

# SORPTION AND LEACHING OF PER- AND POLYFLUOROALKYL SUBSTANCES IN SOIL

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## Introduction

Per- and polyfluoroalkyl substances (PFASs) have received increasing public attention due to their persistence, bioaccumulative potential, and possible adverse effects on humans and wildlife. As a consequence, perfluorooctane sulfonate (PFOS) and its precursors have been added to the persistent organic pollutants (POPs) list of the Stockholm Convention in May 2009, resulting in global restrictions on its use and production.<sup>1</sup> After the voluntary phase-out of PFOS, the production shifted to shorter-chained PFASs and PFAS precursors.<sup>2,3</sup> PFAS precursors can be degraded under aerobic and anaerobic conditions to perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs) which are the final degradation products and extremely persistent in the environment.<sup>4</sup>

The usage of PFAS-containing aqueous fire fighting foams (AFFFs) at fire training facilities has been linked to the contamination of the environment with PFASs.<sup>5-8</sup> PFOS and 6:2 fluorotelomer sulfonic acid (FTSA) were the dominant PFASs detected at AFFF contaminated sites with maximum concentrations in the  $\mu\text{g L}^{-1}$  to  $\text{mg L}^{-1}$  range for fresh water and groundwater.<sup>6-8</sup> The short-chain PFSAs and PFCAs are potentially more water soluble, whereas long-chain PFSAs and PFCAs seem to bind more strongly to particles.<sup>9,10</sup> However, there is a lack of knowledge about the mobility and transport processes of PFASs in the hydrosphere. Furthermore, a better understanding of the sorption and leaching processes of PFASs in contaminated soil is required to assess the potential risks of PFASs to be released to fresh water and groundwater.

The aims of this study were *i*) to examine the soil-water partitioning of PFASs in laboratory batch experiments, *ii*) to assess their leaching behavior in soil column leaching experiments, and *iii*) to investigate their transport and mobility from contaminated soil to groundwater in the field.

## Materials and methods

The target analytes included C<sub>4</sub>–C<sub>14</sub>, C<sub>16</sub>, C<sub>18</sub> PFCAs (C<sub>n</sub>F<sub>2n+1</sub>COOH, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDODA, PFTriDA, PFTeDA, PFHxDA, PFOcDA), C<sub>4</sub>, C<sub>6</sub>, C<sub>8</sub>, C<sub>10</sub> PFSAs (C<sub>n</sub>F<sub>2n+1</sub>SO<sub>3</sub>H, PFBS, PFHxS, PFOS, PFDS), perfluorooctanesulfonamide (FOSA, C<sub>8</sub>F<sub>17</sub>SO<sub>2</sub>NH<sub>2</sub>), methyl and ethyl FOSAs (C<sub>8</sub>F<sub>17</sub>SO<sub>2</sub>N(C<sub>n</sub>H<sub>2n+1</sub>)H), methyl and ethyl perfluorooctane sulfonamidoethanols (FOSEs, C<sub>8</sub>F<sub>17</sub>SO<sub>2</sub>N(C<sub>n</sub>H<sub>2n+1</sub>)CH<sub>2</sub>CH<sub>2</sub>OH), perfluorooctanesulfonamidoacetic acid (FOSAA, C<sub>8</sub>F<sub>17</sub>SO<sub>2</sub>N(H)CH<sub>2</sub>CO<sub>2</sub>H), methyl and ethyl FOSAAAs (C<sub>8</sub>F<sub>17</sub>SO<sub>2</sub>N(C<sub>n</sub>H<sub>2n+1</sub>)CH<sub>2</sub>CO<sub>2</sub>H), and 6:2 FTSA (C<sub>6</sub>F<sub>13</sub>CH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub>H) plus 16 isotopically-labeled internal standards (IS).

Soil samples were collected from various locations at fire training facilities in the Stockholm-Uppsala region, and Gothenburg in Sweden. The soil samples were characterized in terms of the soil texture, water holding capacity (pore volume), total organic carbon (TOC), cation exchange capacity (CEC), and pH. In addition, groundwater samples were collected in Uppsala to investigate the transport processes of PFASs to groundwater.

Laboratory batch sorption tests were performed by mixing 5 g of soil with 40 mL Millipore water in 50 mL polypropylene (PP) tubes to achieve a liquid to solid ratio of 8. In order to determine the sorption equilibrium time for individual PFASs, an equilibrium test was conducted over 360 h. Both spiked (0.05 mL PFASs standard mix of 80 ng mL<sup>-1</sup>) and non-spiked samples were shaken using a wrist-action shaker at 200 rpm until soil-water equilibrium was reached for the PFASs. After the shaking, the samples were centrifuged at 3000 rpm for 30 min and the supernatant and soil was analysed separately.

Soil column leaching experiments were performed by gravity under near-natural conditions using a polyvinylchloride column ( $\varnothing = 10$  cm, length = 20 cm) filled with 80 g sand (50-70 mm mesh particle size) at

the bottom and ~1400 g of soil. Both spiked (8 mL PFASs standard mix of 2 mg mL<sup>-1</sup> spiked to 1700 g soil) and non-spiked soil samples from PFAS-contaminated areas were used. In addition, the sorption behavior of PFASs was investigated using artificial soil with varying content of black carbon (BC, 2%, 9%, 17%) and TOC (3%, 4%, 6%). The leaching experiments were performed using artificial water (0.01 M CaCl<sub>2</sub> in deionized water) with a continuous flow (approximately one drop per five seconds, by gravity) over a period of up to 46 days. The leachate was collected in 1 L PP bottles and the leachate samples from different time points and soil samples (initial and end concentrations) were analysed for PFASs.

An isotopically-labeled IS mix was spiked to the samples before extraction. The water samples were extracted by solid phase extraction (SPE) using Oasis WAX cartridges (6 cc, 150 mg, 30 μm, Waters) as described previously.<sup>11</sup> The extraction of the soil samples was carried out using solid-liquid extraction as described previously.<sup>10</sup> Duplicate samples, positive control, laboratory and field blanks were included for quality control. All extracts were analysed using high-performance liquid chromatography coupled with tandem mass spectrometry (HPLC-MS/MS) (for details see Ahrens et al. (2009)<sup>11</sup>).

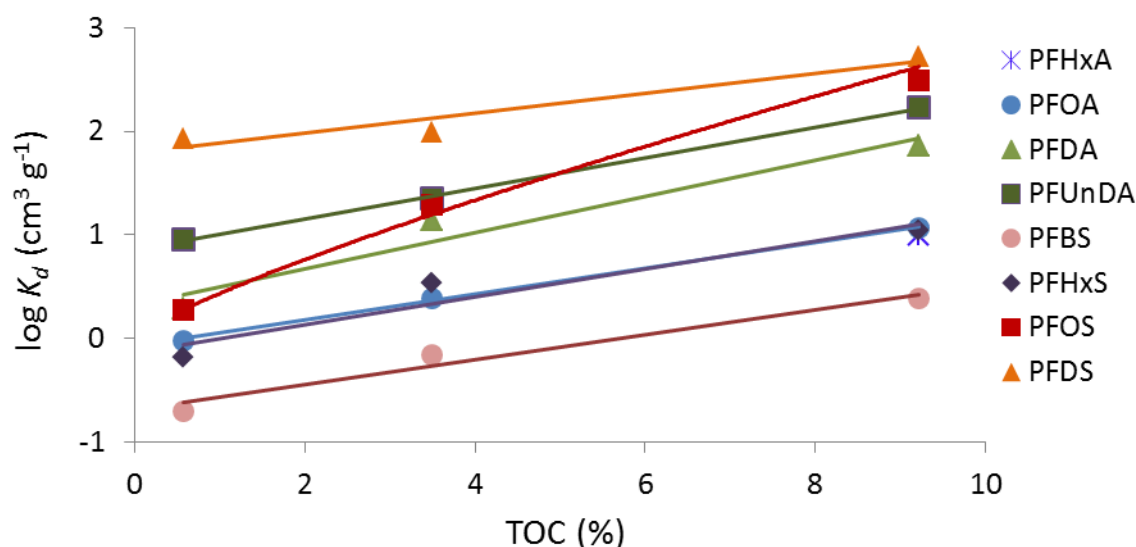
### Results and discussion

The results from the equilibrium tests showed that 48 h of shaking of the spiked soil samples was sufficient for all PFASs. However, the non-spiked soil from PFASs contaminated areas reached equilibrium after 240 h. This indicates that PFASs bind more strongly to aged soil compared to freshly spiked soil. Hence, the strong sorption of PFASs to aged soil can result in lower bioavailability and slower wash out processes into the aqueous environment.

The soil-water partitioning coefficient ( $K_d$ , cm<sup>3</sup> g<sup>-1</sup>) can be used to predict the fate and behavior of a chemical in the hydrosphere and was calculated using Eq. 1.

$$K_d = c_{\text{soil}}/c_{\text{water}} \quad (1)$$

where  $c_{\text{soil}}$  is the concentration of chemical in soil (ng g<sup>-1</sup> dry weight (dw)) and  $c_{\text{water}}$  is the concentration of the target analyte in water (ng cm<sup>-3</sup>). A significant positive correlation was found between the  $K_d$  value for individual PFASs and the TOC content in soil ( $p < 0.05$ , Pearson Correlation) (Figure 1). This indicates that the adsorption mechanism involves an interaction between the respective PFASs and organic carbon content. Furthermore, black carbon in soil and concentrations of Ca<sup>2+</sup> ions had an influence on the sorption behavior of PFASs.

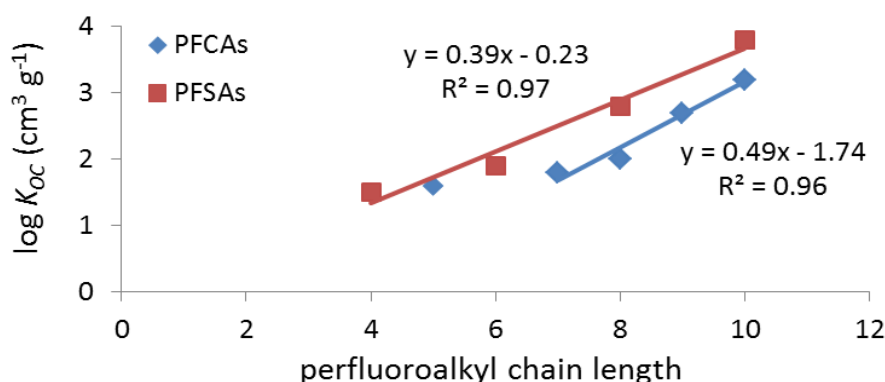


**Figure 1.** Correlation between log  $K_{OC}$  values (cm<sup>3</sup> g<sup>-1</sup>) and TOC (%).

In order to normalize the  $K_d$  values to organic carbon, the organic carbon normalized solid-water distribution coefficient ( $K_{oc}$ ,  $\text{cm}^3 \text{g}^{-1} \text{OC}$ ) was calculated using Eq. 2.

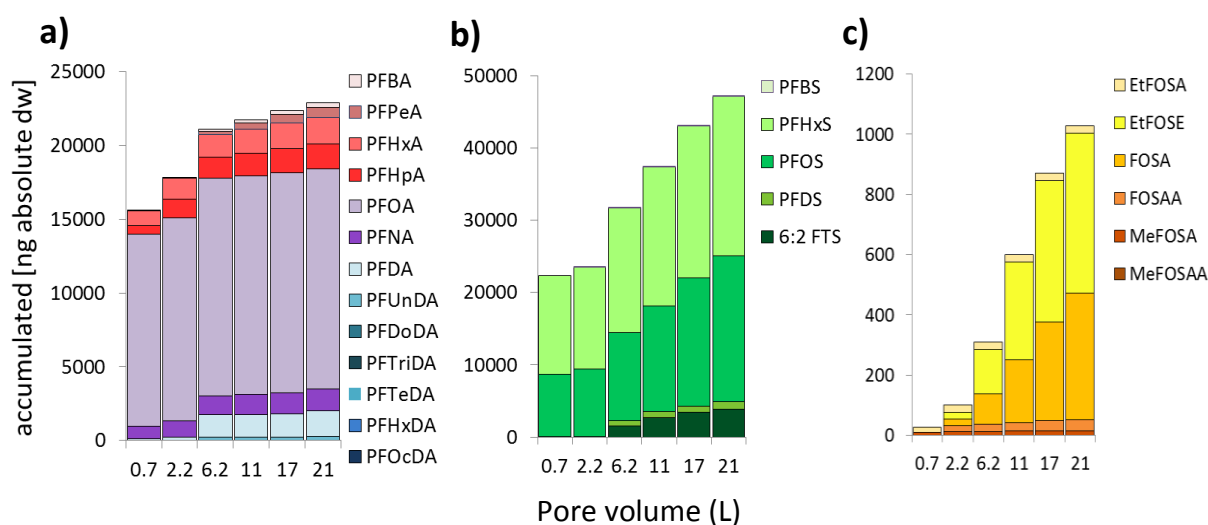
$$K_{oc} = K_d / f_{OC} \quad (2)$$

where  $f_{OC}$  is the fraction organic carbon in soil. The  $\log K_{oc}$  values were plotted against the  $\text{CF}_2$  chain length (Figure 2) to examine the influence of chain length and functional group on the partitioning between water and soil for individual PFASs. The highest average  $\log K_{oc}$  ( $n = 16$ ) was found for PFDS ( $\text{CF}_2 = 10$ ) with  $3.8 \pm 0.3 \text{ cm}^3 \text{g}^{-1}$ , whereas the average  $\log K_{oc}$  for the shorter chain PFBS ( $\text{CF}_2 = 4$ ) was only  $1.5 \pm 0.2 \text{ cm}^3 \text{g}^{-1}$ . For the PFCAs, the  $\log K_{oc}$  decreased from an average of  $3.2 \pm 0.2 \text{ cm}^3 \text{g}^{-1}$  for PFUnDA ( $\text{CF}_2 = 10$ ) to an average of  $1.6 \pm 0.3 \text{ cm}^3 \text{g}^{-1}$  for PFHxA ( $\text{CF}_2 = 5$ ). In general, the  $\log K_{oc}$  values increased by 0.1–0.7 log units for each additional  $\text{CF}_2$  moiety. In addition, the  $\log K_{oc}$  values of PFASs were 0.6–0.8 log units higher compared to the  $\log K_{oc}$  values of PFCAs.



**Figure 2.** Average  $\log K_{oc}$  values ( $\text{cm}^3 \text{g}^{-1}$ ) for PFCAs and PFASs plotted as a function of  $\text{CF}_2$  chain length. The average  $\log K_{oc}$  values were calculated from concentrations of PFASs detected in soil and water for spiked soils 1, 2 and 3 and field contaminated soils C1, C2, C3 and C4 ( $n = 16$ ).

The soil column leaching experiment showed that the chain length of PFASs has an influence on the sorption to soil (Figure 3). PFCAs ( $\text{C}_7$ – $\text{C}_9$ ) had a weaker sorption to soil than PFCAs with a carbon chain length of  $\text{C} \geq 10$ . Furthermore, PFHxS ( $\text{C}_6$ ) had a weaker sorption to soil compared to the longer chained PFOS ( $\text{C}_8$ ). For the PFAS precursors, the leaching occurred in the natural soil samples in the following order of EtFOSA < MeFOSA < FOSA < FOSAA.



**Figure 3.** Accumulated leaching concentrations for a) PFCAs, b) PFASs and c) FOSAs/FOSEs/FOSAA for the soil column leaching experiments.

Alkylated FOSAs such as EtFOSA and MeFOSA desorbed easier than the non-alkylated FOSA. In general, FOSAs can dissociate an acidic amide H in the presence of bases and form amide anions. Since water can serve as a base, FOSAs exist as amide anions in moist soils. Electrostatic interactions between amide anions and cations in the soil lead to ion binding and sorption to the soil. Moreover, FOSAA has an additional possibility to dissociate the carboxylic H-atom, which is more acidic than the amide H-atom and could be the reason for the constant leaching out of FOSAA. Alkylated FOSAAAs, such as EtFOSAA and MeFOSAA, eluted in very low concentrations, consequently they are not presented here. Overall, the leaching experiments simulated a precipitation time period of 20 months for Gothenburg (in total 11123 mm) and 53 month for Stockholm (in total 2194 mm). The results showed a high mobility for the shorter chain PFASs, and thus they tend to be more mobile and prone to leach out to fresh water or groundwater systems. Similar leaching behavior of PFASs has been observed in the field. Overall, once released to soil, PFASs are subject to partitioning and transport processes, and pose a potential threat for the aquatic environment such as human drinking water reservoirs.

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