Column experiments to investigate the fate of per- and polyfluoroalkyl substances (PFASs) in the subsurface during soil stabilization with colloidal activated carbon

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Abstract Remediation of sites contaminated with per- and polyfluoroalkyl substances (PFASs) is key to reduce the contamination of drinking water sources and subsequent human exposure. PFAS production and use is increasingly being restricted worldwide, however, legacy contamination plumes in soil and groundwater system are still posing a threat due to their persistence against degradation. One of the most widely studied soil remediation techniques for PFASs is stabilisation, which results in the long-term entrapment of the contaminants with the addition of fixation agents in the subsurface, aiming to prevent their leaching from soil to groundwater. In relation to this, the aim of this study was to identify the leaching behaviour of PFASs in a treatment scenario using activated carbon. Results have shown significantly increased sorption of PFASs in soil amended with activated carbons compared to untreated soil. Additionally, there was a positive correlation between the length of the perfluorocarbon chain and sorption efficiency. The study is a step towards increasing our understanding on the efficiency and longevity of stabilisation with activated carbons as a remediation strategy for PFAS-contaminated soils and groundwater.
Keywords: PFAS, adsorption, contamination, remediation, groundwater

1. Introduction

Per- and polyfluoroalkyl substances (PFASs) are fluorinated surfactants with unique properties that have found applications in many commercial and industrial products, such as in aqueous film-forming foams (AFFF) (Buck *et al.*, 2011). Their extensive use over decades has resulted in widespread environmental distribution (Zhao *et al.*, 2012). Meanwhile, toxic effects such as carcinogenicity have been reported (ATDSR, 2018), while for most compounds the human health effects are still unknown (Sinclair, Long and Jones, 2020). Production and use of PFASs are increasingly being restricted, however, legacy plumes in soils can act as reservoirs from which PFASs can leach, eventually reaching drinking water sources (Ahrens *et al.*, 2014).

A variety of treatment techniques exists for treatment of PFAS-contaminated soils, however, stabilization is considered as the most promising to-date (Ross *et al.*, 2018). Stabilisation is typically achieved through amendment of soils with sorbents, such as activated carbons, on which the species can adhere through hydrophobic and electrostatic interactions (Cousins *et al.*, 2016). For PFASs, affinity to granular (GAC) and powdered activated carbons (PAC) has been well documented in the past 15 years, with reported adsorption capacities q_m in the range of $41 - 560$ mg g^{-1} (Ochoa-Herrera and Sierra-Alvarez, 2008; Yu *et al.*, 2009; Zhang *et al.*, 2016). The vast majority of experimental studies on PFAS adsorption is typically conducted through batch shaking tests. However, miscible displacement column studies can provide more realistic information, as well as providing information on the longevity of the process. A recent study comparing adsorption of perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) to soil using column and batch tests, has demonstrated similar results with both methods (Van Glubt *et al.*, 2021). Still, column tests can improve our mechanistic understanding of the process. Guelfo *et al.* (2020) recently observed that equilibrium sorption parameters are not enough to fully understand 1-D transport of PFASs, but rate-limited sorption should be considered.

Considering the above, the aim of the present study was to evaluate the impact of stabilization with colloidal activated carbon (CAC) on the transportation of PFASs in soil column experiments, as well as to assess the longevity of the method.

2. Methods

2.1. Soil sampling and preparation

Silt loam soil sampled from central Sweden at a depth of ~3 m was used for the experiments. After sampling, soil was air-dried for 10 days, then grounded by mortar, sieved (<2 mm) and homogenised by shaking. The soil was mixed with silica sand at 0.2 soil:sand. Treatment of soil with soil stabilization was tested by mixing soil with colloidal activated carbon (CAC, ®PlumeStop, 1–2 μm) at 0.1% w/w.

2.2. Column experiments

The 1-D transport of PFASs was investigated in PVC columns (L = 15.5 cm, d = 1.85 cm). In total, four column experiments were conducted following guidelines from Lewis and Sjöstrom (2010), with treated soil and untreated soil tested in duplicates (table 1). Water-saturated soil (~300 g dry weight (dw)) was packed in thin layers, ensuring that no air bubbles were trapped. Water flow was directed upwards to facilitate the escape of any residual air bubbles. The uniformity of the packing was validated through non-reactive tracer tests (sodium chloride (NaCl), 0.43 M). Spiked artificial groundwater was prepared with a mixture of 12 PFASs, at a total concentration of 0.8 mg L^{-1}. Major salts which were found in the field (magnesium sulphate $MgSO_4$, calcium chloride $CaCl_2$, calcium carbonate $CaCO_3$) were added to the feed solution to mimic the composition of the natural groundwater at the sampling site. The desorption behaviour after treatment was investigated, by switching the inflow from contaminated to clean water after steady state was achieved. Sacrificial samples were taken from the outlet bi-weekly during the experiments and were stored at -18 °C until analysis.

**Table 1.** Overview of experiments and operational parameters.

Column	Matrix	$C_{\sum 12PFASs}$	Flow rate	pH
A_1	Treated soil	0.8 (mg L^{-1})	288 (mL d^{-1})	7.7
A_2	Treated soil			
B_1	Untreated soil			
B_2	Untreated soil			

2.3. PFAS analysis

Analysis of PFASs was conducted using ultra high-performance liquid chromatography coupled with tandem mass spectrometry (UHPLC-MS/MS) (Quantiva TSQ; Thermo Fischer Scientific, USA) (for details see (Sörengård et al., 2021). Water samples were directly injected after centrifugation (3000 rpm, 15 min) and filtrated through a 0.45 μm recycled cellulose (RC) filter. The target PFASs were: C_4-C_{10} PFCAs (PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA), C_4, C_6, and C_8 PFSAs (PFBS, PFHxS, PFOS), and 6:2 and 8:2 fluorotelomer sulfonic acids (FTSAs). 16 isotopically labeled internal standards (ISs) were used for PFAS quantitation. Negative blanks and positive control samples were included in the analysis.
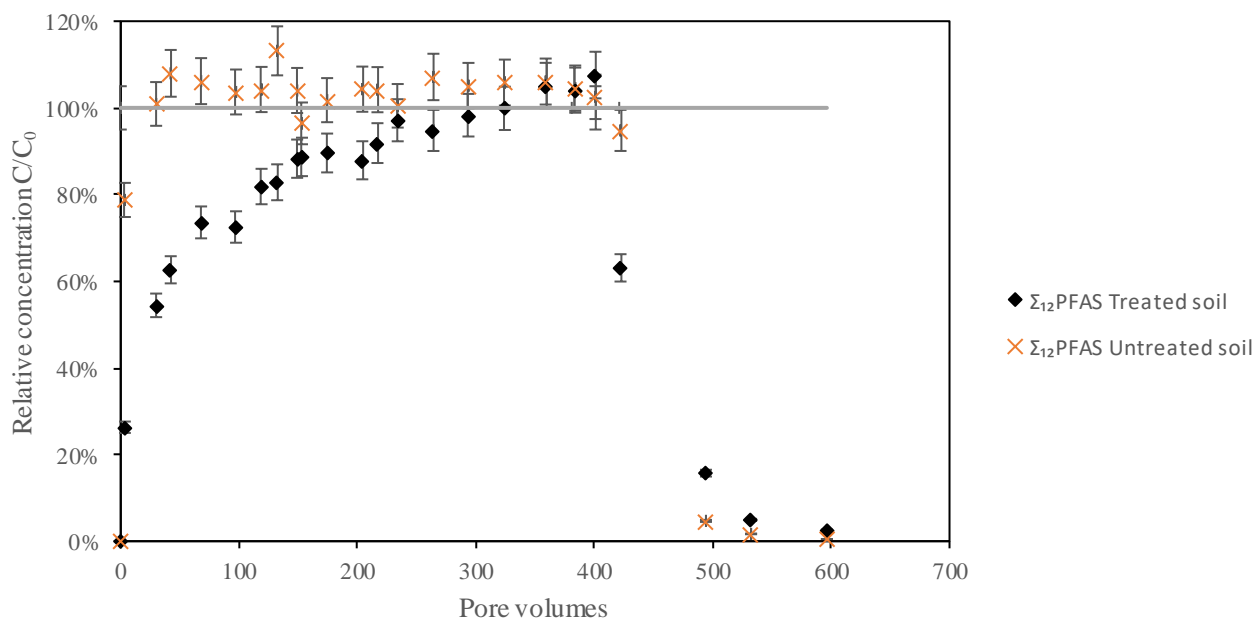
Figure 1. Column breakthrough curves for the sum of 12 PFASs. C/C₀=1 corresponds to same concentration in the outlet as in the inlet. Error bars indicate methodological error as the standard deviation from duplicate columns. After 400 pore volumes inflow switched to non-contaminated water, for testing desorption of PFASs.
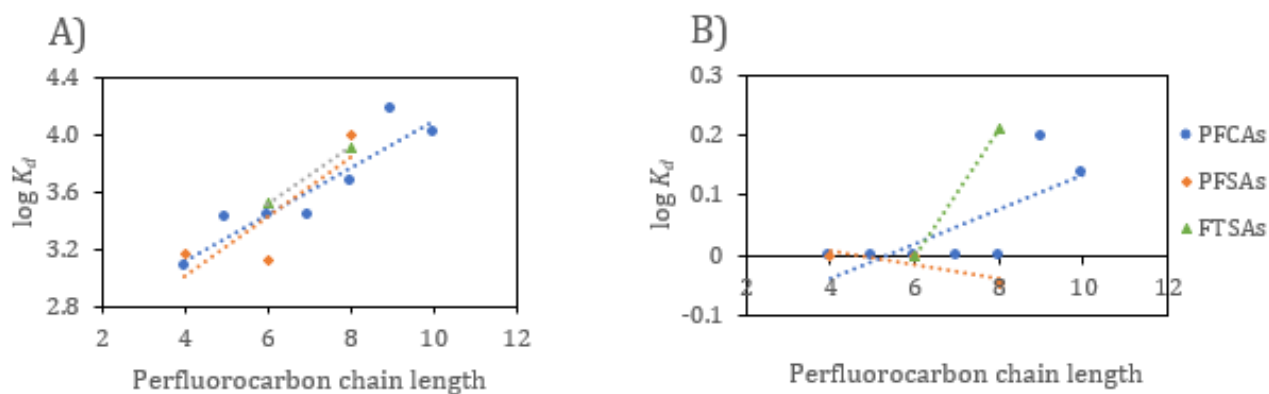
Figure 2. K_d values between soil and aqueous phase based on chain length of PFCAs, PFSAs and FTSAs for A) the CAC fraction (columns A1, A2) and B) for the soil (columns B1, B2)

3. Results and discussion

Sorption behaviour differed between non-treated and treated soil columns. As shown in **Figure 1**, complete breakthrough was much faster in the untreated soil (after 30 PV) than in the treated soil columns (after 233 PV) for $\sum_{12}$PFASs. The retardation was approximately 8 times higher for $\sum_{12}$PFASs in the CAC-treated soil compared to the untreated soil. For the final desorption part of the experiments (after 400 PV), the tail of the breakthrough curves showed a similar behaviour for both setups, however, the drop in concentrations was steeper for the treated soil. This showed strong adherence of PFASs to CAC, reducing the rate of their leaching into groundwater. Still, the outlet water reached a concentration of 0 for the $\sum_{12}$PFASs at the same time for both the treated and untreated soil. For individual compounds, the differences were more noticeable. Specifically, short-chain PFASs leached faster than long-chain ones, which can be attributed to the higher water solubility in comparison to the long-chain PFASs. To further investigate the effect on individual PFASs, soil-water partitioning coefficients (K_d values) were calculated with the use of retardation factors as $K_d = (R_f - 1) * n_{eff}/\rho$, where:

$R_f = t_{80,tracer\_test}/t_{80,column\_test}$: retardation faction

n_{eff}: effective porosity (0.3)

ρ: bulk density (2.02 g cm^{-3})

The K_d values were positively correlated with the carbon chain length of the compounds (**Figure 2**), increasing an order of magnitude from C_4 to C_{10} PFCAs, both for CAC and soil. K_d values were higher than previously reported in batch tests of PFAS sorption to CAC (Sörengård, Kleja and Ahrens, 2019). Also, no retardation was noticed for most PFASs for the untreated soil, when compared to the non-reactive tracer. Only long-chain PFASs (PFDA, PFUnDA, PFOS, 8:2 FTSA) showed signs of retardation in soil. Longer contact times could result in higher sorption of short-chain PFASs. Aging of PFASs in soil is reportedly an important factor when it comes to sorption of contaminants to soil and should be considered for

CAC as well (Alexander, 2000). However, competition effects with long-chain PFASs should be considered in the long-term.

Additionally, K_d was many orders of magnitude higher for CAC than for soil, showing that the sorbent was largely responsible for the retardation of PFASs. Higher dosage of CAC could therefore possibly result in higher adsorption efficiency, as the number of sorption sites would increase, potentially extending the longevity of the treatment. For other organic contaminants, such as polychlorinated buphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs), carbon dosage has been shown to not only significantly increase the remediation efficiency, but also to reduce their bioaccumulation potential (Zimmerman *et al.*, 2005). Such aspects should be taken into account when estimating the efficiency of a treatment barrier. Further research steps should therefore focus on identifying the effect of available sorption sites on the adsorption of PFASs and their toxicity, as well as on potential effects of major groundwater constituents, such as dissolved organic carbon (DOC).

4. Conclusions

The efficiency of using stabilization as a treatment approach for PFAS-contaminated soils was validated. Treatment of soil with 0.1% w/w CAC resulted in 8 times higher retardation of PFASs compared to reference soil and desorption of the compounds was not significant for treated soil. K_d values for CAC were shown to be higher than relevant batch tests for CAC have shown and there was a positive correlation between chain length and K_d.

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