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Sorbent amendment as a remediation strategy to reduce PFAS mobility and leaching in a contaminated sandy soil from a Norwegian firefighting training facility

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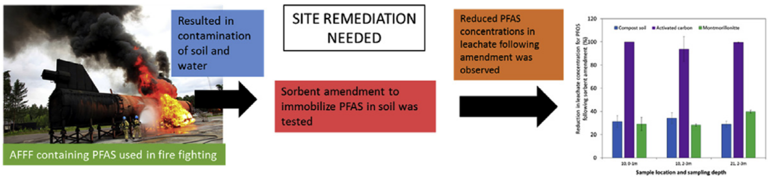
HIGHLIGHTS

- Perfluorooctanesulfonate (PFOS) concentrations up to 2600 μg/kg were measured in soil.
- Sorbent amendment was tested using activated carbon (AC), montmorillonite and compost soil.
- PFOS was immobilised in soil following sorbent amendment.
- PFOS leaching was reduced by 99% for AC and 35% for montmorillonite and compost soil.
- Sorbent + soil-water partitioning coefficients for AC were estimated as 16,940 L/kg.

GRAPHICAL ABSTRACT



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ABSTRACT

Aqueous film-forming foams (AFFF) containing poly- and perfluoroalkyl substances (PFAS) used for firefighting have led to the contamination of soil and water at training sites. The unique physicochemical properties of PFAS results in environmental persistency, threatening water quality and making remediation of such sites a necessity. This work investigated the role of sorbent amendment to PFAS contaminated soils in order to immobilise PFAS and reduce mobility and leaching to groundwater. Soil was sampled from a firefighting training facility at a Norwegian airport and total and leachable PFAS concentrations were quantified. Perfluorooctanesulfonic acid (PFOS) was the most dominant PFAS present in all soil samples (between 9 and 2600 μg/kg). Leaching was quantified using a one-step batch test with water (L/S 10). PFOS concentrations measured in leachate water ranged between 1.2 μg/L and 212 μg/L. Sorbent amendment (3%) was tested by adding activated carbon (AC), compost soil and montmorillonite to selected soils. The extent of immobilisation was quantified by measuring PFAS concentrations in leachate before and after amendment. Leaching was reduced between 94 and 99.9% for AC, between 29 and 34% for compost soil and between 28 and 40% for the montmorillonite amended

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Montmorillonite
AFFF

samples. Sorbent + soil/water partitioning coefficients (K_D) were estimated following amendment and were around 8 L/kg for compost soil and montmorillonite amended soil and ranged from 1960 to 16,940 L/kg for AC amended soil. The remediation of AFFF impacted soil via immobilisation of PFAS following sorbent amendment with AC is promising as part of an overall remediation strategy.

1. Introduction

Poly- and perfluoroalkyl substances (PFAS) have been produced since the 1950s and used in industrial and consumer products as protective coatings for textiles and paper, in the production of semi-conductors, as chemicals in aqueous film-forming foams (AFFF), as polymer additives, in herbicide and insecticide formulations and in cosmetics (Wang et al., 2014; Lindstrom et al., 2011). Perfluorocarboxylic acids (PFCA), perfluorosulfonic acids (PFSA), fluorotelomer alcohols (FTOH), fluorotelomer sulfonates (FTS), and fluoroalkyl sulfonamides are widely researched and this has, in part, led to the regulation of the environmental presence of certain PFCA and PFSA (United Nations Environment Programme, 2001). The unique chemical properties of the substances including hydrophobicity, oleophobicity, and resistance to chemical, biological and physical degradation processes, in addition to their high production levels, have led to a high environmental persistence (Arp et al., 2006) and ubiquitous environmental presence. They have been detected in rainwater (Loewen et al., 2005; Filipovic et al., 2015a), freshwater (Hansen et al., 2002; Skutlarek et al., 2006), seawater, groundwater (Moody and Field, 1999), landfill leachates (Ahrens et al., 2011a), soil, sediment, waste water treatment plant sludge, wildlife and in the atmosphere in urban and remote areas (Giesy and Kannan, 2001; Prevedouros et al., 2006; Jahnke et al., 2007; Armitage et al., 2009). In addition to the very wide array of PFAS precursors found in the environment, it has been documented that certain precursor substances such as FTOH and perfluoroalkyl sulfonamido alcohols can abiotically and biologically degrade to other PFAS, for example the biodegradation of 8:2 FTOH to PFOA (Armitage et al., 2006; Wania, 2007; Oono et al., 2008; Wang et al., 2009).

Over the last decade, the toxicity of PFAS to human health and the wider ecosystem has been investigated and summarized in several review articles (Lau et al., 2007; DeWitt et al., 2009). The uncertainty related to long-term impacts of PFAS has led America, Norway and the Netherlands to set stringent environmental quality guidelines that have resulted in an increased focus on site remediation. Two particular compounds, perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), often drive regulation owing to their bioaccumulative and toxic potential to aquatic and mammalian species (Lau et al., 2007) and ability to reach water bodies. Soil and water clean-up targets have been set based on European water regulation in order to protect these precious resources (European Commission, 2000).

The extensive use of AFFF at firefighting training facilities has resulted in legacy pollution hot spots. PFAS are added to AFFFs to reduce their surface tension owing to the surfactant properties PFAS possess (Rahman et al., 2014) and this ensures a better spreading of AFFF on water and oil resulting in an exclusion of oxygen from the fire source. Previous studies from airport sites in America, Sweden, Norway, Canada, The Netherlands and Germany have reported the following levels of PFAS in groundwater; low milligram per liter, in surface water; nanograms per liter, in biota; nanograms per gram, and in soil; microgram per kilogram as a result of firefighting activities at the sites. (U.S. Army Corps of Engineers, 1994; Chapelle et al., 1996; Moody and Field, 1999; de Solla et al., 2012; Weiss et al., 2012; Houtz et al., 2013; Gewurtz et al., 2014; Kwadijk et al., 2014; McGuire et al., 2014; Ahrens et al., 2015; Baduel et al., 2015; Filipovic et al., 2015b; Kupryianchyk et al., 2016). These environmental burdens are unacceptable and remediation of such contaminated sites is desirable. Traditional soil remediation often relies on dig and dump strategies, however owing to the high cost of landfilling of contaminated soils and the current lack of proper handling and disposal facilities that can receive PFAS contaminated soils, this option has a very limited application. Alternative remediation methods must be found that are both sustainable, cost effective and minimise the environmental burdens.

A very small body of literature related to the treatment of PFAS contaminated soils exists (Das et al., 2013; Kupryianchyk et al., 2016). The difficulty in understanding the behaviour of these compounds in the saturated and unsaturated soil zone has hindered the development of remediation technologies able to treat large soil volumes. On the other hand, the treatment of PFAS contaminated water is well established and is most often carried out via adsorption to activated carbon (AC) filters in pump and treat systems (Qu et al., 2009; Appleman et al., 2013). A similar approach could be taken for PFAS contaminated soil is AC was added to the soil in order to immobilise PFAS pollution. This so called sorbent amendment has been tested in the field for PAH, PCB, DDT and TBT contaminated soils and sediments with the use of AC (Brandli et al., 2009; Cornelissen et al., 2011; Ghosh et al., 2011). AC has a very large surface area and thus sorption capacity for organic pollutants, rendering it ideal for use in sorbent amendment applications. The addition of the sorbent material to the contaminated soil results in a stabilisation or immobilisation of the pollutants making them unavailable to leach to the surroundings and to be taken up by organisms (McLeod et al., 2007; Janssen and Beckingham, 2013).

The previous studies that have investigated sorbent amendment in order to immobilise PFAS in natively impacted soils (rather than just a quantification of the sorption capacity of a sorbent for PFAS without adding the material to a soil) are limited and mostly focused on PFOS (Das et al., 2013; Kupryianchyk et al., 2016). Several studies have quantified the sorption of PFOS to a diverse range of clay and other mineral materials including; montmorillonite (Zhou et al., 2010; Zhang et al., 2014), kaolinite (Zhang et al., 2014; Zhao et al., 2014), hematite (Zhao et al., 2014), alumina (Wang and Shih, 2011), boehmite (Wang et al., 2012) as well as a modified commercial clay adsorbent (Das et al., 2013) in the absence of soil. In addition, the sorption of PFOS to AC and biochar (a material similar to AC but produced via the pyrolysis of biomass) in the absence of soil have been reported (Ochoa-Herrera and Sierra-Alvarez, 2008; Hansen et al., 2010; Deng et al., 2015; Kupryianchyk et al., 2016). However only two studies have investigated the sorption efficiency for these materials in the presence of soil; one where a modified commercial clay adsorbent was used and the other where AC was tested. Both studies reported an almost complete stabilisation of PFOS in the tested soils (Das et al., 2013; Kupryianchyk et al., 2016). These previous studies suggest that sorbent amendment, either when the sorbent is added *in-situ* or *ex-*

situ, could provide one remediation method for PFAS contaminated soils. In order to verify this the identification of suitable sorbent materials, a quantification of their sorption capacity in the presence of real world soils impacted with a cocktail of PFAS from AFFF contamination must be carried out.

The aim of this study was therefore to investigate the role sorbent amendment could play in the immobilisation of PFAS in an AFFF contaminated soil, thus providing information related to whether such a strategy could be considered in a wider remediation context. A case study site was chosen at an airport firefighting training facility in Norway where sandy soils are known to be contaminated by a cocktail of PFAS. Total soil concentrations were determined and a selection of soils were chosen to investigate the extent to which sorbent amendment resulted in an immobilisation of PFAS. The soils were amended with AC, montmorillonite and compost soil in the laboratory and the degree of PFAS immobilisation was quantified by carrying out a batch leach test before and after amendment, and determining PFAS concentrations in the leachate. The batch leach test was used as it represents a theoretical maximum leached concentration owing to the large amount of water used compared to field conditions in the unsaturated soil zone. A one dimensional model was then used in order to translate the results observed in the laboratory to what could be expected in the field.

2. Materials and methods

2.1. Site description

The firefighting training facility site is located at the west of the Oslo airport site, Gardermoen, Norway (60°12′10″N, 11°5′2″E). This facility was established in 1989 and has been used for firefighting training activities prior to this. AFFF has been used extensively at the site. In 2007, the use of AFFF containing PFOS was banned at the facility and a complete ban on the use of organofluorine AFFF was enforced in 2011. In 2001 the site owner ceased using AFFF containing PFOS. It is known that different types of AFFF, with different concentrations of PFAS have been used at the site over time. The soil is known to be contaminated with a range of perfluorinated compounds resulting from this historical contaminant input.

2.2. Soil

Soil was sampled in June 2015 from 6 different sampling points around the firefighting training facility as shown in the supporting information (SI) page S3, section 1. Soil was sampled by digging holes with a small digger and using a spade to take a representative sample from the 0–1 m, 1–2 m, 2–3 m and 3 to groundwater table level (which was in all cases above 4 m) from several locations (referred to by the following location numbers: 4, 5, 6, 10, 17 and 21). The metal spade was rinsed with methanol before sampling at each point and the soil was transferred in to nylon-11 sampling bags before being taken back to the laboratory. Cross contamination in the field and in the laboratory was avoided by rinsing equipment with methanol. In total 21 samples were taken from the site and soil was stored at 4 °C prior to use. All soil samples were classified as medium sand (results for grain size distribution are shown in the SI–Fig. S1).

2.3. Sorbents

Three sorbent materials were chosen based on material availability for a full scale remediation project: activated carbon (AC), montmorillonite and compost soil. Powdered aquasorb BP2 bituminous coal based AC was obtained from Jacobi Carbon (Kalmar, Sweden). The BP2 AC has a surface area of 726 m^2/g and a pH of 8–11. Additional physicochemical parameters can be found in a previous publication (Amstaetter et al., 2012). Montmorillonite K 10, CAS number 1318-93-0, was purchased from Sigma Aldrich as a powder (Norway). The montmorillonite had a surface area of 220–270 m^2/g. Compost soil was purchased from a Norwegian garden shop (http://www.plantasjen.no/kompostjord-40l-200017081-no) and had a high content of nitrogen, phosphate and potassium. All materials were used as received.

2.4. Sorption studies

In order to quantify the leaching of PFAS from the soil with and without sorbent amendment, a standard one step batch leach test was carried out according to method EN 12457-2 with a few modifications before and after sorbent amendment. Details can be found in the SI, page S4, section 2. Briefly soil (90 g taken from a homogenised subsample of soil) was shaken with water for 8 days at a liquid to solid ratio of 10 and then filtered (through 0.7 μm polyethersulfone membrane) before analysis. For sorbent amended samples, 3% of each sorbent material was homogenously mixed with soil and the procedure repeated. Leachate water was stored at 4 °C prior to analysis. The concentration of each individual PFAS in the filtered water at the end of the experiment (C_{water}, μg L^{-1}) was measured, and the concentration leached per dry weight of soil, $C_{leached}$ (μg kg^{-1}) was calculated as follows:

$$C_{leached} = C_{water} \cdot V_{water} / M_{solid,dw} \quad (1)$$

where V_{water} (L) is the volume of water in the batch system, and $M_{solid,dw.}$ is the solid (soil or soil + sorbent) dry weight (kg).

Based on the batch leach tests for soils, three soil samples with low PFOS concentrations were further selected for the batch leach tests following sorbent amendment. Although the focus of this work was on immobilisation of PFAS in soil, for the overall remediation of AFFF impacted sites, additional strategies such as excavation or soil washing may also be necessary. Soil washing is able to reduce soil concentrations following the addition of a large amount of water, however low residual concentrations often persist. In such cases sorbent amendment could be used to immobilise the residual concentrations. Currently excavation is not feasible for large amounts of soil contaminated with high PFAS concentrations. However if sorbent amendment was carried out and resulted in an immobilisation of PFAS then excavation and landfilling may become a more viable solution.

2.5. PFAS analysis

The PFAS investigated in this work were: perfluorobutanoic sulfonate (PFBS, C4), perfluorobutanoic acid (PFBA, C4), perfluoropentanoic acid (PFPeA, C5), perfluorohexanoic sulfonate (PFHxS, C6), perfluorohexanoic acid (PFHxA, C6), perfluoroheptanoic acid (PFHpA, C7), 6:2 fluorotelomer sulfonate (FTS, C8) (H4PFOS), perfluorooctanoic sulfonate (PFOS, linear C8), perfluorooctanoic acid (PFOA, C8), perfluorononanoate (PFNA, C9), 8:2 fluorotelomer sulfonate (FTS, C10) and perfluorodecanoic acid (PFDeA, C10). All analyses were carried out at the accredited laboratory Eurofins GfA Lab Service GmbH (in Germany). For soil, PFAS was quantified using method DIN 38414-S14 based on a methanol or acetonitrile ultrasonic extraction with a multi-step solvent clean up using SPE, followed by analysis using liquid chromatography coupled with mass spectrometry (LC/MS-MS). Leachate was analysed for PFAS following method DIN 38407-F42 and quantification using LC/MS-MS.

2.6. Additional soil and leachate water chemical characterisation

The content of iron (Fe), calcium (Ca), chloride (Cl), manganese (Mn), sulfate (SO_4), total organic carbon (TOC) and pH were quantified in soil samples at accredited Eurofins laboratories. Fe, Ca and Mn were analysed according to EN ISO 11885, Cl and SO_4 were analysed following method EN ISO 10304-1, pH was measured according to method EN 12176 and TOC was measured according to method AM 374.02. Leachate water samples were analysed for the same properties apart from TOC, which was substituted for the determination of content of dissolved organic carbon (DOC). Fe and Mn were analysed according to EN ISO 17294-2 after digestion, Cl was analysed following method EPA Method 325.2, pH was measured according to method EN ISO 10523 and DOC was measured according to EN 1484. Ca and SO_4 were analysed sulfate was analysed according to the methods above.

2.7. Quality control and assurance

All batch leach tests and PFAS analysis were carried out in triplicate. For a selection of samples, triplicate soil and leachate additional chemical characterisation were carried out. PFAS analysis was carried out at an accredited laboratory. 13 internal isotopically labelled standards were added to all soil and leachate samples prior to PFAS analysis. PFAS identification was based on retention time and molecule or fragment ions and quantification was carried out by comparison with the internal isotopically labelled standards. Analytical detection limits were 1 μg/kg for PFAS in soil and 5 ng/L for PFAS in leachate. Previous work in the laboratory where the batch leach tests were carried out has investigated sorption of PFAS to both the 2 L PE bottles and the 0.7 μm polyethersulfone membrane used in the tests (Kupryianchyk et al., 2016). Negligible sorption to both materials was observed.

2.8. Data analysis

The reduction in leachate concentrations of PFAS following sorbent amendment was determined by comparing the C_{water} before and after sorbent amendment (reduction = C_{water} after amendment/C_{water} before amendment).

In addition the fraction of PFAS leached, $f_{leached}$, was also calculated as follows

$$f_{leached} = C_{leached}\left(\mu g\ kg^{-1}\right) \Big/ C_{soil,0}\left(\mu g\ kg^{-1}\right) \tag{2}$$

where $C_{soil,0}$ is the initial soil concentration of PFAS in soil before the batch leach test.

Soil-water partitioning coefficients K_D (L/kg) were estimated using mass balances for soils with sorbent amendments when possible according to:

$$K_D(L/kg) = \left(C_{soil,0} - C_{leached}(\mu g/kg)\right) / C_{water}(\mu g/L) \tag{3}$$

For the AC amendment batches there were several replicates where C_{water} was below the analytical method limit of detection (LOD). In such cases, half of the analytical LOD was used as the measured concentration to calculate K_D as a conservative assumption.

2.9. One dimensional box model

A one dimensional box model was used to simulate the influence of adding sorbent in this sandy soil on C_{soil} and C_{water} over time, where no further PFAS is added, and PFAS is removed from the soil over time by the infiltration of rain water, which then percolates to the groundwater. This 1-D model has the form:

$$C_{soil}(t) = C_{soil,0}e^{-kt} \tag{4}$$

$$C_{water}(t) = C_{water,0}e^{-kt} \tag{5}$$

where k is the rate constant:

$$k = \frac{Rainfall \cdot IF}{h_{soil}(K_D\rho_b + n)} \tag{6}$$

where rainfall (m/y) is the amount of precipitation in the area, IF (unit less) is the infiltration factor which describes the fraction of rain water that makes it to the groundwater, h_{soil} is the height of the unsaturated soil column, ρ_b is the bulk density and n the soil porosity. The derivation of this model is presented in the SI on page S6, section 3.

For sandy soils a typical ρ_b of 1.51 kg/L was assumed, which corresponds to porosity of 0.43 (Klonowski et al., 2008). For the study area, the rainfall is 0.73 m/y, the IF is unknown but is assumed to be 0.5 to account for evapotranspiration and pavement in the area, an average h_{soil} is 3 m is used. The model was used to investigate the influence of increasing K_D with different sorbent amendment, as well as the percolation rate (by increasing rainfall).

3. Results and discussion

3.1. Concentration of PFAS in soil

PFOS was the most dominate PFAS detected in all soil samples and for this reason PFOS data are presented most prominently here (Fig. 1 and Table S1). The PFOS concentration ranged from 6.4 to 2400 μg/kg (samples 21, 2–3 m and 17, 1–2 m). The highest concentrations were typically found in soil samples taken at 1–2 m depth (except for location 4 at 2–3 m depth and location 21 at 0–1 m depth), and not at 0–1 m depth, suggesting a downwards migration of PFOS in the soil profile over time. This presence of PFOS in the environment after the ban on its use highlights PFOS′ inherent environmental persistence, as observed in previous studies (Key et al., 1997; Filipovic et al., 2015b). Total soil concentration of all analysed PFAS are shown in Fig. S2 and Table S2 in the SI. Differences in the fingerprint of PFAS in soil samples from different locations could suggest a different pattern of use for the various AFFFs used over time. There were four PFAS that were not observed in any of the soil samples: PFBS, PFBA, PFHxA and PFHpA. The compounds that were detected in the soil samples included PFPeA (one sample at 2.8 μg/kg), PFHxS (36% of samples, range 3.0–25.3 μg/kg), 6:2 FTS (12% of samples, range 13–92.4 μg/kg), PFOA (19% of samples, range 3.0–13 μg/kg), PFNA (40% of samples, range 2.8–41.3 μg/kg), 8:2 FTS (7% of samples, range 3.8–116 μg/kg) and PFDeA (26% of samples, range 2.6–72.1 μg/kg).

The concentration of PFOS at this firefighting training facility is within the range reported from similar sites worldwide. Concentrations of 118–8520 μg/kg PFOS were reported at a firefighting training facility at Tullinge, Sweden (Filipovic et al., 2015b), while at the Ellsworth Air Force Base (South Dakota, USA) soil PFOS concentrations between 21 and 2400 μg/kg were measured (Houtz et al., 2013) (although a peak concentration of 36,000 μg/kg was reported near a burning pit at the site, (McGuire et al., 2014). At three firefighting training facilities at Norwegian airports (Kristiansand, Bergen and Harstad/Evenes), concentrations of 21 μg/kg, 85 μg/kg and 120 μg/kg have been reported (Kupryianchyk et al., 2016). As a comparison, Strynar et al. (2012) estimated a global

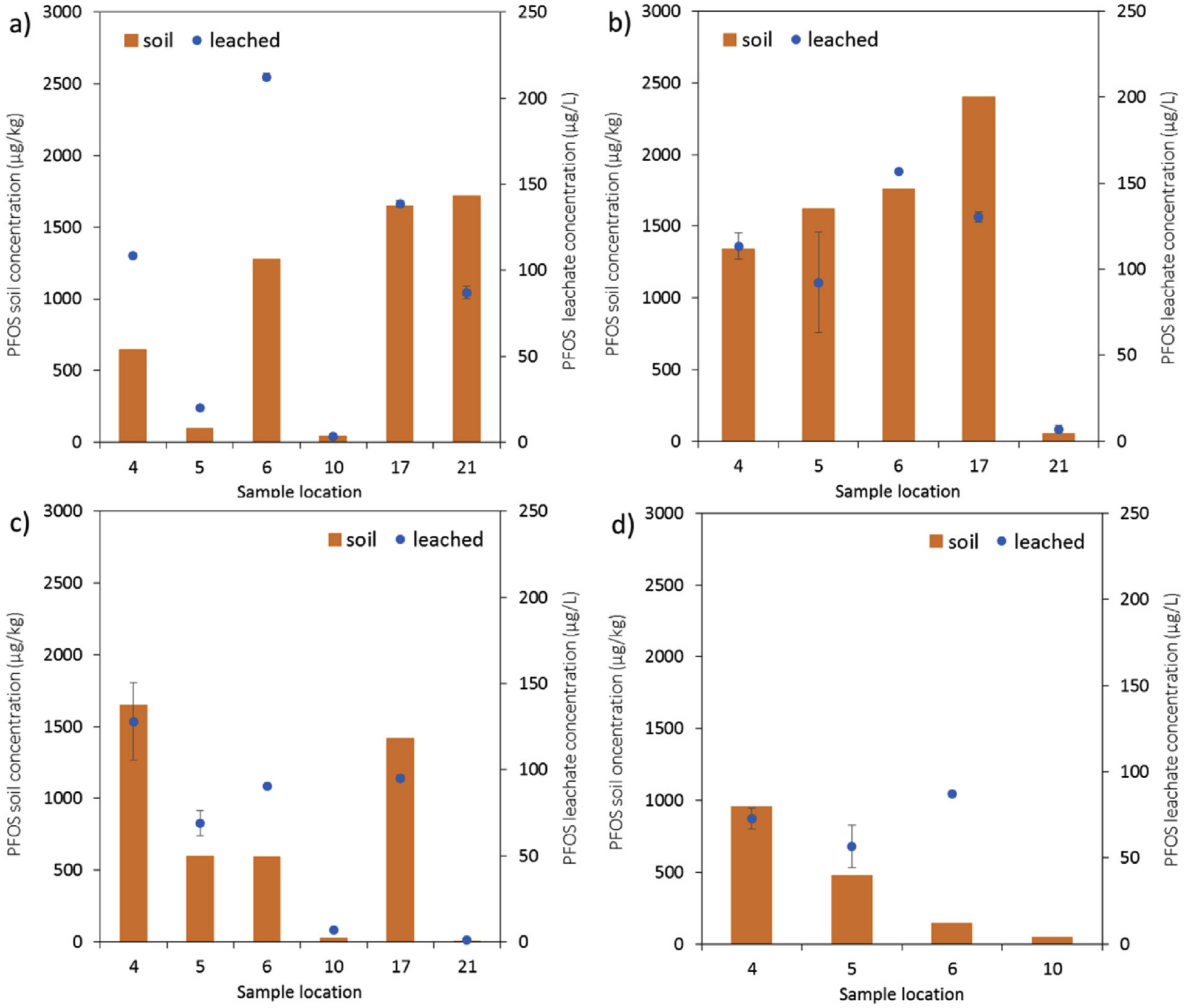

Fig. 1. PFOS soil concentration (µg/kg) and PFOS leachate concentration (µg/L) for a) 0–1 m samples, b) 1–2 m samples, c) 2–3 m samples and d) 3 m to groundwater level samples. Standard deviations represent triplicate measurements.

mean PFOS soil concentration based on samples taken in America, China, Norway, Japan, Greece and Mexico of 0.47 µg/kg, around 12 times lower than the lowest concentration measured in this study.

The additional soil parameters measured (Fe (mg/kg), Cl (mg/kg), Ca (mg/kg), Mn (mg/kg), SO_4 (mg/kg), pH (–) and TOC (%)) are shown in Table S3. In order to investigate whether there was a correlation between the PFOS concentration in soil and these additional physicochemical parameters, they were plotted against each other (see Fig. 3 in the SI). None of the parameters were well correlated with the concentration of PFOS in soil (R^2 ranged from 0.002 to 0.12), suggesting that these single factors alone cannot explain the observed PFOS soil concentrations.

3.2. Leaching of PFAS from soil before sorbent amendment

The concentration of PFOS in the leachate (both in µg/kg and µg/L) along with the percentage of total PFOS leached from the soil is given in Fig. 1 and Table S1. The percentage of total PFOS leached from the soil was calculated by comparison of the concentration in the soil in µg/kg before and after leaching. Leachate concentrations of PFOS varied from 1.2 µg/L (location 21 2–3 m) to 212 µg/L (location 6 0–1 m) and the percentage of PFOS leached from the soil itself varied between 23 and 601%. For 10 samples, greater than 100% leaching was observed. This (impossible) result is likely a result of analysis method artefacts, where the solvent extraction used for the soil analysis was less exhaustive than the water extraction that was carried out through the use of the batch leach test. This implies that the measured soil concentrations are underestimated and that true values are higher. This explanation is also supported by the fact that more PFOS was detected in the soil (using the solvent extraction method) following the batch leach test than before the test. Another possible explanation for this observation is related to the composition of AFFFs, where most AFFF contain just a few percent PFAS, being composed of water, glycols and ethoxylates (Yeung and Mabury, 2013). These additional components are likely to affect the way in which PFAS bind to the soils. In addition, despite efforts to homogenise the soil samples before use, it cannot be ruled out the soil samples were heterogeneous and thus the result is due to this. For these reasons only a qualitative comparison between results is appropriate for this data.

The additional physicochemical parameters that were measured for the leachate following the batch test (Fe mg/L, Ca mg/L, Cl mg/L, Mn mg/L, SO_4 mg/L, pH (–) and DOC mg/L) are shown in Table S4. As for the soil samples, there were no apparent correlations between these leachate water properties and the concentration of PFOS in the leachate (see Fig. S4, R^2 values ranged from 0.008 to

0.02). The leachate concentrations of all individual PFAS expressed as a percentage of the total PFAS in the samples are shown in Fig. S5 and Table S5. Following the batch leaching tests more individual PFAS were detected in the leachate water than in the soil itself following the solvent extraction, again supporting the notion that water extraction provides a more representative extraction method for these soils and compounds reducing the interference from other AFFF components. PFBS was the only PFAS not to be detected in any leachate water samples; therefore being the only analysed PFAS not found in any leachate or soil samples. PFBA, PFHxA and PFHeA were detected in some leachate samples while they were below the LOD in the corresponding soil sample, likely due to the higher LOD in soil. The percentage of samples with detections and concentration ranges for other compounds were as follows: PFBA - 20%, range 0.01–0.02 μg/L, PFPeA - 43%, range 0.01–0.78 μg/L, PFHxS - 100%, range 0.02–9.03 μg/L, PFHxA - 81% of samples, range 0.01–0.49 μg/L, PFHpA – 25% of samples, range 0.02–0.10 μg/L, 6:2 FTS - 38%, range 0.10–5.97 μg/L, PFOA – 60% of samples, range 0.06–3.13 μg/L, PFNA - 71% range 0.02–16.93 μg/L, 8:2 FTS - 10% range 0.13–1.23 μg/L and PFDeA - 48%, range 0.01–2.20 μg/L (Fig. S5). The concentration profiles varied with depth and with sample location and were not systematically affected by the chain length of the PFAS or whether the acid or sulfonate was present. This again, as for the soil could be due to different use patterns at different parts of the site.

To the best of our knowledge this is one of the first studies in which soils natively contaminated by the use of AFFF containing PFAS have been subjected to batch leaching tests in order to quantify PFAS leaching in this way. Previous studies have employed column tests in order to probe the fate and transport of PFAS in soils (Gellrich et al., 2012; Stahl et al., 2013; McKenzie et al., 2015, 2016). Column tests provide information about leachate breakthrough and simulate kinetic field conditions more closely than batch leaching tests, which provide information about equilibrium concentrations (as more energy is applied to batch leachate systems).

3.3. *Leaching of PFAS from soil following sorbent amendment*

The soil samples chosen for the sorbent amendment test contained 6.4 μg/kg to 54.5 μg/kg PFOS. The concentration of PFOS in the leachate water following sorbent amendment are given in Table 1, while Table S6 contains the concentration of all individual PFAS in the leachate water following sorbent amendment. The reduction in PFOS leaching following sorbent amendment, and thus the level of immobilisation of PFAS (compared to the respective non amended sample) calculated as follows:

$$\text{Reduction}(\%) = \left(C_{\text{leachate(soil)}} - C_{\text{leachate(sorbent+soil)}}\right) \Big/ C_{\text{leachate(soil)}} \qquad (7)$$

is shown in Fig. 2.

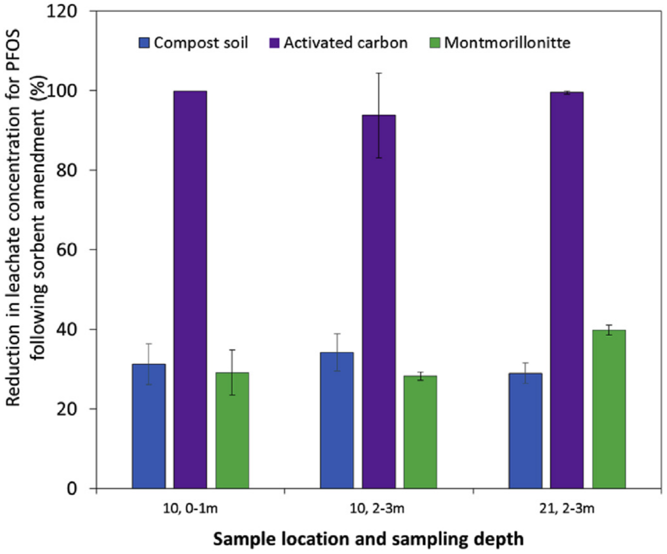

Fig. 2. Relative reduction in PFOS leachate concentration after sorbent amendment. Standard deviations represent triplicate measurements.

Leaching of PFOS was reduced between 28 and 34% following the amendment of compost soil, between 28 and 40% for the montmorillonite amendment and between 94 and 99.9% for AC. There were very few other PFAS where it was possible to quantify the change in leachate concentration following sorbent amendment as concentrations were below the LOD either before, after or both before and after sorbent amendment (65% of cases, see Table S7). For those compounds where it was possible to quantify changes, mixed results, independent of sorbent (including AC) and compound were observed. In some cases there was a reduction in concentration following amendment as expected, but in others an increase was observed. This increase may have been related to working close to the analytical LOD (from 0.31 μg/L down to 0.01 μg/L).

Despite this, the exceptionally strong remediation efficacy of AC for PFOS demonstrated here agrees with a previous study

Table 1

PFOS leachate water concentrations after sorbent amendment (μg/L), the reduction in leaching following sorbent amendment (as compared to the respective unamended sample) and partitioning coefficients (K_D, L/kg) for soil amended with compost soil, AC and montmorillonite.

Sample location	Depth of sampling M	Sorbent material	PFOS concentration in leachate water after amendment μg/L	Reduction in leaching following sorbent amendment **%**	Partitioning coefficient (K_D) (L/kg)
10	0–1	Compost soil	2.26 ± 0.17	31.2 ± 6.7	8.8 ± 1.4
	0–1	AC	0.003 ± 0	99.9 ± 0.002	16,940 ± 0
	0–1	Montmorillonite	2.33 ± 0.19	29.1 ± 5.9	8.2 ± 1.4
	2–3	Compost soil	4.54 ± 0.32	34.2 ± 2.8	[a]
	2–3	AC	0.43 ± 0.74	93.9 ± 10.5	>7287 ± 6287 [b]
	2–3	Montmorillonite	4.95 ± 0.07	28.0 ± 5.5	[a]
21	2–3	Compost soil	0.82 ± 0.03	28.2 ± 10.7	[a]
	2–3	AC	0.01 ± 0.005	99.6 ± 0.4	>1889 ± 1126 [b]
	2–3	Montmorillonite	0.70 ± 0.01	39.5 ± 5.4	[a]

[a] Values are not given as C_{leached} (μg/kg) was higher than $C_{\text{soil,0}}$ (μg/kg).

[b] The leachate water concentration was below LOD, therefore values of half of the LOD were used as a conservative assumption, resulting in large standard deviations.

(Kupryianchyk et al., 2016) in which AC was amended to three Norwegian soils (with high levels of organic carbon). Kupryianchyk et al. (2016) observed an almost complete removal of PFAS from soil porewater following AC amendment (over 99%). Das et al. (2013) investigated the remediation efficiency of a modified clay material (MatCARE, a palygorskite based material modified with oleyamine) and an AC in a PFOS impacted soil. MatCARE was observed to have a higher sorption capacity for PFOS (0.093 mmol/g) than a commercially available AC.

The additional leachate parameters measured following sorbent amendment: Fe, Ca, Cl, Mn, SO_4, pH and DOC can be compared to those for the unamended soil samples, and are given in Table S8. In most cases AC effectively reduced the concentration of the measured parameters (a few exceptions were seen for Fe, Cl and Ca in some samples) and increased the pH of the leachate water, as has been observed previously (Brandli et al., 2008). The amendment with compost soil generally increased the concentration of the measured parameters (a few exceptions were seen for Fe, Mn and SO_4). Variable results were observed for montmorillonite where Cl and SO_4 concentrations were increased and Fe, Ca, Mn and DOC concentrations were both increased and decreased depending on the sample.

3.4. *Determination of partitioning coefficients following sorbent amendment (K_D)*

It was not possible to determine partitioning coefficients for soil samples without sorbent amendment due to the efficiency of the water extraction in the batch leach test which sometimes led to a higher concentration of PFOS in the leachate water than in the soil extract using methanol or acetonitrile (when both values were calculated in μg/kg). Zareitalabad et al. (2013) report a compilation of K_D and K_{OC} values for the sorption of PFOS to various soils and sediments. K_D values ranged between <1 and 35.3 L/kg with the adsorption of PFOS to Ottawa sand reported to be 2.8 L/kg (Johnson et al., 2007) possibly reflecting a K_D value that could be expected for these samples. Previous studies have concluded that the length and substitution of the PFAS's chain (Higgins and Luthy, 2006) and the octanol-water partitioning coefficient of the PFAS (Arp et al., 2006) are related to K_D. Longer chains are known to have higher K_D values and perfluorosulfonate sorb stronger than the perfluorocarboxylate analogues (and a positive relationship between K_D and K_{OW} has been observed).

The correlation of the fraction of PFOS leached, $f_{leached}$, following the batch leach tests with all of the additional leachate water parameters quantified is shown in Fig. S6. There was no real correlation between these parameters, in concurrence with the previous observations for soil and leachate parameters. Higgins and Luthy (2006) noted that sediment organic carbon was the dominant sediment physico-chemical parameter explaining the sorption of PFOS to five sediments with organic carbon contents varying from 0.56 to 9.66%. A positive correlation has also been observed for the sorption capacity of PFOS to river sediments with organic carbon content (Rayne and Forest, 2009). The soils in the present study have low DOC contents (0.68–5.83 mg/L) and this may be the explanation for the overall lack of correlation observed in this study. Both soil pH and calcium content have been shown to affect the sorption of cationic compounds to soils, as these parameters influence the degree of deprotonation of organic matter and can thus alter the cation exchange capacity of a soil. (Jafvert, 1990; Higgins and Luthy, 2006; You et al., 2010; Ahrens et al., 2011b), where an increase in H^+ or Ca^{2+} concentration has been shown to be able to increase sorption of PFOS. You et al. (2010) reported a threefold increase in PFOS sorption onto sediment as $CaCl_2$ concentration increased from 0.005 to 0.5 mol/L at pH 7 and an almost factor 6 increase at pH 6. These ionisable PFAS (e.g. PFOS, PFAS) are strongly acidic (Arp and Goss, 2009), and as the pH values measured in these soil samples (5.1–7.4, Table S2) are near neutral, it is expected that a change in pH would lead to a change of the surface charge of the sorbents (here soil organic matter and mineral surfaces), rather than a protonation of the PFAS molecules themselves (Goss, 2008). The addition of AC was the only amendment to increase pH consistently (i.e. decrease H^+), while the addition of compost soil was the only amendment to consistently increase Ca concentrations. Fe and OC were observed in these soils and this may indicate elevated anion exchange capacity that could affect sorption of PFAS (Jafvert, 1990; Ahrens et al., 2011a). However, based on the observations in this study for a limited selection of soil, none of these parameters had a clear effect on $f_{leached}$ levels.

It was possible to determine partitioning coefficients for soil samples with sorbent amendment (K_D (L/kg)) in some cases (Table 1), as sufficiently less PFOS was extracted in the batch leach test following sorbent amendment. One value of 8.8 L/kg could be calculated for the compost soil, one value of 8.2 L/kg could be calculated for the montmorillonite and values from 1889 ± 1126 to 16,940 ± 0.00 L/kg were calculated for AC. Soil + AC/water partitioning coefficients reported for three other Norwegian soils varied between 5888 L/kg and 37,154 L/kg, overlapping with the values measured here (Kupryianchyk et al., 2016). Jeon et al. (2011) investigated the sorption of PFOS to montmorillonite (in the absence of soil) and reported partitioning coefficients of 5–10 L/kg, agreeing with the values measured here for the soil-montmorillonite mixture.

The sorbent amendment materials used in this study likely exhibit different types of bonding mechanisms that allow PFAS to interact with them. Montmorillonite contains one octahedral silica sheet fused to two tetrahedral alumina sheets. Adsorption of PFOS to it has been ascribed to specific and non-specific electrostatic interactions. PFOS mainly forms outer-sphere surface complexes in addition to some interactions between the sulfonate group of PFOS and the hydroxyl group of montmorillonite through Ca^{2+} bridging and interlayer adsorption (Zhang et al., 2014; Zhao et al., 2014). AC has a high surface area and pore network providing a multitude of sorption sites for PFAS. Sorption has been postulated to occur via direct (specific) polar interactions, hydrophobic (non-specific) interactions and ion exchange mechanisms (Yu et al., 2009). Compost soil was expected to provide additional PFAS binding sites via the contribution of additional functional groups contained in organic matter (Schumacher et al., 2006). Evidentially, AC was the only amendment that resulted in a substantial increase in available sorption sites for PFOS.

3.5. *Modelling*

To illustrate the role of sorbent amendment as part of an overall remediation strategy, the 1D model described above was applied considering a status quo “no amendment” scenario where a K_D of 2.8 L/kg (corresponding to the sorption of Ottawa Sand, which is likely typical of the sandy soils in this area) and a C_{soil} of 54.5 μg/kg from location 10 (which is on the low end of the soils sampled in the area, and the maximum considered in the batch tests), were used leading to a corresponding C_{water} of 19.5 μg/L (calculated as $C_{water} = K_D/C_{soil}$). The results from this scenario were then compared to an AC amendment that was chosen to increase overall sorption to the soil + AC by a factor of 50 (corresponding to a K_D of 140 L/kg). In addition a substantial increase in water percolation in the soil (e.g. by installing sprinklers) was modelled by increasing the rainfall rate of 0.73 m/y to 7.3 m/y. These three scenarios were chosen as illustrative examples and results are presented in Fig. 3 for modelled changes in C_{soil} and C_{water} over time.

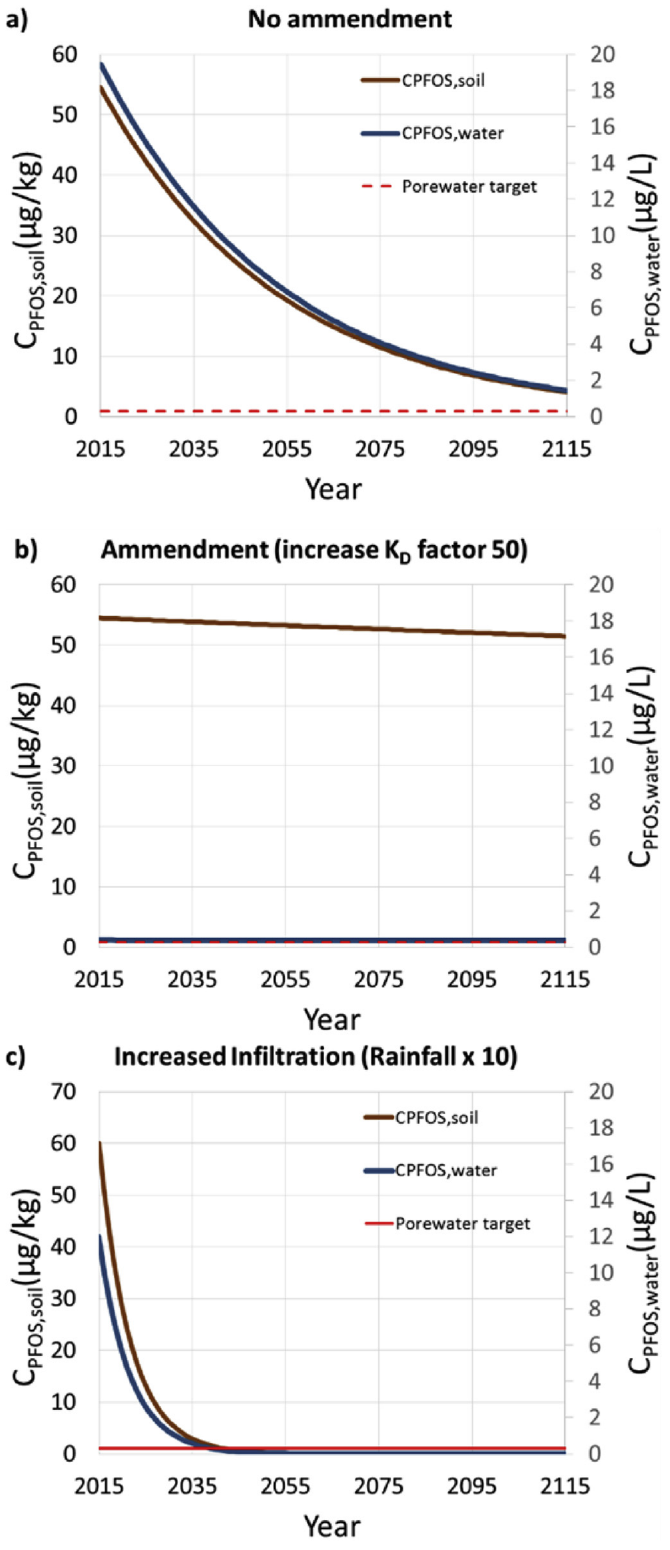

Fig. 3. 1D Model output scenarios for PFOS concentrations in soil and water over time for a) unamended Ottawa Sand (K_D 2.8 L/kg) containing a concentration of 54.5 µg/kg of PFOS; b) increased sorption by a factor 50 via an AC amendment, and c) increased soil percolation by a factor 10. The changes in water concentration are compared to an arbitrary water target, C_{water}, of 0.3 µg/L PFOS which has been recommended for use by the Norwegian Environmental Agency.

Also shown in Fig. 3 is an arbitrary water clean-up target of 0.3 µg/L. As evident from the baseline "no amendment" scenario, C_{soil} and C_{water} will only gradually decrease overtime, with C_{water} taking more than 100 years to decrease from 19.5 µg/L to the arbitrary target of 0.3 µg/L. Considering the AC amendment, C_{soil} will decrease even more slower over time, however the C_{water} will instantly decrease to just above the clean-up target at 0.4 µg/L. If the K_D was increased further for this scenario then the C_{water} would become even lower initially after amendment. Finally, removing PFOS from soil modelled by increasing the amount of water percolation lead to a more rapid decrease in both C_{soil} and C_{water} as compared to no amendment and the clean-up target is reached in just over 25 years.

This illustrates how sorbent amendment could serve as part of an overall remediation strategy. If the overall strategy was to contain and stabilise the PFOS contamination and diminish emissions from the contaminated area to the surrounding environment, sorbent amendment could be used. In addition, this result suggests that sorbent amendment would be suitable to decrease PFOS release from soil after *ex situ* soil washing or following the excavation of soil to a landfill. If the overall remediation strategy was focused on decreasing C_{soil} and thus removing PFOS from the area, flushing would be more effective and could be achieved by adding water to the soil. By flushing with water PFOS is removed from the soil to the water phase itself and so long as flushing is carried out in a controlled manner to allow all of the percolating contaminated water to be captured and treated, increased environmental emissions are prevented.

4. Environmental implications

Immobilisation of PFAS in soils provides one method to reduce the spreading of these hazardous pollutants to the surrounding aqueous environment and to be taken up by native organisms. Bioaccumulation of PFAS in organisms as well as spreading of PFAS to water bodies (which in some cases can be used for drinking water) must be avoided in order to protect human health. The efficiency of sorbent amendment to immobilise PFAS in an impacted sandy soil was investigated here by quantifying leaching of PFAS from soil before and after sorbent amendment using AC, montmorillonite and compost soil. Promising results suggest that immobilisation of PFAS in soil via the addition of a strongly sorbing material could be used as part of a wider remediation strategy. As well as sorbent amendment, other possible remediation methods such as chemical oxidation and soil washing can be considered (Vecitis et al., 2009). When using soil washing to reduce the concentration of PFAS in soil it is paramount that the water used to wash is also itself collected and treated in order to avoid additional environmental spreading.

Future laboratory work related to sorbent amendment will benefit from larger scale tests being carried out on undisturbed soil columns in order to obtain more information about the suitability of the method for field application. The batch tests presented here were carried out on soils that had lower concentrations of PFOS (up to 54.5 µg/kg); therefore, the effect of sorbent amendment for soils containing higher concentrations are not clear. Further testing of soils with higher PFAS concentrations will expand the application domain of sorbent amendment for complete PFAS immobilisation to other airport sites which are typically characterised by high concentrations of PFAS. Within this study AC had the highest sorption capacity for PFOS (and other PFAS) and resulted in an up to 99.9% reduction in leaching and K_D values up to 16,940 L/kg. When selecting a material to use in sorbent amendment, remediation efficacy is not the only variable to be considered. Availability of materials, cost of material and the amendment itself, the long term treatment efficiency and the wider environmental effect of the process must be investigated. The longevity of AC in soil, both with respect to degradation of the AC itself and subsequent release of sorbed PFAS must be investigated. The use of tools such as life cycle analysis and cost benefit analysis in order to compare different methods have an important role in site remediation decisions.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.chemosphere.2016.12.057.

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