PFOS where both left and right panels refer to the same model. The left-hand panels show the x-loading weights of the models and the right-hand panel shows the cross validation regression. (n = 20 for (A) and n = 19 for (B) and (C).

However, aging in soils can be a significant process of decreasing bioavailability for many other organic contaminants, such as anthracene, atrazine, fluoranthene, naphthalene, phenanthrene, pyrene and 4-nitrophenol (Hatzinger and Alexander 1995, Kelsey and Alexander 1997, Chung and Alexander 1998, Tang et al. 1998). For instance, after 200 days incubation in 16 different soils, phenanthrene and atrazine mineralisation was found to be significantly lower, but the rate of mineralisation was different for both chemicals, 9.6–35.0% and 48.4–89.8%, respectively (Chung and Alexander 1998). The significant aging observed for atrazine and phenanthrene is in contrast to the PFAAs tested in this current study, despite the similar time frames (200 days is equivalent to six and a half months). However, the results in Chung and Alexander (1998) indicate that soil characteristics and residence time influence the bioavailability of both atrazine and phenanthrene.

4.2.2 Bioaccumulation factors

The Log BAF values for *P. vulgaris* shoots ranged from 0.1–1.6 for PFOA, 0.3–1.4 for PFHxS and 0.1–0.7 for PFOS dependent on soil type (Table 2 and Table S4). The average Log BAF values for PFOS were approximately 3.5–4.5 times lower than those for PFOA and PFHxS, where the general order of bioaccumulation between the chemicals was PFOS<PFOA<PFHxS. This general order is the inverse of the sorption coefficients (Log K_d) (Table S4). While translocation factors (TFs – shoot concentration/root concentration) were not measured in our study, it has been suggested that the lower accumulation of PFOS into plant shoots compared to PFOA and/or PFHxS could be due to the higher lipophilicity and hydrophobicity of PFOS to PFOA and/or PFHxS (Felizeter et al. 2012, Wen et al. 2016). The BAF values for PFOA and PFOS were of a similar magnitude to those of Wen et al. (2016), who reported BAF values of 0.3–1.9 for PFOA and 0.2–0.8 for PFOS, in a study investigating uptake into several plant species (alfalfa, lettuce, maize, mung bean, radish, ryegrass and soybean) from biosolid-amended soil (Wen et al. 2016).

In relation to other studies, the uptake of PFOA and PFOS in lettuce leaves from a soil amended with compost found Log BAF values of 0.27 and 0.19 for PFOA and PFOS, respectively (Bizkarguenaga et al. 2016). Blaine et al. (2013) found Log BAF values of 1.13 for PFOA, 1.03 for PFHxS and 0.51 for PFOS for lettuce plants grown in a biosolids-amended soil. However, Blaine et al. (2013) also found Log BAF values of 1.40 for PFOA, 1.88 for PFHxS and 1.22 for PFOS for lettuce plants grown in an industrially impacted soil (soil amended with PFAA-contaminated biosolids). The lettuce plants grown in the industrially impacted soil had higher Log BAF values for PFOS and PFHxS than the range of our study. Log BAF values for PFOA, PFHxS and PFOS were 0.04, 0.93 and 0.41, respectively for wheat shoots grown in soil spiked with a range of PFAAs (Zhao et al. 2014b).

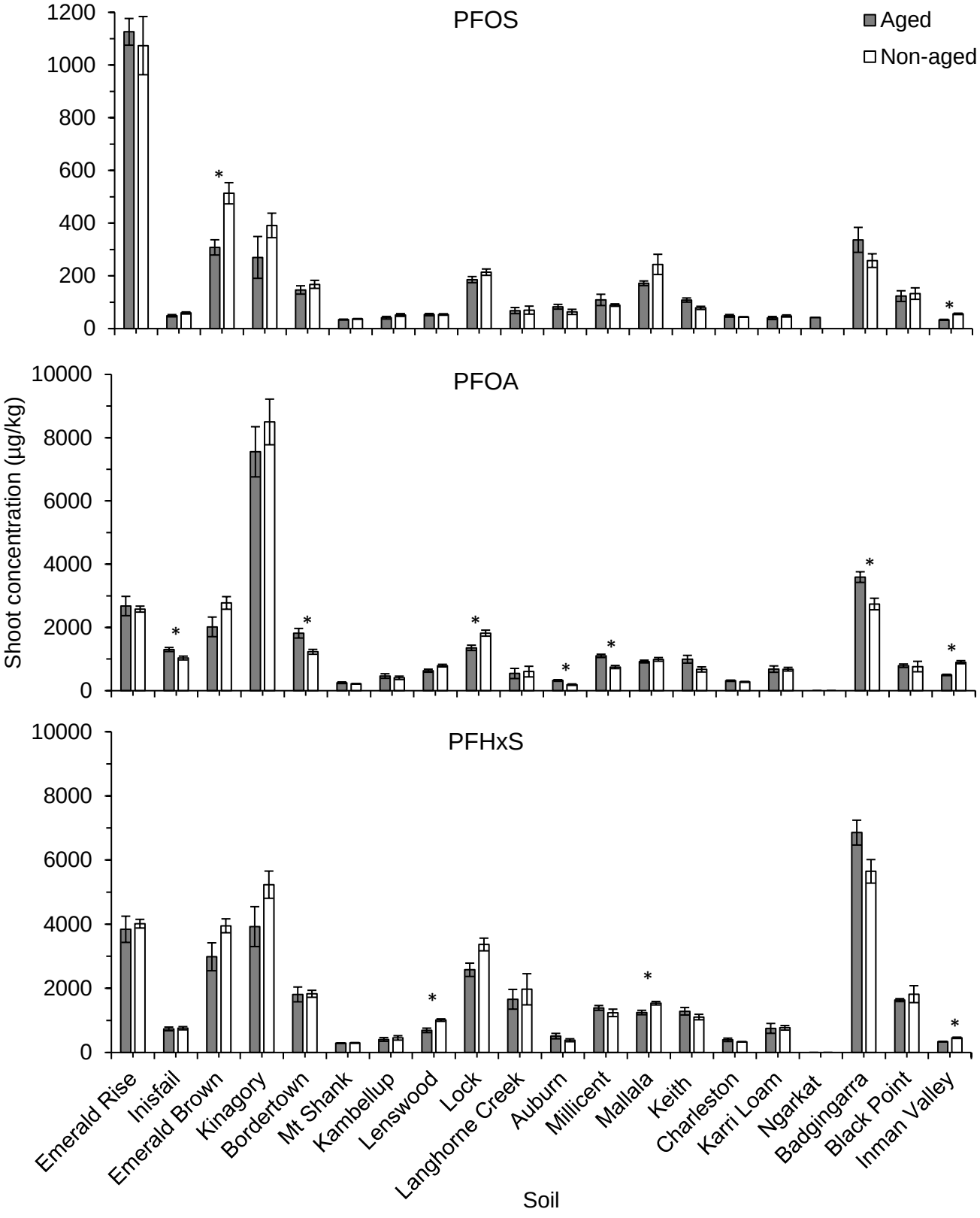

Figure 3: Average concentrations of PFOS (A), PFOA (B) and PFHxS (C) into Phaseolus vulgaris shoots after plants were grown in PFAAs-spiked aged (6 months) and non-aged soils (n = 20). Error bars represent standard error (n = 4). Asterisks indicate significant differences between shoot concentrations for aged and non-aged soils.

4.2.3 Bioaccumulation – Multiple linear regression

All multiple linear regression (MLR) models initially included 11 soil properties (OC, pH, Clay, CEC, exchangeable Ca, Mg, Na, K and oxalate-extractable Al, Fe, Mn). A principal component analysis (PCA) model was produced first to determine if any Log BAF values highly influenced the models - these were excluded from the MLRs. As for the MLR of sorption with soil properties, the same method of removing soil properties with the least significance was employed for MLR to predict BAFs.

The MLR modelling of PFOA Log BAF values in relation to soil properties resulted in an R^2 of 0.25, with significant (p <0.05) negative correlations with OC and exchangeable K^+ and a positive correlation with CEC (Figure 4A and B). The bioaccumulation of PFHxS was most significantly influenced by a negative correlation with OC, R^2 = 0.50 (Figure 4B and C), whereas for PFOS Log BAF values there was a negative correlation with OC and positive correlation with exchangeable Ca^{2+}, R^2 = 0.36 (Figure 4E and F).

The MLR models for all three PFAAs had a significant negative correlation with OC (Figure 4), and can easily be explained by the inverse relationship between BAF values and K_d values, where correlation r values are -0.7 for PFOA, -0.6 for PFHxS and -0.2 for PFOS (Table S5). In other words, the greater the OC content in soil, the greater the sorption which would lead to a decrease in uptake and thus, bioaccumulation into the plant. However, the BAF values of PFHxS was affected by OC alone, whereas other soil properties also affected the BAF values of PFOS and PFOA.

Secondary to the hydrophobic interactions occurring between OC and the C-F hydrophobic chain, electrostatic interactions between exchangeable cations and the functional group of the PFAAs appear to be influencing the bioaccumulation of PFOS and PFOA. The positive correlation between exchangeable Ca^{2+} and the Log BAF values for PFOS could potentially be from Ca-bridging with other organic chemicals or dissolved organic matter and hence remaining soluble and available for plant uptake. However, the same cannot be true for exchangeable K^+, a monovalent cation found previously not to influence the sorption and hence uptake of PFAAs (Higgins and Luthy 2006). Several soil properties tend to correlate with each other, which makes it difficult to isolate their individual contributions. For example, co-correlations of OC and CEC (r = 0.7) as well as exchangeable K^+ with CEC (r = 0.5) were noted.

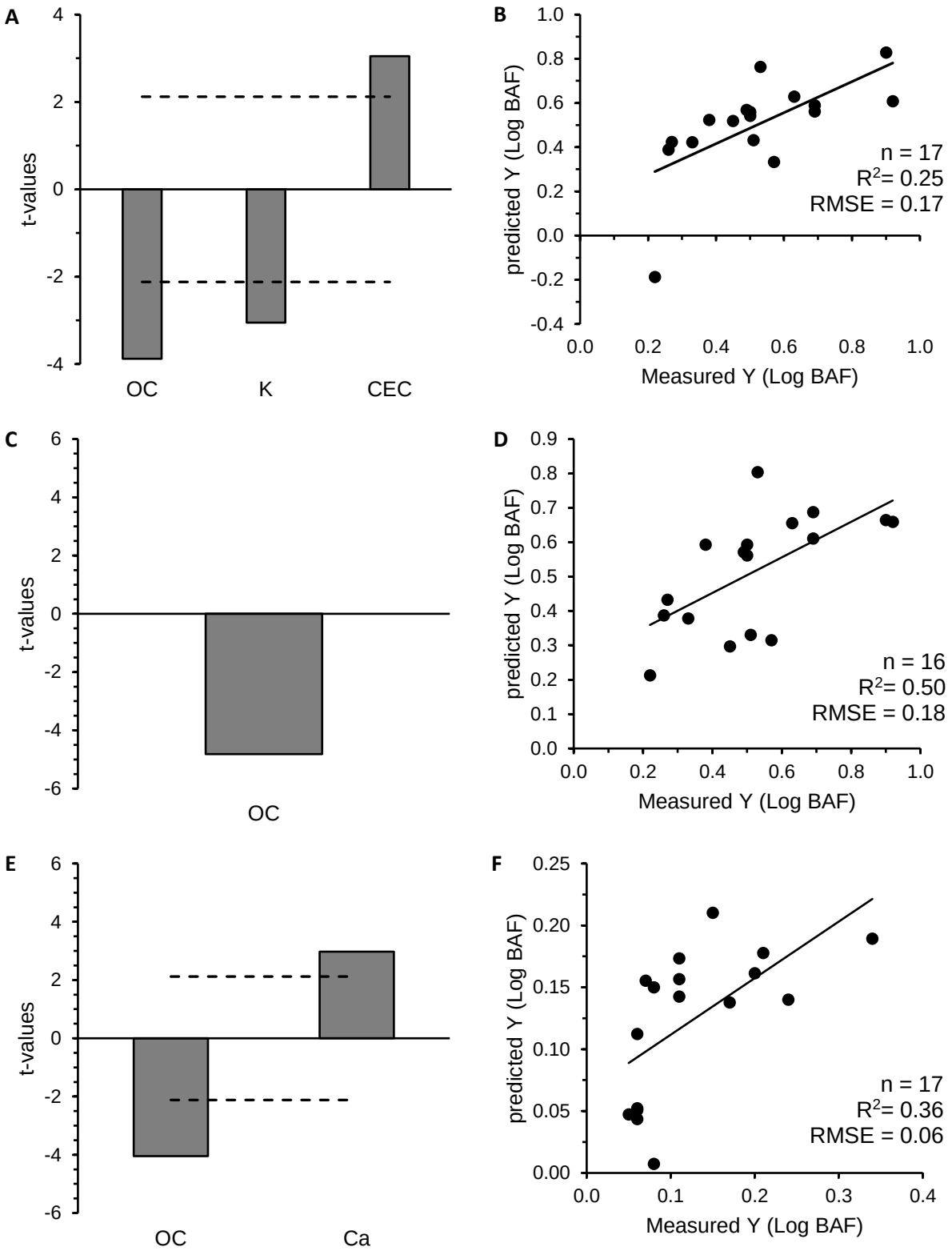

Figure 4: The t-values for significant soil properties in relation to the Log BAF of PFOA, PFHxS and PFOS, (A), (C) and (E) respectively, developed using multiple linear regression models. The dashed lines in (A) and (E) above and below the x-axis represent the critical t-value. Regression plots (B), (D) and (F) correspond to models developed with the soil properties displayed in (A), (C) and (E).

4.2.4 Bioaccumulation – DRIFT-partial least squares regression

Similar to the DRIFT-PLSR sorption models, a PCA model was produced to test for Log BAF value outliers. Three samples were considered outliers and were not included in the modelling. Individual DRIFT-PLSR models were produced for each of the PFAAs using soil spectra (4000–450cm^{-1}). Cross validation models between soil spectra and Log BAF values were very low, R^2 = 0.04 for PFOA, R^2 = 0.20 for PFHxS and R^2 = N/A for PFOS (Figure S1). The lack of any significant correlation between Log BAF values and the soil spectra is likely a result of the narrow range of Log BAF values and the small set of data values (n = 17).

5. Conclusions

This study has provided evidence (through sorption and BAF values) that there is little or no effect of aging of the three PFAAs (PFOA, PFOS and PFHxS) in soils over a six-month study period. The BAF values in this study indicated that the bioaccumulation (in plants) of PFOS from soil was lower than for PFOA and PFHxS; BAF values increased in the following order: PFHxS>PFOA>PFOS, which is consistent with, and inversely related to, sorption. However, K_d values in this study were generally low and narrow in range, suggesting that these PFAAs could potentially leach past the roots zone in a field situation or be easily taken up by plants (e.g. potential for phytoremediation). However, this study is limited to the suite of PFAAs tested, their concentration, the time period (six months) and the plant species.

The modelling of the sorption coefficients with soil properties found that OC, pH and some cations (oxalate Al, exchangeable Mg^{2+}, Ca^{2+} and Na^{+}), influenced the sorption to soils. The modelling of PFAA BAF values and soil properties indicated that OC mitigates the uptake of all three compounds (PFOS, PFOA and PFHxS) as well as exchangeable K^{+} and CEC for PFOA and exchangeable Ca^{2+} for PFOS. The range of Log BAF values was also narrow and this limited the ability to accurately predict bioaccumulation using soil spectra (DRIFT-PLSR) for all three PFAAs. Using a greater number of different soils is needed to confirm this result. Currently, limited research has been conducted to further understand how soil properties affect the uptake of PFAAs from soils as well as the plant mechanisms involved.

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8. Supplementary information

An investigation into the long-term binding and uptake of PFOS, PFOA and PFHxS in soil - plant systems

Table S1: Soil characteristics measured for test soils.

					Particle size (%)			Oxalate Extractable (mg/kg)			Exchangeable cations ($cmol^+/kg$)				
Soil Name	**Soil classification**	**OC (W&B) %**	**pH ($CaCl_2$)**	**CEC (NH_4)**	**Clay**	**Sand**	**Silt**	**Al**	**Fe**	**Mn**	**Ca**	**Mg**	**Na**	**K**	**Total**
Emerald Rise	Sandy loam	0.8	7.8	8.1	12.0	83.0	5.4	610	541	68	4.5	0.8	1.3	1.7	8.3
Inisfail	Loam	0.8	5.0	5.3	12.0	76.0	13.0	999	4270	301	2.2	1.8	0.6	0.3	4.9
Emerald Brown	Silty clay	0.8	7.3	27.8	45.0	23.0	32.0	1370	1640	645	10.5	3.7	1.2	0.9	16.2
Kingaroy	Clay	0.9	5.5	10.3	60.0	20.0	20.0	2540	2710	1030	6.3	2.5	0.3	0.2	9.3
Bordertown	Loamy sand	1.1	4.9	4.9	6.6	87.0	6.6	289	1290	13	2.7	1.1	0.5	0.4	4.7
Mt Schank	Loamy sand	11.0	6.5	41.6	5.6	79.0	16.0	13200	9460	257	38.4	9.9	1.1	2.0	51.3
Kambellup	Loamy sand	3.3	4.6	8.6	5.6	88.0	6.4	300	1350	13	3.7	2.7	0.9	0.7	8.0
Lenswood	Silty loam	3.9	4.6	7.9	7.6	66.0	27.0	802	2340	64	3.9	1.9	0.4	0.4	6.6
Lock	Sand	0.4	8.0	2.5	6.6	89.0	4.7	139	189	13	2.1	0.7	0.9	0.3	3.9
Langhorne Creek	Sand	0.9	7.3	3.6	3.6	94.0	2.1	157	214	13	2.0	0.4	0.9	0.6	3.9
Auburn	Silty loam	2.6	7.5	20.7	9.6	60.0	30.0	874	810	135	10.8	1.7	0.9	1.7	15.1
Millicent	Loam	2.2	5.9	15.3	18.0	70.0	13.0	2300	1550	153	10.4	2.7	0.5	0.3	14.0
Mallala	Silty loam	2.0	7.5	23.3	12.0	62.0	26.0	1120	625	194	11.1	1.7	1.0	1.8	15.6
Keith	Sandy clay loam	2.0	5.0	11.8	21.0	74.0	5.4	595	1300	30	6.8	3.3	0.5	0.7	11.4
Charleston	Loamy sand	4.2	5.0	11.3	1.6	86.0	12.0	462	2490	151	7.9	2.1	0.4	0.8	11.2
Karri Loam	Loamy sand	2.3	5.7	8.1	1.6	87.0	12.0	8760	2010	102	4.9	2.1	0.5	0.4	7.8
Ngarkat	Sand	0.3	5.7	2.1	2.6	97.0	1.0	111	469	13	1.3	0.3	0.3	0.0	2.0
Badgingarra	Sand	0.6	4.5	2.3	1.6	97.0	1.9	62	76	13	1.3	0.2	0.3	0.1	1.9
Black Point	Loam	0.8	7.6	16.0	13.0	68.0	19.0	987	705	186	7.4	1.9	1.1	1.2	11.6
Inman Valley	Silty clay loam	5.2	4.9	25.0	32.0	41.0	28.0	1230	3300	269	11.7	7.0	0.8	0.9	20.5

Table S2: Analyte name, abbreviation and the multiple reaction monitoring (MRM) transitions (parent, quantifiers and qualifiers) for LC-QQQ and LC-QTOF. The bolded transitions are those that were used for quantification. Unavailable transitions are written as N/A.

	MRM transitions		
PFAA	Parent	Quantifier	Qualifier
PFOA	413	369	169
$^{13}C_4$-PFOA	417	373	N/A
$^{13}C_8$-PFOA	421	377	N/A
PFOS	499	99	80
$^{13}C_8$-PFOS	507	99	N/A
PFHxS	399	99	80
$^{18}O_2$-PFHxS	403	103	N/A

Table S3: The limits of detection (LODs) and quantification (LOQs) of PFOA, PFOS and PFHxS in three matrices; soil, plant and porewater. The LODs and LOQs were calculated as 3x and 10x the standard deviation of the lowest standard (0.1 µg/kg for plant and soil and 1 µg/kg for porewater). Average internal standards recoveries (R (%) – of all samples run) are plus or minus the standard deviation for plant and soil matrices only.

	Soil (µg/kg)			Plant shoots (µg/kg)			Porewater (µg/L)	
	LOD	LOQ	R (%)	LOD	LOQ	R (%)	LOD	LOQ
PFOS	0.12	0.16	82 ± 24	0.12	0.16	86 ± 15	2.34	2.59
PFOA	0.13	0.16	77 ± 17	0.13	0.17	73 ± 10	1.42	2.11
PFHxS	0.13	0.16	82 ± 20	0.13	0.17	87 ± 11	1.08	1.41

Table S4: The average (± standard error (n = 4 for Log K_d and Log BAF, n = 2–3 for Log BAF (porewater))) Log K_d and Log BAF values for PFOA, PFOS and PFHxS in 20 soils. The Log K_d and Log BAF (porewater) values are for 0 month measured porewater concentrations.

	Log K_d			Log BAF			Log BAF (plant/porewater)		
Soil Name	**PFOS**	**PFOA**	**PFHxS**	**PFOS**	**PFOA**	**PFHxS**	**PFOS**	**PFOA**	**PFHxS**
Emerald Rise	1.51 ± 0.03	0.48 ± 0.01	0.29 ± 0.01	0.65 ± 0.02	0.92 ± 0.04	1.13 ± 0.04	2.05 ± 0.02	0.85 ± 0.02	0.63 ± 0.02
Inisfail	1.28 ± 0.15	0.20 ±0.01	0.14 ± 0.00	0.07 ± 0.01	0.63 ± 0.02	0.52 ± 0.03	0.58 ± 0.02	0.04 ± 0.00	0.03 ± 0.00
Emerald Brown	1.99 ± 0.13	0.33 ± N/A	0.53 ± 0.34	0.34 ± 0.02	0.90 ± 0.02	1.07 ± 0.03	2.06 ± 0.05	0.38 ± 0.03	0.37 ± 0.03
Kingaroy	0.98 ± 0.36	0.17 ± 0.03	0.13 ± 0.01	0.34 ± 0.04	1.46 ± 0.03	1.22 ± 0.05	0.82 ± 0.06	0.18 ± 0.02	0.14 ± 0.02
Bordertown	1.66 ± 0.04	0.40 ± 0.02	0.22 ± 0.00	0.17 ± 0.01	0.69 ± 0.03	0.83 ± 0.03	1.33 ± 0.03	0.21 ± 0.01	0.12 ± 0.01
Mt Schank	2.03 ± 0.10	1.06 ± 0.03	0.75 ± 0.01	0.05 ± 0.00	0.22 ± 0.01	0.29 ± 0.01	1.12 ± 0.01	0.32 ± 0.01	0.18 ± 0.00
Kambellup	1.55 ± 0.03	0.64 ± 0.02	0.45 ± 0.00	0.06 ± 0.00	0.33 ± 0.03	0.36 ± 0.03	0.76 ± 0.03	0.15 ± 0.01	0.10 ± 0.01
Lenswood	1.47 ± 0.14	0.57 ± 0.02	0.42 ± 0.01	0.08 ± 0.00	0.51 ± 0.03	0.58 ± 0.04	0.78 ± 0.02	0.16 ± 0.01	0.11 ± 0.00
Lock	1.40 ± 0.04	0.42 ± 0.03	0.23 ± 0.01	0.20 ± 0.01	0.69 ± 0.03	0.96 ± 0.04	1.16 ± 0.02	0.25 ± 0.01	0.14 ± 0.01
Langhorne Creek	1.74 ± 0.29	0.58 ± 0.05	0.38 ± 0.02	0.08 ± 0.01	0.38 ± 0.05	0.76 ± 0.06	0.97 ± 0.06	0.17 ± 0.02	0.10 ± 0.01
Auburn	1.80 ± 0.07	0.59 ± 0.05	0.42 ± 0.03	0.11 ± 0.01	0.27 ± 0.03	0.42 ± 0.03	1.26 ± 0.04	0.23 ± 0.02	0.16 ± 0.01
Millicent	1.40 ± 0.31	0.36 ± 0.04	0.25 ± 0.02	0.11 ± 0.01	0.53 ± 0.02	0.67 ± 0.02	0.79 ± 0.04	0.12 ± 0.01	0.08 ± 0.01
Mallala	1.65 ± 0.16	0.38 ± 0.03	0.24 ± 0.01	0.21 ± 0.02	0.57 ± 0.02	0.73 ± 0.03	1.42 ± 0.04	0.25 ± 0.02	0.17 ± 0.01
Keith	1.69 ± 0.32	0.49 ± 0.02	0.34 ± 0.03	0.11 ± 0.01	0.50 ± 0.04	0.67 ± 0.04	1.03 ± 0.03	0.17 ± 0.01	0.12 ± 0.01
Charleston	1.91 ± 0.02	0.76 ± 0.00	0.62 ± 0.02	0.06 ± 0.00	0.26 ± 0.01	0.33 ± 0.02	1.09 ± 0.02	0.20 ± 0.01	0.16 ± 0.01
Karri Loam	1.11 ± 0.01	0.40 ± 0.01	0.23 ± 0.00	0.06 ± 0.01	0.49 ± 0.03	0.55 ± 0.05	0.46 ± 0.02	0.08 ± 0.01	0.04 ± 0.00
Ngarkat	1.13 ± 0.22	0.27 ± 0.00	0.13 ± 0.00	N/A	N/A	N/A	0.61 ± 0.26	0.13 ± 0.10	0.07 ± 0.06
Badgingarra	1.09 ± 0.04	0.29 ± 0.03	0.15 ± 0.00	0.24 ± 0.02	0.92 ± 0.03	1.24 ± 0.03	0.97 ± 0.04	0.22 ± 0.02	0.12 ± 0.01
Black Point	1.78 ± 0.19	0.35 ± 0.08	0.20 ± 0.03	0.15 ± 0.02	0.50 ± 0.04	0.80 ± 0.04	1.33 ± 0.04	0.15 ± 0.01	0.09 ± 0.01
Inman Valley	2.00 ± 0.03	0.68 ± 0.14	1.28 ± 0.38	0.06 ± 0.01	0.45 ± 0.04	0.34 ± 0.02	1.14 ± 0.04	0.15 ± 0.01	0.41 ± 0.03
Average	***1.56 ± 0.06***	***0.47 ± 0.03***	***0.37 ± 0.05***	***0.16 ± 0.01***	***0.58 ± 0.02***	***0.70 ± 0.03***	***1.09 ± 0.03***	***0.22 ± 0.01***	***0.17 ± 0.01***
Median	***1.60***	***0.41***	***0.27***	***0.11***	***0.51***	***0.67***	***1.08***	***0.19***	***0.13***
Minimum	***0.98***	***0.17***	***0.13***	***0.05***	***0.22***	***0.29***	***0.46***	***0.04***	***0.03***
Maximum	***2.03***	***1.06***	***1.28***	***0.65***	***1.46***	***1.24***	***2.06***	***0.85***	***0.63***
Skewness	***-0.25***	***1.13***	***2.17***	***2.21***	***1.41***	***0.37***	***0.77***	***2.54***	***1.99***

Table S5: Cross correlation matrix of soil properties with Log K_d, soil BAF values and porewater BAF values for PFOA, PFOS and PFHxS. Correlations are represented by the Pearson's coefficient r values and the units for the different soil properties are stated in the first and second column from the left.

		Oxalate extractable								Exchangeable cations						Log K_d			Soil Log BAF			Log BAF (plant/porewater)		
		Al	Fe	Mn	OC	pH	Clay	Sand	Silt	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Total	CEC	PFOA	PFOS	PFHxS	PFOS	PFOA	PFHxS	PFOS	PFOA	PFHxS
Oxalate cations (mg/kg)	Al	1.0	0.8	0.2	0.7	0.0	-0.1	0.0	0.1	0.8	0.7	0.1	0.3	0.8	0.6	0.5	0.1	0.2	-0.2	-0.2	-0.3	-0.2	0.0	-0.1
	Fe		1.0	0.3	0.8	-0.2	0.1	-0.2	0.2	0.8	0.8	0.1	0.3	0.8	0.6	0.6	0.3	0.5	-0.3	-0.2	-0.5	-0.2	-0.1	0.0
	Mn			1.0	0.0	0.1	0.9	-0.9	0.5	0.2	0.3	0.0	0.0	0.2	0.4	-0.3	-0.1	0.1	0.3	0.6	0.3	0.1	0.0	0.1
	OC				1.0	-0.2	-0.1	0.0	0.3	0.9	0.9	0.2	0.5	0.9	0.7	0.9	0.5	0.7	-0.4	-0.6	-0.7	-0.1	0.0	0.1
	pH ($CaCl_2$)					1.0	0.0	-0.1	0.2	0.2	-0.1	0.7	0.6	0.2	0.3	0.0	0.3	-0.1	0.4	0.0	0.3	0.6	0.4	0.3
	Clay (%)						1.0	-0.9	0.5	0.1	0.3	0.1	0.0	0.1	0.3	-0.3	0.0	0.2	0.4	0.7	0.4	0.2	0.1	0.3
	Sand (%)							1.0	-0.8	-0.2	-0.4	-0.2	-0.2	-0.3	-0.5	0.2	-0.2	-0.3	-0.2	-0.4	-0.2	-0.3	-0.1	-0.3
	Silt (%)								1.0	0.4	0.4	0.3	0.4	0.4	0.7	0.1	0.4	0.4	-0.1	0.0	-0.2	0.3	0.0	0.2
Exchangeable cations ($cmol^{+}/kg$)	Ca^{2+}									1.0	0.9	0.4	0.7	1.0	0.9	0.7	0.5	0.5	-0.2	-0.3	-0.4	0.1	0.1	0.2
	Mg^{2+}										1.0	0.3	0.5	0.9	0.8	0.6	0.5	0.7	-0.3	-0.3	-0.5	0.0	0.0	0.2
	Na^{+}											1.0	0.8	0.4	0.5	0.3	0.6	0.3	0.3	-0.2	0.0	0.6	0.5	0.5
	K^{+}												1.0	0.7	0.7	0.5	0.7	0.4	0.2	-0.3	-0.3	0.5	0.5	0.5
	Total													1.0	0.9	0.7	0.6	0.6	-0.2	-0.4	-0.4	0.1	0.1	0.2
	CEC (NH_4)														1.0	0.5	0.7	0.6	-0.1	-0.3	-0.4	0.3	0.2	0.3
Log K_d	PFOA															1.0	0.7	0.7	-0.4	-0.7	-0.7	0.0	0.2	0.2
	PFOS																1.0	0.7	-0.2	-0.6	-0.5	0.4	0.2	0.3
	PFHxS																	1.0	-0.3	-0.4	-0.6	0.1	0.1	0.4

Soil Log BAF	PFOS																		1.0	0.7	0.8	0.7	0.8	0.8
	PFOA																			1.0	0.9	0.3	0.3	0.3
	PFHxS																				1.0	0.5	0.4	0.3
Log BAF (plant/porewater)	PFOS																					1.0	0.8	0.8
	PFOA																						1.0	0.9
	PFHxS																							1.0

25

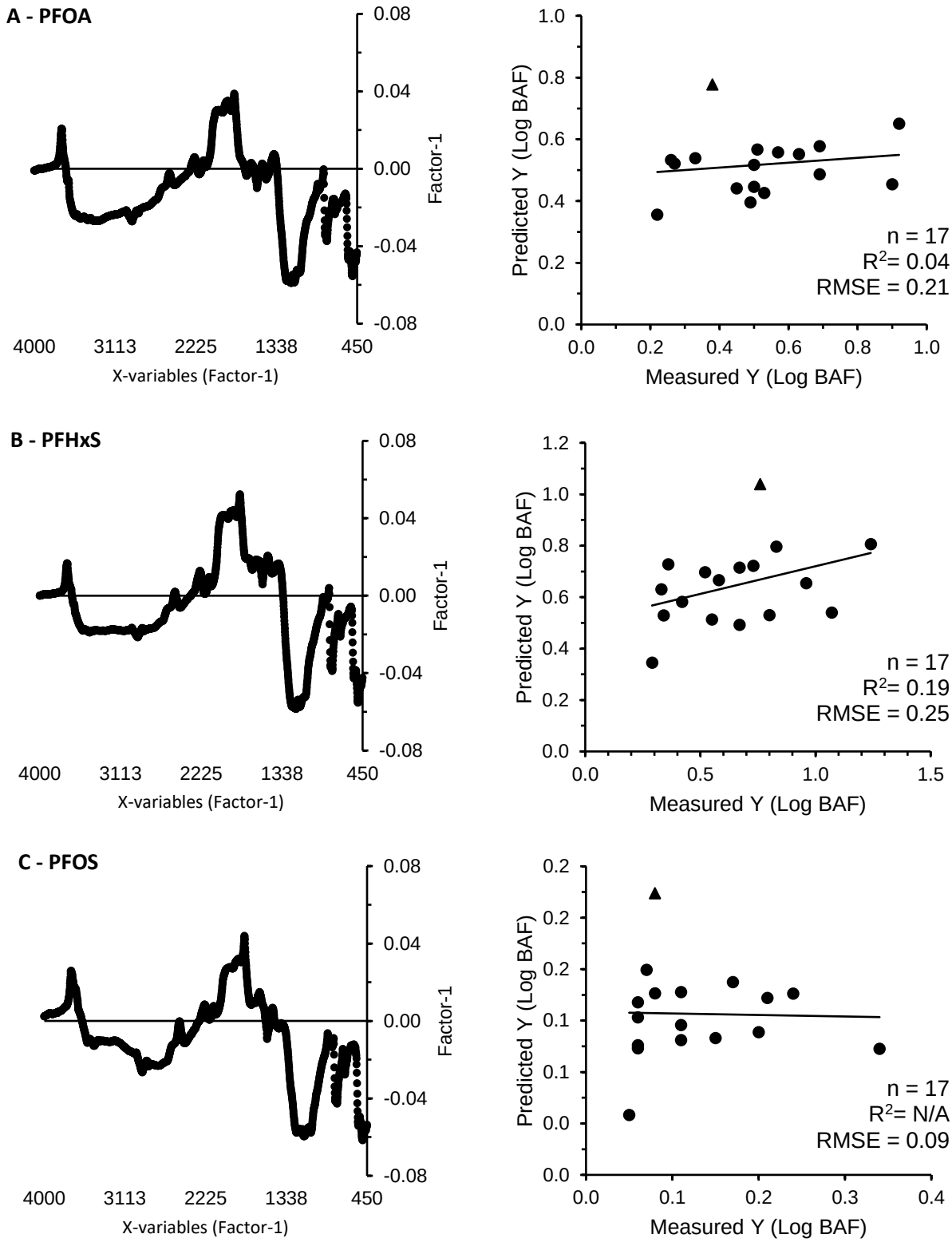

Figure S1: DRIFT-PLSR of soil spectra in relation to Log BAF values for (A) PFOA, (B) PFHxS and (C) PFOS where both left and right panels refer to the same model. The left-hand panels show the x-loading weights of the models and the right-hand panel shows the cross validation

Chapter 6. Conclusions and Future Research Directions

1. Summary of thesis outcomes

The historical contamination of PFASs from aqueous film forming foams (AFFF) and from the manufacturing of various stain- and water-resistant items, their subsequent leaching into soil, surface- and ground-waters has led to widespread contamination of PFASs in the environment. This group of substances have unique characteristics that make them resistant to natural biodegradation (and hence persistent), highly mobile in the environment, available to bioaccumulate in plants and other organisms, as well as potentially toxic. These characteristics have led some PFASs (e.g. PFOS, PFOA) to be classed as persistent organic pollutants (Stockholm Convention) and contaminants of emerging concern (USEPA). However, despite the decades of pollution, little is understood about how PFASs behave in the soil environment, which has meant that regulators are unable to effectively regulate or manage for potential risks to humans and the environment. This thesis investigated the sorption, aging and uptake of three common PFASs: PFOS, PFOA and PFHxS.

1.1 PFOA sorption losses observed on different laboratory consumables.

This study brings attention to the potential PFAS sorption losses that could occur during routine laboratory procedures and could lead to significant analytical bias if not properly accounted for, including the suitability testing of chosen consumables. Observations during preliminary studies with radiolabeled ^{14}C-PFOA indicated that losses on polypropylene (PP) laboratory consumables was in contrast to reports in published literature and USEPA procedures, where PP was recommended over glassware. To explore these losses further, the testing of ^{14}C-PFOA sorption was conducted on tubes made of different materials and syringe filter membranes under various conditions, including pH, ionic strength and differing concentrations. For tubes, PP had significantly lower recoveries compared to other tubes materials (polystyrene, polycarbonate and glass), whereas glass tubes had the highest recoveries. These findings are on contrast to much of the PFAS-related literature. For syringe filter membranes, the lowest recovery was 21% for nylon membrane and highest recoveries ranged from 70–75% (PP, regenerated cellulose, glass-fibre and PVDF membranes). These recoveries indicate that a large percentage of losses can occur during filtration and could lead to an underestimation of solution concentrations.

1.2 Many different soil properties influence the sorption of PFOA in soils.

Radiolabeled ^{14}C-PFOA was used to calculate the soil-water partitioning coefficient (K_d) in 100 soils (surface- and sub-soils) with differing properties. This published work greatly increased the number of K_d values for PFOA in soils available in the literature and used two different modelling techniques to further investigate the influence of different soil properties on the sorption of PFOA. The K_d values in this study, while low and narrow in range, were still comparable to those previously published in

the literature. Simple linear regressions of soil properties and K_d values did not show significant relationships except with soil depth, where a significant decrease in K_d values occurred with an increase in depth. This highlights that in these soils, sorption is less likely in subsurface soils. As there was no single soil chemical property significantly influencing sorption of PFOA in soils, multiple linear regression (MLR) was employed. The MLR modelling of both top-soils and sub-soils found that the organic carbon (OC) and silt+clay content was significantly influencing sorption, whereas for top-soils, OC, silt+clay content and pH were the key properties determining sorption. Diffuse reflectance mid-infrared spectroscopy combined with partial least squares regression (DRIFT-PLSR) was also used to model soil spectra and K_d values, which indicated that quartz and pyrophyllite minerals were influencing sorption of PFOA in soils. A comparison between MLR and DRIFT-PLSR models found similar results, indicating that DRIFT-PLSR could be used as a rapid and cost-effective modelling technique compared to soil chemical analysis and MLR.

1.3 Many different soil properties influence the sorption of PFOS and PFHxS in soils.

This study investigated the sorption of two perfluorosulphonic acids (PFSAs), PFOS and PFHxS, in 172 diverse Australian surface- and subsoils. In the absence of availability of ^{14}C-labelled compounds, the study was conducted using unlabelled compounds and LC/MS-MS for analysis. The K_d values for PFOS were found to be higher than those of PFHxS with averages of 4.37 and 1.23 L/kg, respectively, which is generally consistent with those reported in the literature. This was expected due to the increase in chain length from C_6 to C_8 for PFHxS and PFOS resulting in an increase in hydrophobic interactions in the soils. For simple linear regression, a significant relationship between PFOS and PFHxS K_d values and OC, despite low R^2 values, was observed but no other significant relationships between K_d values and other soil characteristics were seen. Modelling of K_d values for PFOS and PFHxS using MLR and DRIFT-PLSR was unreliable which could be due to the low K_d values (<20% sorption) for both PFOS and PFHxS and thus resulted in exclusion of those soils from the modelling. It is suspected that the sorption in these Australian soils was low due to low OC contents, in relation to other countries. However, the exact reason(s) for the poor correlations between soil characteristics and K_d values for PFOS and PFHxS is unclear. Based on the small and narrow range of K_d values observed, this suggests that PFHxS would be extremely susceptible to leaching or have greater mobility in the soil environment in Australia, compared to PFOS.

1.4 Limited aging of PFAAs occurs in soils over a six-month time period.

This study investigated the long-term binding (aging) in soils of PFOS, PFOA and PFHxS over a six-month time period, through the evaluation and modelling of both sorption (K_d) and bioaccumulation factors (BAFs). Aging is a process whereby the contaminant in contact with soil becomes less bioavailable over time and this process can be significant for other organic contaminants, like

polycyclic aromatic hydrocarbons (PAHs). This study found that over the six-month incubation period there was no evidence of aging for PFOS, PFHxS and PFOA in 20 different soils. This limited aging was evidenced by a lack of consistent significant increases in K_d values over the incubation period but also by the inconsistent changes in uptake by bean plants from soils that were aged and those that were freshly spiked before planting. Modelling of the K_d values using MLR and DRIFT-PLSR showed that each PFAA was influenced by different soil properties, but overall, the models were comparable with similar soil properties influencing sorption – OC and oxalate extractable Al. Concentrations of the PFAAs in the plant shoots varied with soil type but concentrations generally increased, with some exceptions, in the following order: PFHxS>PFOA>PFOS. The BAF values for PFOS were approximately 3.5–4.5 times lower compared to PFOA and PFHxS. Modelling using MLR found that OC content in soil was negatively correlated to the BAF values for all three PFAAs, where the BAF values for PFOS also had a positive correlation with exchangeable Ca^{2+} and the BAF values for PFOA also had a negative correlation with exchangeable K^+ and a positive correlation with cation exchange capacity (CEC). It was also evident that K_d values and BAF values were inversely related. This study adds to the limited research that so far has been conducted on which soil properties may be affecting BAFs besides OC.

2. Conclusions

This thesis investigated the sorption and bioavailability of three PFAAs in a wide range of soils and over an extended period of time, with the intention of predicting which soil characteristics influence these parameters. It has become clear that working with these substances is challenging, due to their surfactant-like properties, and furthermore complex once in the soil environment.

Laboratory challenges associated with working with PFAAs were first observed in Chapter 2. Contrary to what is reported in the literature, the use of PP tubes was found to be a considerable source of sorption losses for PFOA in laboratory procedures. However, the use of PP tubes in laboratories is quite common due to their versatility (non-brittle, resistant to high temperature and high-speed centrifugation) and low cost compared to other tube materials e.g. polycarbonate and polystyrene. This study was limited to only one PFAA, PFOA, and did not consider the likelihood that PFAAs are often found in the environment in mixtures containing many other PFASs, which could have their own sorption affinity to different tube or filter membrane surfaces. While the prior testing of appropriate consumables for any new methodologies is recommended, it is not always possible. This is where consistency with whichever materials or laboratory consumables used is advised, along with the use of appropriate quality assurance and control measures to account for

any sorption losses that could be observed from the use of consumables through current and future methodologies.

Sorption of PFAAs in the soil environment was found to be extremely complex and related to several factors – soil properties, PFAA species and chain length. For instance, when modelling with MLR in Chapter 3, the sorption of PFOA was significantly influenced by silt-plus-clay content and OC, whereas in Chapter 4 the sorption of PFOS was influenced by OC and PFHxS by OC, clay content and exchangeable Ca^{2+} and Mg^{2+}. These results are similar to the most recent research, suggesting that sorption of PFASs in soils is influenced by a few soil properties, unlike the sorption of many other organic contaminants (like PAHs) where OC alone is important for sorption (Luo et al. 2012). However, this is in contrast with early research investigating sorption of PFASs in soils and sediments, that found OC was the most significant soil parameter influencing sorption (Higgins and Luthy 2006). While the research in this thesis is limited in the number of PFAAs tested, the results may have implications for potential management strategies for these compounds. For instance, the low K_d values and the decrease of K_d values for PFOA with increasing soil depth (Chapter 3) indicate for a highly contaminated site, like a fire-fighting training ground, that PFOA would be very mobile in surface soils, but even more so in subsoils, where leaching into ground waters could be very rapid. This would then further increase the spread of PFOA in the environment, away from the source. The extremely low K_d values of PFHxS in Australia soils indicate that a similar scenario, as for PFOA, is also likely. The implications of offsite contamination have become an issue to regulators and since starting this PhD, two Australian states, South Australia and Queensland, have implemented bans on the use of aqueous film forming foams (AFFF) containing PFASs. These bans are an attempt to reduce the exposure of PFASs to both humans and the environment, but the legacy of these compounds continues far beyond the intended purpose, with their lack of biodegradation and potential bioaccumulation into plants.

Plant uptake of organic contaminants is affected by the plant species, soil type, PFAS chain length, functional group and concentration. For many organic contaminants in soil, there is a likelihood they will undergo biodegradation or transition further into the soil matrices (aging), which reduces their potential for uptake into plants or leaching into ground waters. However, the results from this thesis indicate that the aging of PFOS, PFOA and PFHxS did not occur, at least over a six-month time period. The lack of aging was evidenced by no distinguishable difference in uptake into bean plants (*Phaseolus vulgaris*) from aged and freshly spiked soils. Therefore, there is a greater chance of continued uptake or leaching of these compounds compared to other hydrophobic organic compounds that age in soils. Thus, the use of natural attenuation to reduce contamination risks, often observed with other organic contaminants due to biodegradation or ageing in soils, is unlikely

to occur for these compounds. Legacy sites contaminated by PFOS, PFOA or PFHxS will thus continue, over long periods, to pose risks of contaminant leaching or contaminant uptake into the food chain, until remediated.

3. Future research recommendations

The findings in this thesis are a small part of the larger picture in terms of understanding PFAAs in the soil environment. To further advance this area of research the following areas of future work are recommended.

3.1 Further investigation of sorption/desorption behaviour of a larger suite of PFASs, including precursors

Further investigation of sorption for a much larger suite of PFASs in soils could be explored to improve the understanding PFAS fate and behaviour in the soil environment. There are 1000s of different PFASs and yet there are many studies (including in this thesis) that have focused only on the most prevalent two or three. This information is especially important as longer-chained compounds, such as PFOS and PFOA, are being phased out and replaced by shorter-chained compounds which could be more bioaccumulative (Krippner et al. 2015, Bizkarguenaga et al. 2016). Another aspect to consider is the sorption and biodegradation of precursor molecules, such as fluorotelomer alcohols (FTOHs), into the more stable and persistent PFASs. Understanding of the larger suite of PFASs and their precursor compounds in the soil environment could provide information to regulators who can then implement better management strategies and lower the risk of further exposure to humans and the environment.

3.2 Longer-term binding mechanisms

While in this thesis limited aging occurred over a six-month time period, it would be interesting to investigate aging over a much longer time period, for example three years or longer. For example, for PAHs aging occurs a lot quicker, over a few months (Chung and Alexander 1998), but perhaps for PFASs this process could take much longer. If this process does take a much longer period of time, then there would also be a higher chance of the PFASs being leached into ground water or taken up by plants before moving deeper into the soil matrix. The soil mechanisms responsible for aging of other organic contaminants could still be responsible for PFAS aging, just over a longer time frame and could be measured through both a decrease in PFAS soil pore water concentrations or through a decrease in plant uptake. This would provide a much clearer understanding if PFASs become less bioavailable over time. This would be valuable information as the further understanding of the aging

or bioavailability over time could potentially have implications for both further environment monitoring or exposure to humans and the environment.

3.3 Other plant species and potential for phytoremediation

In this thesis only one plant species was investigated for uptake, *P. vulgaris* (common green bean), to highlight the potentially worst case scenario, as it has been reported that PFASs are taken up in greater concentrations by plants with higher protein contents (Wen et al. 2016). However, to better understand the risks associated with uptake of PFAAs in plants and the potential transfer into edible plant portions, multiple plant species need to be investigated. Many plant studies have investigated more than one plant species, but they have been limited by the number of PFASs tested (Wen et al. 2013, Krippner et al. 2015, Bizkarguenaga et al. 2016). The uptake of PFASs into plants is likely to be different for different plant species due to their inherently different root uptake and translocation mechanisms as well as environmental conditions such as soil moisture, transpiration, evaporation and temperature. Having a clear understanding of the accumulation potential for many different plant species means that the risk of exposure through consumption of contaminated crops or foods can be managed effectively. This management could include regulations on the base level contamination allowed in soil for agricultural crops but also for grazing livestock.

In Chapter 5, the lack of aging of three PFAAs indicated that their bioavailability does not change with time. This could mean that phytoremediation could be an interesting aspect to investigate in the future, particularly for contaminated sites. This type of remediation would also need to be tested for viability on many different plant species to find a species that would be the greatest accumulator of PFAS concentrations.

3.4 DRIFT interpretation and database

While writing and modelling the sorption data from this thesis I realised that understanding the DRIFT spectra and relating it back to the soil properties in the soils of interest is not straightforward. Soil spectra contain large amounts of information, absorbance of IR energy of a certain wavelength may occur for several different soil components, and calibrations of new soil properties with spectra are highly influenced by the calibration soil set used. Determining the soil components active in sorbing any contaminant by spectral analysis relies on accurate identification of spectral regions related to specific mineral and organic components of soil. Unlike transmission IR (Van der Marel and Beutelspacher 1976), there is no agreed reference library of diffuse reflectance IR spectral regions associated with specific minerals or soil components i.e. specific clay minerals, types of OM, etc. An updated reference work (hard copy or online) of soil and mineral diffuse reflectance spectra

is therefore very much needed, as this would standardise and facilitate rapid interpretation of diffuse reflectance spectra from soils.

4. References

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