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Leaching and bioavailability of selected perfluoroalkyl acids (PFAAs) from soil contaminated by firefighting activities

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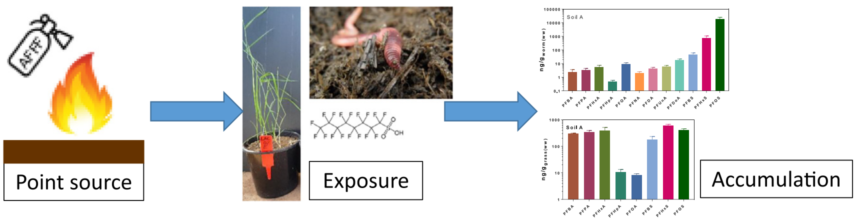
HIGHLIGHTS

- Batch leaching tests showed high desorption of PFAAs from contaminated soil.
- Bioaccumulation factors highest for shorter chain PFAAs in wheat grass
- Bioaccumulation factors highest for long chain PFAAs in earthworms
- PFCA accumulation decreased then increased with increasing carbon chain length.

GRAPHICAL ABSTRACT



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ABSTRACT

Historical usage of aqueous film-forming foam (AFFF) at firefighting training grounds (FTGs) is a potential source of perfluoroalkyl acids (PFAAs) to the surrounding environment. In this study the leaching of PFAAs from field contaminated soil and their uptake into biota was investigated. Soil was sampled from FTGs at two airports and the total as well as the leachable concentration of 12 PFAAs was determined. A greenhouse study was carried out to investigate the uptake of PFAAs from soils into earthworms (*Eisenia fetida*) and wheat grass (*Elymus scaber*). Perfluorooctane sulfonate (PFOS) and perfluorohexane sulfonate (PFHxS) were the most dominant PFAAs in all soils samples, with concentrations of PFOS reaching 13,400 ng/g. Leachable concentrations of PFOS and PFHxS reached up to 550 μg/L and 22 μg/L, respectively. In earthworms concentrations of PFOS reached 65,100 ng/g after a 28-day exposure period, while in wheat grass the highest concentration was measured for uptake of PFHxS (2,800 ng/g) after a 10-week growth-period. Bioaccumulation factors (BAFs) for earthworms ranged from 0.1 for perfluorohexanoic acid (PFHxA) to 23 for perfluorododecanoic acid (PFDoA) and initially showed a decreasing trend with increasing perfluoroalkyl chain length, followed by an increase with increasing perfluoroalkyl chain length for perfluoroalkyl carboxylic acids (PFCAs). In wheat grass the highest BAF was found for perfluorobutanoic acid (BAF = 70), while the lowest was observed for perfluorononanoic acid (BAF = 0.06). BAFs in wheat grass decreased with increasing perfluoroalkyl chain length for both PFCAs and perfluoroalkyl sulfonic acids (PFSAs). The results show that PFAAs readily leach from impacted soils and are bioaccumulated into earthworms and plants in an analyte dependent way. This shows considerable potential for PFAAs to move away from the original source either by leaching or uptake into ecological receptors, which may be a potential entry route into the terrestrial foodweb.

1. Introduction

Perfluoroalkyl acids (PFAAs), including perfluoroalkyl sulfonic acids (PFSAs) and perfluoroalkyl carboxylic acids (PFCAs), are organic compounds characterised by their fully fluorinated hydrophobic carbon

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chain and a hydrophilic functional end group (Kissa, 2001). Due to their unique properties PFAAs have been used in a wide variety of consumer products and industrial applications and as key ingredients in aqueous film-forming foams (AFFFs) (Buck et al., 2012). Their widespread use and environmental persistence has led to PFAAs being ubiquitously found in water, soil, wildlife and humans. They are potentially toxic, have the ability to bioaccumulate and potentially biomagnify (Ahrens and Bundschuh, 2014; Ding and Peijnenburg, 2013; Giesy and Kannan, 2001; Giesy et al., 2010; Tomy et al., 2004).

AFFFs have excellent fire-extinguishing properties for flammable fluids and were used since the 1960s for emergency responses and fire and rescue training purposes (Tuve and Jablonski, 1966). The frequent use and uncontrolled releases and/or spillages of AFFF has led to the contamination of different environmental media such as soil, groundwater and surface water in the vicinity of firefighting facilities, particularly airport firefighting training grounds (FTGs) and fire stations (Ahrens et al., 2015; Baduel et al., 2017; Baduel et al., 2015; Bräunig et al., 2017; Moody and Field, 2000; Oakes et al., 2010). AFFFs are known to contain a diverse mix of per- and poly-fluoroalkyl substance (PFAS) classes, some of which have the potential to transform to stable PFAAs (so called PFAA precursors) under environmental conditions (Backe et al., 2013; D'Agostino and Mabury, 2013; Place and Field, 2012).In addition to a wide variety of PFASs, areas of high AFFF-use are also impacted by co-contaminants, such as hydrocarbon surfactants, or fuels and chlorinated solvents which were extinguished using the AFFF (Backe et al., 2013; Guelfo and Higgins, 2013; Moody and Field, 2000). Such co-contaminants have been shown to have varying influence on the sorption and environmental fate of PFAAs (Guelfo and Higgins, 2013).

Generally, environmental behavior of PFAAs depends on their perfluoroalkyl chain length and functional group. Long chain PFAAs ($C_nF_{2n+1}COOH$, $n \geq 7$ and $C_nF_{2n+1}SO_3H$, $n \geq 6$) show higher sorption to soils and sediments compared to short chain PFAAs. Sorption processes of PFAAs to soils are complex and have shown to not be predictable by single soil properties (Barzen-Hanson et al., 2017; Li et al., 2018). Hydrophobic interactions between PFAAs and organic carbon, ligand binding through divalent cations, electrostatic interactions between the functional end groups of PFAAs and mineral and organic phases and oxides in soils all play a role in sorption (Higgins and Luthy, 2006; Jeon et al., 2011; Li et al., 2018). However, still to date there are many uncertainties when it comes to predicting how these differing soil properties interact with each other and influence PFAA sorption. It has been observed that with increasing pH PFAA sorption decreases, whereas sorption increases with increasing organic carbon content and chain length of PFAAs (Higgins and Luthy, 2006; Prevedouros et al., 2006). However, Li et al. (2018) found that both pH and organic carbon alone could not effectively predict sorption of PFOS and PFOA, whereas OC, pH and/or clay content together effectively predicted sorption for a few PFAAs. While there are a number of studies that have investigated the sorption/desorption of PFAAs from soils many have used spiked soils (Enevoldsen and Juhler, 2010; Milinovic et al., 2015) and only few have used field contaminated soils (Hale et al., 2017).

Moreover, PFAAs have the potential to accumulate from contaminated soil into both biota (Navarro et al., 2016; Rich et al., 2015; Wen et al., 2015; S. Zhao et al., 2013) and plants (Blaine et al., 2014a; Lechner and Knapp, 2011; Stahl et al., 2009; Wen et al., 2014; H. Zhao et al., 2013). Short chain PFAAs show higher accumulation in plants such as lettuce, tomatoes and wheat (Blaine et al., 2013; Blaine et al., 2014b; Felizeter et al., 2012; Zhao et al., 2014), while long chain PFAAs show higher potential to bioaccumulate from soil into earthworms (Rich et al., 2015, Wen et al., 2015, S. Zhao et al., 2013). This accumulation in biota and plants provides an additional bridge for contaminants to move away from the source and can be a potential entry route into the terrestrial food web.

To date there is a paucity of systematic studies investigating the desorption of PFAAs from contaminated soils and their bioavailability and bioaccumulation in plants and animals at highly contaminated sites around FTGs. The use of field contaminated soils increases the environmental relevance, as the presence of a diverse mix of PFASs, including potential PFAA precursors, and other co-contaminants present in AFFF impacted soils, which can influence the sorption and bioavailability of PFAAs (Baduel et al., 2017; Guelfo and Higgins, 2013), is incorporated.

The aim of this study was to understand the mobility and bioavailability of PFAAs in AFFF-contaminated soils which may serve as long-term sources to groundwater and biota in the surrounding environment. Specific objectives were to (1) study the leaching potential of PFAAs from soils by using laboratory based batch experiments, (2) determine the uptake of PFAAs into wheat-grass grown in these contaminated soils, and (3) determine the bioavailability of PFAAs to earthworms from such soils. This information will add to the understanding of potential off-site transport of PFAAs from contaminated soils into both the aquatic and terrestrial environment.

2. Methods

2.1. Soils

Three soils were sampled at two airports. Two of these soils, A and B, were collected directly from AFFF-impacted airport sites, and a third was collected from a remote site at the airport where Soil A was collected, and was used as an uncontaminated reference soil. Soil A was collected from a FTG, while Soil B was collected from a stockpile of waste soil removed from a fire station during reconstruction works. It is understood that 3M Light Water, containing PFOS and PFHxS as active ingredients, as well as PFAA precursors (3M Company, 1997; Backe et al., 2013; Barzen-Hanson and Field, 2015) was used at sites A and B for around two decades. This product was replaced by Ansulite® (Ansul), which was used for another 7 years. Ansulite® contains fluorotelomers as key ingredients, which can degrade to form carboxylic acids (ANSUL, 2016; Houtz et al., 2013; Place and Field, 2012). Nowadays, RF6 produced by Solberg and sold as being fluorine free, is used at the investigated sites.

The soils were transported back to the lab in polypropylene (PP) buckets, air-dried, sieved to <2 mm and thoroughly mixed. Soil characteristics including total organic carbon content (OC; Dumas combustion), particle size analysis and soil pH (1:5 water extraction) were determined according to NATA accredited procedures by the Chemistry Centre at the Department of Science, Information Technology and Innovation, Queensland.

2.2. Batch desorption experiments

Batch experiments were set up to determine the leaching of PFAAs from soil. All soils were dried at 60 °C and sieved using a 1.18 mm mesh to further rid the soil of little stones. For each soil three independent batches were prepared on separate days. An aliquot of 2 g of soil was weighed into a 50 mL PP centrifuge tube and 40 mL of deionized water, adjusted to a pH of 7 using potassium hydroxide to represent environmental conditions, was added to the tube and the samples were shaken for 24 h on a vertical shaker. While the leaching solution had an initial pH of 7 the buffering capacity of the soils changed the pH in the course of the extraction to those listed in Table 1. After shaking

Table 1
Summary of soil characteristics. The sum of PFAA concentrations excludes the ones below the LOQ.

	$\sum_{12}$ PFAAs ng/g dw	OC %	pH	Particle Size analysis (%)			
				Coarse sand 0.2–2 mm	Fine sand 0.02–0.2 mm	Silt 2–20 μm	Clay <2 μm
Soil A	14,000	2.9	6.3	32	31	25	20
Soil B	2,400	0.5	8.5	26	66	4	5
Soil C	9	1.1	6.9	23	31	16	33