Science of the Total Environment 646 (2019) 471–479

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

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

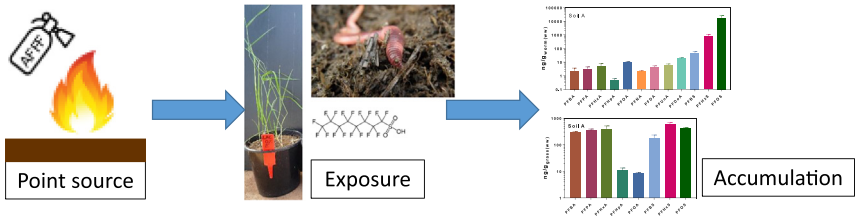
Jennifer Bräunig [a,*], Christine Baduel [a,1], Craig M. Barnes [b], Jochen F. Mueller [a]

[a] Queensland Alliance for Environmental Health Sciences, The University of Queensland, 20 Cornwall Street, Woolloongabba, QLD 4102, Australia
[b] Airservices Australia, 25 Constitution Avenue, Canberra, ACT 2601, Australia

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



ARTICLE INFO

Article history:
Received 20 April 2018
Received in revised form 17 July 2018
Accepted 17 July 2018
Available online xxxx

Editor: Jay Gan

Keywords:
Bioavailability
PFAAs
Earthworm
Wheat grass
Leaching
Contaminated soils

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

* Corresponding author.
E-mail address: j.braeunig@uq.edu.au (J. Bräunig).
[1] Present address: Université Grenoble Alpes, IRD, CNRS, Grenoble INP, IGE, Grenoble, France.

https://doi.org/10.1016/j.scitotenv.2018.07.231
0048-9697/

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

the tubes were centrifuged for 20 min at 1455 RCF and subsequently 1 mL of the supernatant was spiked with 4 ng of isotopically labelled PFAA standard mix and vortexed. The sample was then passed through a 0.45 μm syringe filter (Phenomenex, RC membrane) and 600 μL filtrate was added to 400 μL of methanol. Finally, the performance standards $^{13}C_8$-PFOS (2 ng) and $^{13}C_8$-PFOA (2 ng) were added to the vial to account for volume corrections and compensate for instrumental drift. Further details on chemicals and sample preparation can be found in the Supplementary information (S1 and S2).

2.3. Experimental setup: bioavailability of PFAAs to wheat grass

The common wheat grass (*Elymus scaber*), indigenous to Australia, is a perennial C3 grass, adapted to low soil fertility, and frequently used for revegetation, as it has a very short germination period (7–10 days) and thus establishes quickly. *E. scaber* seeds were provided by Natural Seeds (Cheltenham, VIC, Australia).

Soil was filled into 125 mm (1 L) polypropylene (PP) pots up to the brim and gradually rehydrated with deionized water, using capillary forces on a wetted capillary mat. This procedure reduced leaching of water from the pots. Soil moisture content was adjusted to approximately 60% maximum water holding capacity (WHC) for optimum growth of grass seedlings, and maintained at this throughout the experiments. For each soil three replicate pots were prepared. Grass seeds were sown around 0.5 mm deep in trays of autoclaved sand for pre-germination. Four seedlings were transferred to each pot 5 days after germination. Pots were then transferred to a greenhouse where temperatures averaged 26 °C during the day and 19 °C during night throughout the experimental period. Pots were distributed on a table and randomized weekly to ensure even light and temperature conditions. The grasses were watered every 3rd day and weight adjusted to approximately 60% WHC once per week. Grass was harvested after a growth period of 10 weeks. Roots and shoots were carefully removed from the soil, washed in deionized water and dried with clean tissues. Roots were separated from the shoots and the weight was determined for each. Grass samples were stored at −20 °C until analysis.

2.4. Experimental setup: bioavailability of PFAAs to earthworms

Earthworms (*Eisenia fetida*) were obtained from Wormlovers Pty Ltd. (St. Kilda, VIC, Australia) and subsequently cultured in the laboratory at room temperature in hydrated coir for 2 months prior to experiments. The worms were fed three times a week a diet of mixed vegetables. Before the start of the experiments three pools of 10 earthworms each were analysed for their PFAA content to determine background levels. Concentrations of all PFAAs investigated in the worms prior to the experiments were below the LOD (i.e. 0.03–0.1 ng/g, depending on the specific congener, see Supplementary information, Table S1). Before exposing the worms they were depurated in the dark for 24 h on wet filter paper, washed with deionized water and the initial weight of pools of ten worms was recorded. The earthworm bioaccumulation experiment was conducted following a modified version of the OECD standard procedure No. 222 (OECD, 2004). Modifications included a non-temperature controlled and non-light controlled environment. The experiment was performed in 125 mm (1 L) PP pots. Soil equating to 700 g of dry weight was transferred to each pot, with triplicate pots prepared for each soil. Soils were rehydrated with deionized water through the use of capillary forces on a wet capillary mat and then adjusted to approximately 40% WHC. A pre-weighed pool of ten depurated worms was added to each container and the pots were covered with punctured aluminum foil to retain worms and soil moisture. The pots were set up in the greenhouse where temperatures averaged 26 °C during the day and 19 °C during night throughout the experimental period. Pots were watered every 3 days and pot weight was monitored once weekly in order to keep soil moisture at 40% WHC. Worms were incubated in the soil for 28 days and then carefully removed from the soil, washed with deionized water and placed in petri dishes on wet filter paper for 24 h to depurate their guts. Next they were washed again in deionized water, lightly patted dry, weighed and then frozen at −20 °C until analysis.

2.5. Sample extraction and analysis

PFAAs investigated in this study include perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnA), perfluorododecanoic acid (PFDoA), perfluorobutanesulfonate (PFBS), perfluorohexane sulfonate (PFHxS), and perfluorooctane sulfonate (PFOS). Further details on the chemicals and reagents can be found in the Supplementary information.

All samples were extracted and analysed in triplicate. Detailed extraction protocols as well as limits of detection (LOD) and quantification (LOQ) for each analyte and internal standard recovery are reported in the Supplemental information Table S1. Mass-labelled PFAAs were used as isotope dilution standards. For those target analytes without corresponding mass-labelled standard quantification was done using the internal standard presenting the closest structural similarity. Soil samples were extracted using a 1% ammonia solution in methanol and cleaned up using a graphitized carbon cartridge (Bond Elut Carbon, Agilent). Earthworms were homogenized using a mortar and pestle and extracted with a mixture of 4 mL acetonitrile and 0.4 mL 200 mM NaOH in methanol. Samples were cleaned up by liquid-liquid extraction with n-hexane, followed by percolation through a carbon cartridge. Wheat grass samples were homogenized in an electric blender and soaked in 1.4 mL 200 mM NaOH in methanol for 10 min before an additional 3.5 mL methanol were added. Samples were soaked overnight before sonication extraction. The samples were cleaned up by percolation through a Bond Elut (Agilent) carbon cartridge.

The PFAAs of interest were analysed using high performance liquid chromatography (Nexera HPLC, Shimadzu Corp., Kyoto Japan) coupled to a tandem mass spectrometer (QTRAP 5500 Sciex, Concord, Ontario, Ca) operating in negative electrospray ionisation mode and using multiple reaction monitoring (MRM). A 5 μL aliquot of the sample was injected onto a Gemini NX C18 column (50 × 2 mm, 3 μm particle size, 110 Å pore size, Phenomenex, Lane Cove, Australia) held at a constant temperature of 50 °C, with a flow rate of 0.3 mL/min. Separation of PFAAs was achieved by gradient elution from the column. Mobile phases consisted of methanol:water (1:99, v:v), and methanol:water (90:10, v:v), each with 5 mM ammonium acetate. A pre-column (C18, 50 × 4.6 mm, 5 μm particle size, Phenomenex, Lane Cove, Australia) was installed between the solvent reservoirs and the injector to trap and delay the background of PFAAs originating from the HPLC system. Identification and confirmation of peaks was done using retention times and comparing the ratios of MRM transition area between the samples and the calibration standards in the same batch of analysis. Quantification was conducted using mass-labelled PFAAs. Calibration standards were made up in 1000 μL (400 μL methanol and 600 μL 5 mM ammonium acetate in water). The concentration range of the eight point calibration standards was 0.1–100 μg/L (0.1; 0.4; 1; 4; 10; 20; 40; 100 μg/L).

2.6. Analytical quality assurance and quality control (QA/QC)

Calibration standards were injected three times in each batch of samples and only regression coefficients (r^2) higher than 0.993 were accepted. Quality control standards, including duplicate samples, native spikes and deionized water procedural blanks were added to each batch and treated in the same way as real samples. No PFAAs were detected in procedural and instrument blanks. Quantification of PFAAs was performed using a linear regression fit analysis weighted by 1/x of the calibration curve. Quantification of PFAAs was done by

comparison with calibration curves constructed using the linear isomer of each compound. Instrumental detection limits (LOD) were set according to three times the standard deviation of the concentration of the lowest standard after eight injections with a signal to noise superior to 10. Limits of quantification (LOQ) were set at 10 times the standard deviation of the lowest standard after 8 injections with a signal to noise superior to 10. Matrix specific LODs and LOQs as well as recoveries are listed in the Supplementary information (Table S1). All values reported are corrected for recovery of the internal standards. The authors have further successfully taken part in two interlaboratory studies run by the National Measurement Institute of Australia targeting PFOS and PFOA and have with this reported accurate concentrations in soil, water and biota.

2.7. Data analysis

Bioaccumulation factors were calculated for all earthworm (BAF) and wheat grass (GAF) samples analysed. Concentrations in soil (C_s) were calculated for soil dry weight (ng/g dw), while concentrations in earthworms (C_{ew}) and wheat grass (C_g) were calculated as wet weight (ng/g ww). The effects of uptake of PFAAs could therefore be assessed by relating the BAFs/GAFs for the different PFAAs to each other. BAFs/GAFs were calculated according to Eq. (1).

$$\text{BAF or GAF} = \frac{C_{ew,ww} \text{ or } C_{g,ww}}{C_{s,dw}} \quad (1)$$

BAF/GAF was not derived if the concentration of PFAAs measured in earthworms/grass or soil were below the LOD. Where PFAAs were below the LOQ in soil but above the LOQ in earthworm/grass, a minimum BAF/GAF_{min} was estimated using ½ the LOQ of C_s. Values where this was the case are marked with one asterisk (*) Where PFAAs were below the LOQ in earthworm/grass but above the LOQ in soil, a maximum BAF/GAF_{max} was estimated using ½ the LOQ of C_{ew} or C_g. Values where this was the case are marked with two asterisk (**). Where both C_{ew}/C_g and C_s were below the LOQ no BAFs were derived.

3. Results and discussion

3.1. Soil properties

Soil A and Soil C showed similar pH and particle sizes, reflecting their geographic proximity, however Soil A had a 2.6-fold higher organic carbon content (2.9%) compared to Soil C (1.1%) (Table 1). The most apparent difference between the two soils concerns the contamination with PFAAs with $\sum_{12}$ PFAAs of 14,000 ng/g dw for Soil A and 9 ng/g dw for Soil C. Soil B had the lowest organic content (0.5%) and the highest pH with 8.5. The soil showed a high content of fine sand, contrary to the other two soils and low content of silt and clay. The $\sum_{12}$ PFAAs was 2,400 ng/g dw in Soil B. Concentrations of PFOS measured in Soil A are at the higher end of concentrations found in soils from FTGs worldwide, most likely due to the regulated firefighting training regimes that applied to Australian Airports. Filipovic et al. (2015) found concentrations of PFOS between 4 and 555 ng/g dw at a firefighting training facility in Sweden, while in Norway concentrations of 273 ng/g dw of PFOS were measured (Kärrman et al., 2011). Houtz et al. (2013) recorded PFOS concentrations between 11 and 8,300 ng/g with the median at 2,400 ng/g and one site that had a concentration of 20,000 ng/g at an air force base in the U.S. Anderson et al. (2016) measured 16 PFASs at locations of AFFF release other than fire-training areas and found maximum concentrations of PFOS in surface and subsurface soils in the same order of magnitude of the ones found in this study in soil from the fire station (Soil B).

A diverse mixture of PFAAs was detected in all three soils investigated (Table 2). Soils were analysed in triplicate and the coefficient of variance (% CV) was below 16% for all samples, with the majority being below 10%. Concentrations of PFOS were 13,400 ng/g in Soil A, 2,200 ng/g in Soil B and 6.8 ng/g in Soil C. After PFOS the most dominant PFAA in all three soils was PFHxS, which was 30-fold lower in Soil A, nearly 18-fold lower in Soil B and 7-fold lower in Soil C. Concentrations of PFAA congeners roughly followed the order of PFOS ≫ PFHxS ≫ PFHxA > PFOA > all other PFAAs investigated. Judging from the contamination profile, it is apparent that the use of 3M Light Water™, which was based primarily on PFOS and PFHxS (Backe et al., 2013) is likely the main source of PFAS contamination at the sites, which agrees with available site information.

3.2. Leaching of PFAAs

Batch leaching tests were performed in triplicate for each soil, with the results showing a CV of <10% for all but one sample (PFBA from Soil A with 15% CV). PFAAs were detected in leachate from Soil A and Soil B with a pattern similar to the concentrations measured in the soils; i.e. PFOS ≫ PFHxS ≫ PFHxA > all other PFAAs (Table 2). In leachate of Soil C solely PFOS and PFHxS were detected at concentrations below 0.5 μg/L. PFOS concentrations in the leachate of Soil A and B were 550 μg/L and 90 μg/L, respectively. PFHxS concentrations were more than an order of magnitude lower than PFOS, with 22 μg/L in leachate of Soil A and 6.2 μg/L in leachate of Soil B. PFHxA was 5-fold lower than PFHxS in leachate of Soil A (3.4 μg/L) and 2-fold lower in leachate of Soil B (2.5 μg/L). The concentration of all other PFAAs was below 1 μg/L for Soil B, while in Soil A PFOA and PFBS had leaching concentrations of 2.6 μg/L and 2 μg/L. Only PFUnA and PFDoA were not detected in leachate of either Soil A or Soil B. Due to the long carbon chain and thus high sorption potential as well as a lower water solubility these chemicals would likely stay bound to the soil. Similar batch desorption tests on field contaminated soils collected at FTGs were conducted by Hale et al. (2017). A liquid to solid ratio of 10 as well as a longer shaking time (8 days) was used. Highest leaching concentrations were observed for PFOS (212 μg/L) from a soil concentration of 1,280 μg/kg which was around ½ of the concentration of our Soil B.

While our experimental design did not allow for the derivation of proper distribution coefficients (K_d), as the concentration of PFAAs was not determined in the soil after partitioning, a discussion on the soil to water distribution can be found in the Supplementary information S3. Instead, a mass balance calculation (Supplementary information, S4) was performed to determine the percentage of PFAAs that leached from the soil into the water phase by determining the total amount of PFAAs in 2 g of soil and the total amount in 40 mL of water after 24 h. Around 100% of all short chain PFAAs in the soil leached into the water (Table 3). For some, values higher than 100% were derived, which could be an artefact of heterogeneous soil concentrations, or formation of PFAAs from precursors during the leach tests. Nevertheless, the leaching percentage reflects the high water solubility of short chain PFAAs and their high potential to leach into the environment by transport with water. With increasing perfluoroalkyl chain length lower percentages of PFAAs were recovered in the leachate solution, with around 82% of PFOS leaching from the soils. Using a similar approach Hale et al. (2017) found that between 51 and 601% of PFOS had leached from different soils after 8 days.

While the initial pH of the leaching solution was 7 the buffering capacity of Soil A changed it to 6.3 and to pH 8.5 in Soil B. Nonetheless, very similar percentages of leached chemicals were found despite the different pH values.

International guideline values on reference concentrations of PFAAs in water vary depending on the approach chosen for deriving the values as well as the subject to be protected. In Australia, health based drinking water guidance values are set at 0.07 μg/L for the sum of PFOS and PFHxS and 0.7 μg/L for recreational waters (Australian Government, 2017). The German Drinking Water Commission issued a strictly health-based guidance value for safe lifelong exposure of 0.3 μg/L for the sum of PFOS and PFOA, and a higher precautionary action value

Table 2
Average triplicate soil, leachate, earthworm and wheat-grass concentration. Standard deviation is shown (n = 3). For samples below the LOQ the LOQ is shown preceded by a < sign.

	Concentration in soil ng/g dw C_s			Concentration in leachate in μg/L C_l			Concentration in earthworms ng/g ww C_{ew}			Concentration in wheat-grass ng/g ww C_g		
	Soil A	Soil B	Soil C	Soil A	Soil B	Soil C	Soil A	Soil B	Soil C	Soil A	Soil B	Soil C
PFBA	11.0 ± 1.0	5.80 ± 0.50	0.16 ± 0.03	0.61 ± 0.09	0.37 ± 0.03	<0.08	18.0 ± 9.4	2.30 ± 1.40	0.37 ± 0.15	766 ± 206	296 ± 19	2.0 ± 1.0
PFPeA	16.0 ± 1.0	11.0 ± 1.00	0.10 ± 0.01	0.83 ± 0.08	0.59 ± 0.02	<0.08	22.0 ± 7.9	3.30 ± 1.20	0.24 ± 0.09	466 ± 119	342 ± 50	<LOD
PFHxA	68.0 ± 4.0	45.0 ± 3.8	0.32 ± 0.05	3.40 ± 0.25	2.50 ± 0.06	<0.08	23.0 ± 4.2	5.40 ± 2.20	0.29 ± 0.07	515 ± 141	395 ± 116	0.31 ± 0.07
PFHpA	11.0 ± 0.4	3.60 ± 0.30	<0.17	0.57 ± 0.05	0.20 ± 0.01	<LOD	1.90 ± 0.22	0.49 ± 0.10	<LOD	17.0 ± 6.0	11.0 ± 3.0	<LOD
PFOA	55.0 ± 3.1	14.0 ± 0.4	0.36 ± 0.03	2.60 ± 0.16	0.66 ± 0.03	<0.05	45.0 ± 1.1	9.4 ± 2.0	0.40 ± 0.27	16.0 ± 4.0	8.0 ± 1.0	<0.20
PFNA	12.0 ± 1.1	1.0 ± 0.1	<0.17	0.60 ± 0.04	<0.09	<LOD	12.0 ± 2.9	2.00 ± 0.52	<0.17	0.80 ± 0.11	< 0.34	<LOD
PFDA	10.0 ± 0.8	1.20 ± 0.05	<0.13	0.37 ± 0.08	<0.06	<0.06	17.0 ± 0.8	4.30 ± 1.00	0.15 ± 0.02	< 0.25	< 0.25	<LOD
PFUnA	5.40 ± 0.60	0.68 ± 0.06	<0.11	<LOD	<LOD	<LOD	23.0 ± 3.0	6.30 ± 1.03	0.11 ± 0.03	<LOD	<LOD	<LOD
PFDoA	6.00 ± 0.70	0.79 ± 0.12	<0.12	<LOD	<LOD	<LOD	54.0 ± 1.2	18.0 ± 4.0	0.17 ± 0.18	<LOD	<LOD	<LOD
PFBS	39.0 ± 3.30	10.0 ± 0.52	<0.11	2.00 ± 0.11	0.55 ± 0.04	<LOD	202 ± 45	48.0 ± 12.7	2.70 ± 1.70	550 ± 170	179 ± 54	0.30 ± 0.05
PFHxS	450 ± 44.0	123 ± 14	0.97 ± 0.04	22.0 ± 1.3	6.2 ± 0.26	0.080 ± 0.002	2,700 ± 736	763 ± 311	30.0 ± 10.0	2,790 ± 480	595 ± 76	1.40 ± 0.20
PFOS	13,400 ± 1,900	2,200 ± 120	6.80 ± 0.43	550 ± 49	90.0 ± 6.5	0.30 ± 0.03	65,100 ± 26,400	18,000 ± 7,550	65.0 ± 4.10	1,070 ± 190	406 ± 47	<0.69

<LOD = below limit of detection.

for adults of 5 μg/L (German DWC, 2011). The US EPA issued a lifetime drinking water health advisory for PFOS and PFOA of 0.07 μg/L (U.S. EPA, 2016). Guideline values aiming at the protection of ecological receptors in the receiving environment are usually much lower than the ones quoted above; i.e. in Australia the draft guideline values for the protection of 80% to 99% of species in an aquatic environment lie between 31 μg/L and 0.00023 μg/L for PFOS, respectively (Australian Government, 2016).

The concentrations in leachates from both Soil A and B exceeded any existing drinking water and other water quality guidelines substantially, which is not unexpected as the two soils originate from the vicinity of FTGs with historical use of AFFF. A comparison to guidelines values should however be considered with caution as in the natural environment/undisturbed soils the desorption kinetics is expected to be relatively slow. However, the batch desorption experiments represent a leachate concentration that could possibly percolate through the soil column to eventually be diluted when mixing with underlying groundwater. While predicting a receiving water concentration from leachate concentrations would be highly uncertain, the derived concentrations and high percentages of leached chemicals observed in this work reflect the potential of PFAAs to leach from soil and migrate into the aquatic environment, highlighting the need to remediate such contaminated soils.

3.3. Uptake of PFAAs from contaminated soil into earthworms

Earthworms appeared in good health at the end of the 28-day incubation period. All worms were recovered, except from two Soil B pots, where 3 and 5 worms out of 10, respectively, had escaped the pots, most likely due to the sandy soil which is not a preferred substrate of worms.

In all three replicates of Soil C average worm weight increased (27%). However, the results for Soils A and B were variable between the replicates. Worm weight increased in only one replicate from Soils A and B, and decreased in the other two replicates for both soils. In Soil A there was an average weight decrease of worms of 16% and in Soil B an average weight increase of 3%. Soil concentrations measured were well below established lethal concentrations and also below the no observable adverse effect level (NOAEL) for earthworms exposed to PFOS (LC50, PFOS = 373 mg PFOS per kg soil and NOAEL = 77 mg PFOS per kg soil; Beach et al., 2006).

Earthworms take up PFAAs mainly through ingestion of soil and gut adsorption, as well as through pore water (Sijm et al., 2000). It has been shown that uptake through the gut increases for chemicals with increasing hydrophobicity, whereas those with lower hydrophobicity are taken up mainly by passive diffusion through the skin (Jager et al., 2003). All 12 PFAAs investigated in the present study were detected in earthworms exposed to Soil A and B and all except PFHpA were detected after exposure to Soil C (Table 2 and Supplementary information Fig. S2). Consistent with data for soil and leachate, PFAA concentrations in earthworms were dominated by PFOS ≫ PFHxS. The next highest

Table 3
Percentage of PFAAs leached from soil after 24 h batch desorption tests. Standard deviations represent triplicate measurements.

	% of PFAAs leached from soil to water	
	Soil A	Soil B
PFBA	112 ± 19	127 ± 15
PFPA	102 ± 13	110 ± 11
PFHxA	101 ± 10	111 ± 10
PFHpA	103 ± 10	112 ± 10
PFOA	95 ± 8	97 ± 5
PFNA	99 ± 11	
PFDA	77 ± 9	
PFBS	102 ± 10	109 ± 10
PFHxS	98 ± 11	99 ± 12
PFOS	82 ± 14	82 ± 7

concentration was found for PFBS, which was contrary to soil and leachate concentrations, where PFHxA followed after PFHxS. PFOS concentrations in earthworms were 65,000 ng/g ww, 18,000 ng/g ww and 65 ng/g ww in Soil A, B and C, respectively. Concentrations of PFHxS were around 24-fold lower than PFOS in Soil A and B and 2-fold lower than PFOS in Soil C.

To be able to compare the accumulation of different PFAAs from soil to earthworm BAFs were plotted against PFAA perfluoroalkyl chain length for Soil A and Soil B (Fig. 1 and Supplementary information, Table S4). For Soil C BAFs were not derived for PFHpA and PFNA and BAF_{min} are labelled with an asterisk. With increasing perfluoroalkyl chain length of PFCAs an initial decreasing trend in accumulation was observed with a minimum BAF at PFHpA (Soil A) and PFHxA (Soil B), followed by an increasing trend up to PFDoA for Soil A and Soil B. For Soil C the trend was not as obvious for all PFCAs but also included estimated BAF_{min} for PFPeA and PFCAs >C9.

Soil A has significantly higher BAF compared to Soil B for PFCAs with perfluoroalkyl chains of C5 and less and significantly lower BAFs for PFCAs with perfluoroalkyl chains C8 and longer, which together with the initial decrease in accumulation suggests different sorption mechanisms of the lower versus the higher carbon PFCAs. Interestingly, Guelfo and Higgins (2013) observed a similar initial decreasing and then increasing trend between carbon chain length and log K_d for three soils, detailing that van der Waals effects may be less important for short chain PFCAs and rather ion exchange the dominant sorption driver or that steric effects in OC of soils favour the binding of smaller molecules. Campos Pereira et al. (2018) similarly found that sorption of short chain PFCAs was less dependent on pH and soil organic matter bulk charge than sorption of longer-chained PFASs, and stipulated that short chain PFCAs may preferentially bind to the humic and fulvic acids rather than to the humin fraction of a soil. These differences in sorption may influence the accessibility of PFAAs to earthworms, leading to higher accumulation of the short chain PFAAs up to C6 or C7 in the soils used in our experiment. As this study was conducted with field contaminated soils they may also contain a variety of precursor chemicals (Baduel et al., 2017; Barzen-Hanson et al., 2017; Houtz et al., 2013). Baduel et al. (2017) investigated an AFFF-impacted FTG that had seen a very similar training regime to the ones investigated in this study. Many different PFASs were detected in soil cores from the FTG, including n:2 fluorotelomer sulfonates, n:2 fluorotelomer sulfonate amines and perfluoroalkane sulfonamides (FASAs), some of which have the potential to transform to PFCAs and PFSAs measured in this study. Zhao et al. showed that perfluorooctane sulfonamide (PFOSA) and N-ethyl perfluorooctane sulfonamide ethanol (N-EtFOSE) can biotransform to PFSAs in wheat and earthworms (Zhao et al., 2016; Zhao et al., 2018). PFOSA was also detected in the soil core by Baduel et al. (2017) and is therefore potentially also present in the soils investigated in this study. Similar biotransformation of PFAA precursors were seen in oligochaetes, activated sludge and soil (Higgins et al., 2007; Mejia Avendaño and Liu, 2015; Rhoads et al., 2008). BAFs of PFAAs with precursors found at these sites impacted by AFFF may therefore be higher than BAFs derived in studies using spiked soils.

BAFs of PFSAs agreed well for Soil A and Soil B. An increasing trend was observed with increasing carbon chain length in Soil A and B, with the exception of PFOS in Soil A, which had a slightly lower BAF compared to PFHxS. For Soil C BAFs were derived for PFOS and PFHxS and estimated BAF_{min} for PFBS, which showed a decreasing trend with increasing carbon chain length. A similarly higher accumulation of shorter chain PFSAs compared to longer chain PFSAs, as seen here in Soil C, was also found by Rich et al. (2015). BAFs derived for PFOS increased with decreasing soil concentration. Others have suggested a concentration dependent uptake of PFAAs into earthworms, observing decreasing BAFs with increasing soil concentration (Wen et al., 2015; S. Zhao et al., 2013), stipulating that at lower soils concentrations there are more binding sites for PFAAs in earthworms, and as they get filled with increasing concentration, the BAFs decrease. Such a concentration dependent accumulation was found for PFOS and PFHxS in our study, while it was not as clear for other PFAAs investigated.

For easier comparison with other publications on PFAAs uptake from soil into earthworms BAFs were OC normalised (Supplementary information Table S3). However, it is acknowledged that OC itself is not the only factor controlling sorption and bioavailability of PFAAs in soils (Li et al., 2018) and is therefore generally not a valid normalization approach. Some OC-normalised BAFs from Soil A (PFOS, PFHxS, PFDoA, PFUnA, PFDA, PFOA) were similar to BAFs derived for two AFFF-soils (Rich et al., 2015) and a spiked soil (S. Zhao et al., 2013), albeit different initial soil concentrations were used. Trends such as concentration dependency of accumulation may however not become apparent in this study, as field contaminated soils were used that can contain PFAA precursors which may biotransform to PFAAs upon uptake into worms, as discussed above.

3.4. Uptake of PFAAs from contaminated soil into wheat grass

Wheat grass appeared in good health and grew well throughout the experimental period. Average biomass produced from plants grown in separate pots in Soil A was 2.9 ± 0.1 g, for Soil B 2.2 ± 0.3 g and for Soil C 2.6 ± 0.5 g. Lowest biomass was produced by plants grown in Soil B, perhaps due to the sandy texture and low organic carbon content.

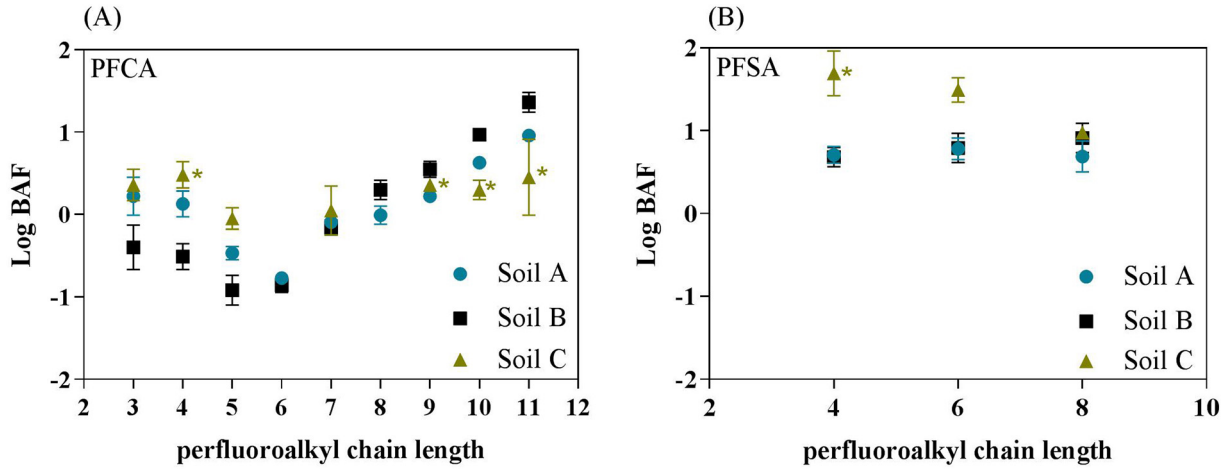


Fig. 1. Relationship between the log bioaccumulation factor (BAF) from Soil A, B and C in earthworms and perfluoroalkyl chain length for PFCAs (A) and PFSAs (B). Average of three replicates with standard deviation are shown. Values labelled with an asterisk (*) are estimated log BAF_{min}.

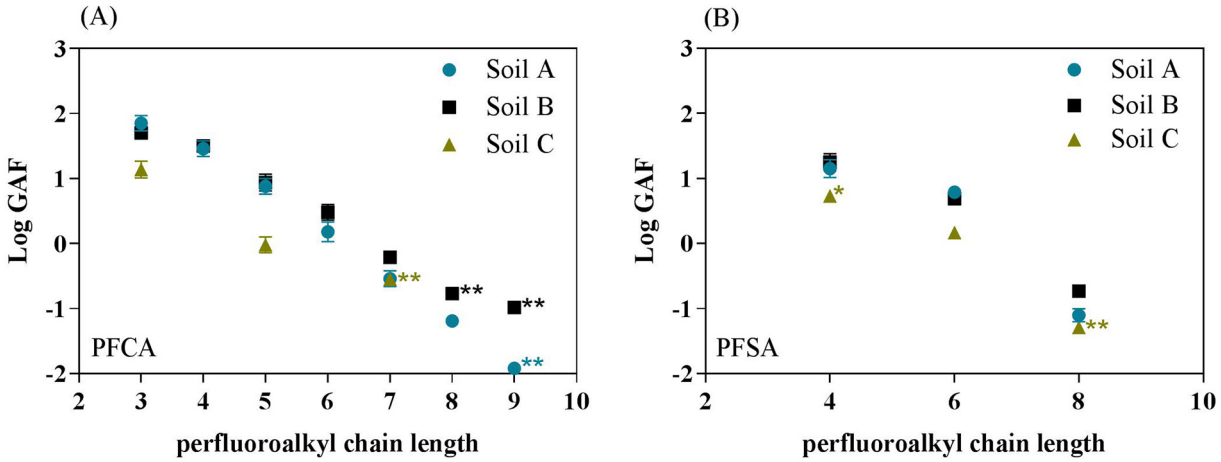


Fig. 2. Relationship between the log accumulation factor (GAF) from Soil A, B and C to grass and perfluoroalkyl chain length for PFCAs (A) and PFSAs (B). Average of three replicates with standard deviation. Values labelled with one asterisk (*) are estimated log GAFmin, values labelled with two asterisk (**) are estimated GAFmax.

Of the 12 PFAAs investigated 10 were detected in wheat grass blades grown in Soil A and Soil B (Table 2 and Supplementary information Fig. S3). Long chain PFDoA and PFUnA were not detected. In Soil C only PFBA, PFHxA, PFOA, PFBS, PFHxS and PFOS were detected. Grass grown in Soil A showed concentrations of PFAAs in the order of PFHxS ≫ PFOS > PFBA > PFBS > PFHxA > all other PFAAs. In Soil B the order was PFHxS > PFOS > PFHxA > PFPeA > PFBA >all other PFAAs. Concentrations of PFHxS were 2,800 ng/g ww and 600 ng/g ww from Soil A, and B, respectively, and 1,100 ng/g ww and 400 ng/g ww for PFOS. The short chain PFAAs PFBA, PFPeA and PFHxA exhibited high concentrations in grass in comparison to initial soil concentrations.

The uptake of PFAAs into plants depends on what is available through the pore-water. In the absence of pore-water concentrations we have used the results from the batch experiments to make comparisons to PFAAs detected in the wheat grass blades. Both long chain PFCAs, PFDoA and PFUnA, that were below the LOD in soil leachate were also not observed to be taken up by wheat grass. Those short chain PFCAs showing high leaching percentages (Table 3), however, were preferentially taken up into wheat grass. Although the batch leachate results are not an ideal comparison, the trends observed were similar in wheat grass and leachate.

Bioaccumulation factors showed a decreasing trend with increasing perfluoroalkyl chain length (Fig. 2 and Supplementary information Table S4). For both Soil A and Soil B the accumulation factors of PFCAs in shoots decreased by around 0.4–0.7 log units per additional CF_2-group. For PFSAs, which also showed an inverse relationship between accumulation and perfluoroalkyl chain length, the decrease was higher, between 0.4 and 1.9 log units per additional CF_2-group. This trend and preferential accumulation of short chain PFCAs in plant shoots has also been observed by others investigating the uptake of PFAAs into the leafy parts of plants (Blaine et al., 2013; Blaine et al., 2014b; Felizeter et al., 2012; H. Zhao et al., 2013).

Accumulation factors derived by others (Lechner and Knapp, 2011) for PFOS and PFOA in cucumber plants were 0.76 for PFOA and 0.12 for PFOS and compared well to the GAFs of 0.61 for PFOA and 0.19 for PFOS derived in the present study. In the same study (Lechner and Knapp, 2011) transfer factors for carrot leaves were determined as 0.53 for PFOA and 0.32 for PFOS, which were within a factor 2 or less of our GAFs. Stahl et al. (2009) did not derive bioaccumulation factors for perennial wheatgrass grown at different soil concentrations of PFOA and PFOS, but provided all of the data to be able to derive them. For comparison with their data we assumed a moisture content of 50% for our wheat grass and thus derived GAF on a dry weight basis of 0.6 and 1.2 for PFOA in and 0.2 and 0.4 for PFOS in Soil A and B, respectively. At similar soil concentrations we calculated GAF between 0.1 and 2.2 for PFOA and 0.08 and 0.7 for PFOS from the data provided by Stahl et al. (2009), which compare well to the GAF derived from our data.

Despite differences in initial soil concentration and soil properties (pH, OC, particle size), the accumulation factors derived for the two soils were very similar. In our study there was no apparent relationship between GAFs and OC content of the soil. In contrast, Blaine et al. (2014b) found lower accumulation with higher OC content, however the authors included soils with substantially higher OC content than we used in our study.

The uptake mechanisms of PFAAs into plants are to date not fully understood. Some research suggests uptake via the soil pore water into the roots by passive diffusion with further translocation into the leafy parts of plants via the transpiration stream (Blaine et al., 2014a; Felizeter et al., 2014), a mechanism that has been observed for hydrophobic organic contaminants (Murano et al., 2010). Wen et al. (2016) found a correlation between the protein content of plants and the concentration of PFOS/PFOA in shoots, suggesting that proteins may play a role in the translocation of these chemicals.

Overall, the results clearly show that uptake of PFAAs into wheatgrass is dependent upon the functional group as well as the carbon chain length. What is most striking is that we found a 2.5-log unit difference between accumulation of PFBA and PFOA and around a 1.5-log unit difference between accumulation of PFHxS and PFOS in grass. The much higher accumulation of shorter chain PFCAs and PFSAs has implications for their movement into the terrestrial food chain. With easy accumulation into grass they can consequently be consumed by grazing animals which in turn will have higher dietary exposure to short chain PFAAs. In humans, PFHxS has a longer elimination half-life compared to PFOS (Olsen et al., 2007). Thus, if PFHxS preferably accumulates in grass it will most likely also accumulate in grazers, especially if their half-life is similarly long to the one in humans. In an effort to reduce the use of long chain PFAAs in AFFF, use of foams which are based on shorter chain fluorinated alternatives is increasing (Wang et al., 2013). While shorter chain PFAAs are similarly persistent as their longer chain analogues (Parsons et al., 2008), they usually express a much higher mobility (Venkatesan and Halden, 2014; Vierke et al., 2014). The results presented here, and supported by other studies (Blaine et al., 2014b; Felizeter et al., 2012), demonstrate that the replacement of long chain PFAAs with short chain PFAAs has the potential to result in a higher PFAA bioaccumulation being evidenced in plants. Cousins et al. (2016) pointed out that the poorly reversible exposure, which applies to both short and long chain PFAAs, should be an incentive for application of the precautionary principle in chemicals management. In light of the greater bioavailability and uptake in plants replacement of long chain PFAAs with shorter equally persistent PFAAs is short sighted.

Acknowledgements

The Queensland Alliance for Environmental Health Sciences, The University of Queensland, gratefully acknowledges the financial support of the Queensland Department of Health. JFM acknowledges funding by an ARC future fellowship (FF120100546). JB received a University of Queensland International Scholarship. The authors would like to thank Prof Susanne Schmidt for advice, Stéphane Guilliou for assistance with plant care and the UQ Central Glasshouse Services for provision of facilities. Native Seeds is acknowledged for provision of grass seeds.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2018.07.231.

References

3M Company, 1997. Material Safety Data Sheet for FC-203CF Light Water brand aqueous film forming foam, St. Paul, MN.
Ahrens, L., Bundschuh, M., 2014. Fate and effects of poly- and perfluoroalkyl substances in the aquatic environment: a review. Environ. Toxicol. Chem. 33 (9), 1921–1929.
Ahrens, L., Norström, K., Viktor, T., Cousins, A.P., Josefsson, S., 2015. Stockholm Arlanda Airport as a source of per- and polyfluoroalkyl substances to water, sediment and fish. Chemosphere 129, 33–38.
Anderson, R.H., Long, G.C., Porter, R.C., Anderson, J.K., 2016. Occurrence of select perfluoroalkyl substances at U.S. Air Force aqueous film-forming foam release sites other than fire-training areas: field-validation of critical fate and transport properties. Chemosphere 150, 678–685.
ANSUL, 2016. Data Sheet: Ansulite A364 3% × 6% AR-AFFF Concentrate, Marinette, WI, USA.
Australian Government, 2016. Commonwealth Environmental Management Guidance on Perfluorooctane Sulfonic Acid (PFOS) and Perfluorooctanoic Acid (PFOA). https://www.environment.gov.au/system/files/pages/dfb876c5-581e-48b7-868c-242fe69dad68/files/draft-environmental-mgt-guidance-pfos-pfoa.pdf.
Australian Government, 2017. Department of Health. Health Based Guidance Values for PFAS. For Use in Site Investigations in Australia. http://www.health.gov.au/internet/main/publishing.nsf/Content/2200FE086D480353CA2580C900817CDC/$File/fs-Health-Based-Guidance-Values.pdf.
Backe, W.J., Day, T.C., Field, J.A., 2013. Zwitterionic, cationic, and anionic fluorinated chemicals in aqueous film forming foam formulations and groundwater from U.S. military bases by nonaqueous large-volume injection HPLC-MS/MS. Environ. Sci. Technol. 47 (10), 5226–5234.
Baduel, C., Paxman, C.J., Mueller, J.F., 2015. Perfluoroalkyl substances in a firefighting training ground (FTG), distribution and potential future release. J. Hazard. Mater. 296, 46–53.
Baduel, C., Mueller, J.F., Rotander, A., Corfield, J., Gomez-Ramos, M.-J., 2017. Discovery of novel per- and polyfluoroalkyl substances (PFASs) at a fire fighting training ground and preliminary investigation of their fate and mobility. Chemosphere 185, 1030–1038.
Barzen-Hanson, K.A., Field, J.A., 2015. Discovery and implications of C2 and C3 perfluoroalkyl sulfonates in aqueous film-forming foams and groundwater. Environ. Sci. Technol. Lett. 2 (4), 95–99.
Barzen-Hanson, K.A., Roberts, S.C., Choyke, S., Oetjen, K., McAlees, A., Riddell, N., McCrindle, R., Ferguson, P.L., Higgins, C.P., Field, J.A., 2017. Discovery of 40 classes of per- and polyfluoroalkyl substances in historical aqueous film-forming foams (AFFFs) and AFFF-impacted groundwater. Environ. Sci. Technol. 51 (4), 2047–2057.
Beach, S.A., Newsted, J.L., Coady, K., Giesy, J.P., 2006. Ecotoxicological evaluation of perfluorooctanesulfonate (PFOS). Reviews of Environmental Contamination and Toxicology. Rev. Environ. Contam. Toxicol. 186. Springer, pp. 133–174.
Blaine, A.C., Rich, C.D., Hundal, L.S., Lau, C., Mills, M.A., Harris, K.M., Higgins, C.P., 2013. Uptake of perfluoroalkyl acids into edible crops via land applied biosolids: field and greenhouse studies. Environ. Sci. Technol. 47 (24), 14062–14069.
Blaine, A.C., Rich, C.D., Sedlacko, E.M., Hundal, L.S., Kumar, K., Lau, C., Mills, M.A., Harris, K.M., Higgins, C.P., 2014a. Perfluoroalkyl acid distribution in various plant compartments of edible crops grown in biosolids-amended soils. Environ. Sci. Technol. 48 (14), 7858–7865.
Blaine, A.C., Rich, C.D., Sedlacko, E.M., Hyland, K.C., Stushnoff, C., Dickenson, E.R.V., Higgins, C.P., 2014b. Perfluoroalkyl acid uptake in lettuce (*Lactuca sativa*) and strawberry (*Fragaria ananassa*) irrigated with reclaimed water. Environ. Sci. Technol. 48 (24), 14361–14368.
Bräunig, J., Baduel, C., Heffernan, A., Rotander, A., Donaldson, E., Mueller, J.F., 2017. Fate and redistribution of perfluoroalkyl acids through AFFF-impacted groundwater. Sci. Total Environ. 596, 360–368.
Buck, R.C., Murphy, P.M., Pabon, M., 2012. Polyfluorinated Chemicals and Transformation Products. In: Knepper, P.T., Lange, T.F. (Eds.), Chemistry, Properties, and Uses of Commercial Fluorinated. Springer Berlin Heidelberg, Berlin, Heidelberg, pp. 1–24 https://doi.org/10.1007/978-3-642-21872-9.
Campos Pereira, H., Ullberg, M., Kleja, D.B., Gustafsson, J.P., Ahrens, L., 2018. Sorption of perfluoroalkyl substances (PFASs) to an organic soil horizon – effect of cation composition and pH. Chemosphere 207, 183–191.
Cousins, I.T., Vestergren, R., Wang, Z., Scheringer, M., McLachlan, M.S., 2016. The precautionary principle and chemicals management: the example of perfluoroalkyl acids in groundwater. Environ. Int. 94, 331–340.
D'Agostino, L.A., Mabury, S.A., 2013. Identification of novel fluorinated surfactants in aqueous film forming foams and commercial surfactant concentrates. Environ. Sci. Technol. 48 (1), 121–129.
Ding, G., Peijnenburg, W.J., 2013. Physicochemical properties and aquatic toxicity of poly-and perfluorinated compounds. Crit. Rev. Environ. Sci. Technol. 43 (6), 598–678.
Enevoldsen, R., Juhler, R.K., 2010. Perfluorinated compounds (PFCs) in groundwater and aqueous soil extracts: using inline SPE-LC-MS/MS for screening and sorption characterisation of perfluorooctane sulphonate and related compounds. Anal. Bioanal. Chem. 398 (3), 1161–1172.
Felizeter, S., McLachlan, M.S., de Voogt, P., 2012. Uptake of perfluorinated alkyl acids by hydroponically grown lettuce (*Lactuca sativa*). Environ. Sci. Technol. 46 (21), 11735–11743.
Felizeter, S., McLachlan, M.S., De Voogt, P., 2014. Root uptake and translocation of perfluorinated alkyl acids by three hydroponically grown crops. J. Agric. Food Chem. 62 (15), 3334–3342.
Filipovic, M., Woldegiorgis, A., Norström, K., Bibi, M., Lindberg, M., Österås, A.-H., 2015. Historical usage of aqueous film forming foam: a case study of the widespread distribution of perfluoroalkyl acids from a military airport to groundwater, lakes, soils and fish. Chemosphere 129, 39–45.
German DWC, 2011. (Drinking Water Commission of the German Ministry of Health at the Federal Environment Agency) Provisional Evaluation of PFT in Drinking Water With the Guide Substances Perfluorooctanoid acid (PFOA) and Perfluorooctane Sulfonate (PFOS) as Examples.
Giesy, J.P., Kannan, K., 2001. Global distribution of perfluorooctane sulfonate in wildlife. Environ. Sci. Technol. 35 (7), 1339–1342.
Giesy, J.P., Naile, J.E., Khim, J.S., Jones, P.D., Newsted, J.L, 2010. Aquatic toxicology of perfluorinated chemicals. Reviews of Environmental Contamination and ToxicologySpringer New York, New York, NY, pp. 1–52.
Guelfo, J.L., Higgins, C.P., 2013. Subsurface transport potential of perfluoroalkyl acids at aqueous film-forming foam (AFFF)-impacted sites. Environ. Sci. Technol. 47 (9), 4164–4171.
Hale, S.E., Arp, H.P.H., Slinde, G.A., Wade, E.J., Bjørseth, K., Breedveld, G.D., Straith, B.F., Moe, K.G., Jartun, M., Høisæter, Å., 2017. Sorbent amendment as a remediation strategy to reduce PFAS mobility and leaching in a contaminated sandy soil from a Norwegian firefighting training facility. Chemosphere 171, 9–18.
Higgins, C.P., Luthy, R.G., 2006. Sorption of perfluorinated surfactants on sediments. Environ. Sci. Technol. 40 (23), 7251–7256.
Higgins, C.P., McLeod, P.B., MacManus-Spencer, L.A., Luthy, R.G., 2007. Bioaccumulation of perfluorochemicals in sediments by the aquatic oligochaete *Lumbriculus variegatus*. Environ. Sci. Technol. 41 (13), 4600–4606.
Houtz, E.F., Higgins, C.P., Field, J.A., Sedlak, D.L., 2013. Persistence of perfluoroalkyl acid precursors in AFFF-impacted groundwater and soil. Environ. Sci. Technol. 47 (15), 8187–8195.
Jager, T., Fleuren, R.H.L.J., Hogendoorn, E.A., de Korte, G., 2003. Elucidating the routes of exposure for organic chemicals in the earthworm, *Eisenia andrei* (Oligochaeta). Environ. Sci. Technol. 37 (15), 3399–3404.
Jeon, J., Kannan, K., Lim, B.J., An, K.G., Kim, S.D., 2011. Effects of salinity and organic matter on the partitioning of perfluoroalkyl acid (PFAs) to clay particles. J. Environ. Monit. 13 (6), 1803–1810.
Kärrman, A., Elgh-Dalgren, K., Lafossas, C., Møskeland, T., 2011. Environmental levels and distribution of structural isomers of perfluoroalkyl acids after aqueous fire-fighting foam (AFFF) contamination. Environ. Chem. 8 (4), 372–380.
Kissa, E., 2001. Fluorinated surfactants and repellents. Surfactant Science Series. Vol. 97 (Marcel Dekker, New York, CRC Press).
Lechner, M., Knapp, H., 2011. Carryover of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) from soil to plant and distribution to the different plant compartments studied in cultures of carrots (*Daucus carota ssp. Sativus*), potatoes (*Solanum tuberosum*), and cucumbers (*Cucumis sativus*). J. Agric. Food Chem. 59 (20), 11011–11018.
Li, Y., Oliver, D.P., Kookana, R.S., 2018. A critical analysis of published data to discern the role of soil and sediment properties in determining sorption of per and polyfluoroalkyl substances (PFASs). Sci. Total Environ. 628-629, 110–120.
Mejia Avendaño, S., Liu, J., 2015. Production of PFOS from aerobic soil biotransformation of two perfluoroalkyl sulfonamide derivatives. Chemosphere 119, 1084–1090.
Milinovic, J., Lacorte, S., Vidal, M., Rigol, A., 2015. Sorption behaviour of perfluoroalkyl substances in soils. Sci. Total Environ. 511, 63–71.
Moody, C.A., Field, J.A., 2000. Perfluorinated surfactants and the environmental implications of their use in fire-fighting foams. Environ. Sci. Technol. 34 (18), 3864–3870.
Murano, H., Otani, T., Seike, N., Sakai, M., 2010. Dieldrin uptake and translocation in plants growing in hydroponic medium. Environ. Toxicol. Chem. 29 (1), 142–148.
Navarro, I., de la Torre, A., Sanz, P., Pro, J., Carbonell, G., Martínez, M.d.l.Á., 2016. Bioaccumulation of emerging organic compounds (perfluoroalkyl substances and halogenated flame retardants) by earthworm in biosolid amended soils. Environ. Res. 149, 32–39.
Oakes, K.D., Benskin, J.P., Martin, J.W., Ings, J.S., Heinrichs, J.Y., Dixon, D.G., Servos, M.R., 2010. Biomonitoring of perfluorochemicals and toxicity to the downstream fish community of Etobicoke Creek following deployment of aqueous film-forming foam. Aquat. Toxicol. 98 (2), 120–129.

OECD, 2004. OECD Guidelines for Testing of Chemicals Section 2: Effecs on Biotic Systems, Test no. 222: Earthworm Reproduction Test (*Eisenia fetida*/*Eisenia andrei*). OECD Publishing.

Olsen, G.W., Burris, J.M., Ehresman, D.J., Froehlich, J.W., Seacat, A.M., Butenhoff, J.L., Zobel, L.R., 2007. Half-life of serum elimination of perfluorooctanesulfonate, perfluorohexanesulfonate, and perfluorooctanoate in retired fluorochemical production workers. Environ. Health Perspect. 115 (9), 1298–1305.

Parsons, J.R., Sáez, M., Dolfing, J., de Voogt, P., 2008. In: Whitacre, D.M. (Ed.), Biodegradation of Perfluorinated Compounds. Reviews of environmental contamination and toxicology 196. Springer US, New York, NY.

Place, B.J., Field, J.A., 2012. Identification of novel fluorochemicals in aqueous film-forming foams used by the US military. Environ. Sci. Technol. 46 (13), 7120–7127.

Prevedouros, K., Cousins, I.T., Buck, R.C., Korzeniowski, S.H., 2006. Sources, fate and transport of perfluorocarboxylates. Environ. Sci. Technol. 40 (1), 32–44.

Rhoads, K.R., Janssen, E.M.L., Luthy, R.G., Criddle, C.S., 2008. Aerobic biotransformation and fate of N-ethyl perfluorooctane sulfonamidoethanol (N-EtFOSE) in activated sludge. Environ. Sci. Technol. 42 (8), 2873–2878.

Rich, C.D., Blaine, A.C., Hundal, L., Higgins, C.P., 2015. Bioaccumulation of perfluoroalkyl acids by earthworms (*Eisenia fetida*) exposed to contaminated soils. Environ. Sci. Technol. 49 (2), 881–888.

Sijm, D., Kraaij, R., Belfroid, A., 2000. Bioavailability in soil or sediment: exposure of different organisms and approaches to study it. Environ. Pollut. 108 (1), 113–119.

Stahl, T., Heyn, J., Thiele, H., Hüther, J., Failing, K., Georgii, S., Brunn, H., 2009. Carryover of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) from soil to plants. Arch. Environ. Contam. Toxicol. 57 (2), 289–298.

Tomy, G.T., Budakowski, W., Halldorson, T., Helm, P.A., Stern, G.A., Friesen, K., Pepper, K., Tittlemier, S.A., Fisk, A.T., 2004. Fluorinated organic compounds in an eastern Arctic marine food web. Environ. Sci. Technol. 38 (24), 6475–6481.

Tuve, R.L. and Jablonski, E.J. (1966) Patent: Method of extinguishing liquid hydrocarbon fires. The United States Patent Office (Patent No. US 3258423).

U.S. EPA, 2016. United States Environmental Protection Agency: drinking water health advisory for PFOS. Office of Water EPA 822-R-16-004.

Venkatesan, A.K., Halden, R.U., 2014. Loss and in situ production of perfluoroalkyl chemicals in outdoor biosolids–soil mesocosms. Environ. Res. 132, 321–327.

Vierke, L., Möller, A., Klitzke, S., 2014. Transport of perfluoroalkyl acids in a water-saturated sediment column investigated under near-natural conditions. Environ. Pollut. 186, 7–13.

Wang, Z., Cousins, I.T., Scheringer, M., Hungerbühler, K., 2013. Fluorinated alternatives to long-chain perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSAs) and their potential precursors. Environ. Int. 60, 242–248.

Wen, B., Li, L., Zhang, H., Ma, Y., Shan, X.-Q., Zhang, S., 2014. Field study on the uptake and translocation of perfluoroalkyl acids (PFAAs) by wheat (*Triticum aestivum* L.) grown in biosolids-amended soils. Environ. Pollut. 184, 547–554.

Wen, B., Zhang, H., Li, L., Hu, X., Liu, Y., Shan, X.-q., Zhang, S., 2015. Bioavailability of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) in biosolids-amended soils to earthworms (*Eisenia fetida*). Chemosphere 118, 361–366.

Wen, B., Wu, Y., Zhang, H., Liu, Y., Hu, X., Huang, H., Zhang, S., 2016. The roles of protein and lipid in the accumulation and distribution of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in plants grown in biosolids-amended soils. Environ. Pollut. 216, 682–688.

Zhao, H., Guan, Y., Zhang, G., Zhang, Z., Tan, F., Quan, X., Chen, J., 2013. Uptake of perfluorooctane sulfonate (PFOS) by wheat (*Triticum aestivum* L.) plant. Chemosphere 91 (2), 139–144.

Zhao, S., Zhu, L., Liu, L., Liu, Z., Zhang, Y., 2013. Bioaccumulation of perfluoroalkyl carboxylates (PFCAs) and perfluoroalkane sulfonates (PFSAs) by earthworms (*Eisenia fetida*) in soil. Environ. Pollut. 179, 45–52.

Zhao, S., Fang, S., Zhu, L., Liu, L., Liu, Z., Zhang, Y., 2014. Mutual impacts of wheat (*Triticum aestivum* L.) and earthworms (*Eisenia fetida*) on the bioavailability of perfluoroalkyl substances (PFASs) in soil. Environ. Pollut. 184, 495–501.

Zhao, S., Ma, X., Fang, S., Zhu, L., 2016. Behaviors of N-ethyl perfluorooctane sulfonamide ethanol (N-EtFOSE) in a soil-earthworm system: transformation and bioaccumulation. Sci. Total Environ. 554-555, 186–191.

Zhao, S., Zhou, T., Wang, B., Zhu, L., Chen, M., Li, D., Yang, L., 2018. Different biotransformation behaviors of perfluorooctane sulfonamide in wheat (*Triticum aestivum L.*) from earthworms (*Eisenia fetida*). J. Hazard. Mater. 346, 191–198.