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Sorption of perfluoroalkyl substances (PFASs) to an organic soil horizon – Effect of cation composition and pH

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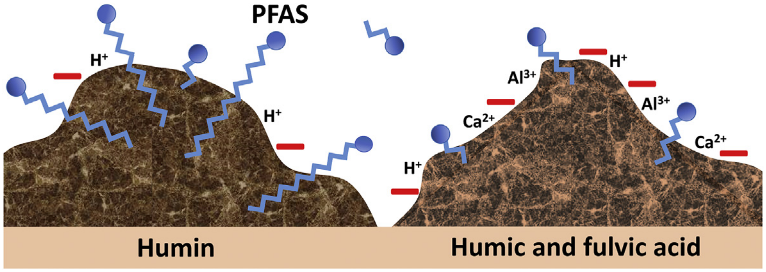
HIGHLIGHTS

- Sorption of PFASs of C_5 or longer depends on the pH or on the SOM bulk net charge.
- For C_5–C_8 PFCAs, SOM bulk net charge is strongly related to sorption.
- For longer-chained PFASs, pH is a better predictor of sorption.
- Cation effects are evident only for shorter-chained PFASs.
- Longer-chained PFASs probably bind preferentially to the humin fraction of SOM.

GRAPHICAL ABSTRACT



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ABSTRACT

Accurate prediction of the sorption of perfluoroalkyl substances (PFASs) in soils is essential for environmental risk assessment. We investigated the effect of solution pH and calculated soil organic matter (SOM) net charge on the sorption of 14 PFASs onto an organic soil as a function of pH and added concentrations of Al^{3+}, Ca^{2+} and Na^{+}. Often, the organic C-normalized partitioning coefficients (K_{OC}) showed a negative relationship to both pH ($\Delta\log K_{OC}/\Delta pH = -0.32 \pm 0.11$ log units) and the SOM bulk net negative charge ($\Delta\log K_{OC} = -1.41 \pm 0.40$ per log unit $mol_c\ g^{-1}$). Moreover, perfluorosulfonic acids (PFSAs) sorbed more strongly than perfluorocarboxylic acids (PFCAs) and the PFAS sorption increased with increasing perfluorocarbon chain length with 0.60 and 0.83 log K_{OC} units per CF_2 moiety for C_3–C_{10} PFCAs and C_4, C_6, and C_8 PFSAs, respectively. The effects of cation treatment and SOM bulk net charge were evident for many PFASs with low to moderate sorption (C_5–C_8 PFCAs and C_6 PFSA). However for the most strongly sorbing and most long-chained PFASs (C_9–C_{11} and C_{13} PFCAs, C_8 PFSA and perfluorooctane sulfonamide (FOSA)), smaller effects of cations were seen, and instead sorption was more strongly related to the pH value. This suggests that the most long-chained PFASs, similar to other hydrophobic organic compounds, are preferentially sorbed to the highly condensed domains of the humin fraction, while shorter-chained PFASs are bound to a larger extent to humic and fulvic acid, where cation effects are significant.

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1. Introduction

Perfluoroalkyl substances (PFASs) have been produced in large quantities for use in a variety of consumer products and industrial applications since the 1950s (Cousins et al., 2016). However, in recent years they have been recognized as environmental contaminants of global concern due to their persistency (Houtz et al., 2013), bioaccumulative potential (Conder et al., 2008) and toxicity (Giesy et al., 2010; Apelberg et al., 2007). PFASs have been found ubiquitously in the environment (Zareitalabad et al., 2013; Ahrens, 2011), and are taken up by organisms including humans (Giesy and Kannan, 2001; Yeung et al., 2006). The environmental behavior of PFASs differs from other persistent organic pollutants (POPs) due to their extreme surface-active properties (Goss and Bronner, 2006) characterized by their hydrophobic (oleophobic) poly- or perfluorinated carbon chain (tail) in combination with the hydrophilic, usually anionic, functional head group. Thus, in contrast to other, non-ionic, POPs, for which the environmental behavior is well predicted solely by their hydrophobic or lipophilic properties, the behavior of the PFASs is governed not only by hydrophobic (oleophobic) but also by electrostatic interactions (Higgins and Luthy, 2007). Due to this complexity of PFAS chemistry, sorption of these substances cannot be predicted from a single sorbent bulk property such as for example organic carbon (OC) content (Barzen-Hanson et al., 2017; Li et al., 2018) and there are still significant uncertainties as regards how various sorbent-specific properties, such as for example pH and surface-bound cations, interact to determine the binding of PFASs to soils (Li et al., 2018). Accordingly, up to date there is a lack of standard protocols to assess the soil chemical properties of PFASs.

Organic matter is known to be an important sorbent for PFASs in soils (Milinovic et al., 2015) and sediments (Higgins and Luthy, 2006). However, the number of studies on PFAS sorption to “pure” phases of soil organic matter (SOM) is scarce. Moreover, studies on sorption in soils have usually included only a limited number of PFASs (e.g. Milinovic et al., 2015). Furthermore, there is still a lack of knowledge as for what fractions of SOM may be important for binding of PFASs. Zhang et al. (2015) reported that the humin fraction accounted for most of the sorption by comparing perfluorooctane sulfonate (PFOS) sorption to untreated soils with that of sodium hydroxide (NaOH)-treated soils. Humic (HA) and fulvic acids (FA) were found to be less important, presumably because of their higher charge, hydrophilicity and polarity (Zhang et al., 2015). However, this contrasts with the results of Zhao et al. (2014), who found that both the humin and the HA/FA fractions may be important for the sorption of PFOS and perfluorohexane sulfonate (PFHxS). Humin has been shown to be an important sorbent also for other hydrophobic organic compounds (HOCs) (Kohl and Rice, 1998; Han et al., 2013). For polycyclic aromatic hydrocarbons (PAHs) the humin fraction contributed more to binding than the HA/FA fraction (e.g. Gunasekara and Xing, 2003; Chen et al., 2017; Kang and Xing, 2005).

In general, the sorption of ionizable, anionic, organic contaminants is promoted by a decrease in pH and by an increase in solution cation concentration (Jafvert, 1990). For PFASs this has been confirmed by e.g. Higgins and Luthy (2006), Chen et al. (2009) and Zhang et al. (2013) concerning the effect of pH and Ca^{2+}, and by Wang et al. (2015) concerning the positive impact of Mg^{2+}, Fe^{3+} and Al^{3+}. However, no significant effect on sorption has been observed for monovalent cations such as Na^{+} and K^{+} (e.g. Higgins and Luthy, 2006; Wang et al., 2015). Under environmental pH values, natural organic matter (NOM) carries a negative net charge due to the presence of dissociated carboxylic and phenolic acid groups (Kinniburgh et al., 1999). Thus, in systems where NOM is present, the increased sorption of anionic organic compounds after adding multivalent cations can be understood in terms of a reduced negative electrostatic potential of NOM caused by cation complexation (Higgins and Luthy, 2006, 2007). The modeling work by Higgins and Luthy (2007) on sorption of PFASs to sediment in the presence of Ca^{2+} and Na^{+} suggested a strong relationship with the electrostatic Donnan potential for sediment organic matter.

The main objective of this study was to assess the effect of solution cation composition on the sorption of 14 PFASs onto SOM. The effect of the modeled bulk net charge of SOM was compared to that of pH, with the hypothesis that the bulk net charge would be the better predictor of PFAS sorption in the presence of variable concentrations of divalent and trivalent ions. In particular we examined the effect of Al^{3+} on PFAS sorption to an organic soil sample and compared it to the effects of Ca^{2+} and Na^{+}, as Al^{3+} has a high charge density (a high valence in combination with small ionic radius) and therefore a high propensity to form complexes with organic functionalities. Accordingly, we hypothesized that the effect of Al^{3+} on PFAS sorption would exceed those of Ca^{2+} and Na^{+}.

2. Materials and methods

2.1. Standards

Fourteen target PFASs (purchased from Sigma Aldrich) were analyzed including $C_3–C_{11}$ and C_{13} perfluoroalkyl carboxylates (PFCAs), C_4, C_6, C_8 perfluoroalkyl sulfonates (PFSAs) and perfluorooctane sulfonamide (FOSA) (Table 1). For quality control, 10 mass-labelled internal standards (ISs) (i.e., $^{13}C_4$-PFBA, $^{13}C_2$-PFHxA, $^{13}C_4$-PFOA, $^{13}C_5$-PFNA, $^{13}C_2$-PFDA, $^{13}C_2$-PFUnDA, $^{13}C_2$-PFDoDA, $^{18}O_2$-PFHxS, $^{13}C_4$-PFOS, $^{13}C_8$-FOSA, purity >99%, Wellington Laboratories, Guelph, ON) and one recovery standard ($^{13}C_8$-PFOA, purity >98%, Wellington Laboratories, Guelph, ON) were included.

2.2. Sample characteristics

A mor layer soil sample with pH(H_2O) of 4.8, containing 45% C, 1.3% N and 3.4% ash content on a dry weight (dw) basis, was used for the experiment. The sample (Risbergshöjden Oe) was collected in 2011 from a Spodosol in central Sweden (Risbergshöjden, 59°43′00″N 15°01′59″E), a site dominated by Scots Pine (*Pinus sylvestris*) vegetation. Soil from this site has been used in several previous studies on metal binding to SOM (Gustafsson and van Schaik, 2003; Gustafsson et al., 2007; Gustafsson et al., 2014), and was selected for our experiment as it is representative for northern latitude organic surface horizons, especially for those of coniferous forest. The sample was sieved (<2 mm) prior to homogenization, and then stored at +5 °C in its field-moist state with 69% water content until further use. The geochemically active concentrations of humic and fulvic acid, Al, Ca, Fe, K, Mg, Mn, Cr and Cu were determined by Gustafsson et al. (2014) and are shown in Table S1 in the Supporting Information.

2.3. Sorption batch experiment

Four batch sorption experiments were conducted using 50 mL polypropylene (PP) tubes (Corning®, nonpyrogenic) with 0.45 g sample (dry weight) to which nitrate (NO_3^-) salts of 10 mM Na^{+}, 3.0 and 5.0 mM Ca^{2+} or 2.0 mM Al^{3+} were added to obtain environmentally relevant ionic compositions within the range of previous studies (Chen et al., 2009; Higgins and Luthy, 2006). Additional sodium nitrate ($NaNO_3$) salt was added to the Ca^{2+} and Al^{3+} series to keep the NO_3^- concentration similar (~10 mM) in all series (for details see Table S2, Supporting Information). In addition, each batch experiment was carried out at four different pH values (3, 4, 5 and 6), which were reached using variable volumes of 20 mM nitric

Table 1
Target PFASs and field- and laboratory-derived soil/sediment organic carbon-normalized partitioning coefficients (log K_{OC}).

Substance	Acronym	Chemical formula (dissociated)	log K_{OC} [mL g^{-1}]
Perfluorobutanoate	PFBA	$C_3F_7COO^-$	1.88[f]
Perfluoropentanoate	PFPeA	$C_4F_9COO^-$	1.37[f]
Perfluorohexanoate	PFHxA	$C_5F_{11}COO^-$	1.31[f], 2.1[a]
Perfluoroheptanoate	PFHpA	$C_6F_{13}COO^-$	1.63[f], 2.1[a]
Perfluorooctanoate	PFOA	$C_7F_{15}COO^-$	1.89–3.5[b,c,d,e,f]
Perfluorononanoate	PFNA	$C_8F_{17}COO^-$	2.36–4.0[a,b,d,f]
Perfluorodecanoate	PFDA	$C_9F_{19}COO^-$	2.96–4.6[a,b,d,f]
Perfluoroundecanoate	PFUnDA	$C_{10}F_{21}COO^-$	3.3–5.1[a,b,d,f]
Perfluorododecanoate	PFDoDA	$C_{11}F_{23}COO^-$	5.6 ± 0.2[a]
Perfluorotetradecanoate	PFTeDA	$C_{13}F_{27}COO^-$	na
Perfluorobutane sulfonate	PFBS	$C_4F_9SO_3^-$	1.22[e], 1.79[f]
Perfluorohexane sulfonate	PFHxS	$C_6F_{13}SO_3^-$	2.05–3.7[a,d,f]
Perfluorooctane sulfonate	PFOS	$C_8F_{17}SO_3^-$	2.6–3.8[a,b,c,d,e,f]
Perfluorooctane sulfonamide	FOSA	$C_8F_{17}SO_2NH_2$[g]	4.2–4.5[c,d]

na = not available.
[a] Labadie and Chevreuil (2011).
[b] Higgins and Luthy (2006).
[c] Ahrens et al. (2011).
[d] Ahrens et al. (2010).
[e] Milinovic et al. (2015).
[f] Guelfo and Higgins (2013).
[g] Non-ionic species predominates within the investigated pH range ($pK_a = 6.52$ (Steinle-Darling and Reinhard, 2008)).

acid (HNO_3) or NaOH. The equilibrium solution chemistries of all soil suspensions were checked to ensure undersaturation with respect to $Al(OH)_3$ soil phases. The suspensions (40 mL) were spiked with 10 μL of a standard stock mixture of 14 PFASs dissolved in methanol (5 μg mL^{-1} of each substance), resulting in 111 ng of each substance per gram dry sample. All four samples in the four cation series were prepared in duplicate yielding in total 31 samples after removing one outlier from the subsequent data treatment. A horizontal 1D-shaker (Gerhardt) was used to equilibrate the suspensions for 7 days (168 h), which has been shown to be sufficient to reach equilibrium (Higgins and Luthy, 2006; Ahrens et al., 2011). After 7 days, the samples were centrifuged for 20 min at 3000 rpm, and the pH was measured in the supernatant using a GK2401C combined pH electrode (Radiometer Analytical).

The aqueous phase was analyzed for PFASs using high-performance liquid chromatography coupled to tandem mass spectrometry (HPLC-MS/MS) and the validated method is described elsewhere (Ahrens et al., 2015) and in the Supporting Information. The sorbed amount of each compound was calculated with the method of aqueous loss. Furthermore, all PFAS sorption was attributed to the organic carbon content of the soil ($f_{OC} = 45\%$) and sorption to mineral phases was thus assumed to be negligible.

2.4. Quality assurance and control

The method detection limits (MDLs) ranged from 0.07 ng L^{-1} (PFHpA, PFDA) to 1.01 ng L^{-1} (PFHxA) using a signal-to-noise ratio of 3. To minimize contamination, no fluorinated material (e.g. tetrafluoroethylene) was used in the experiments. All PFASs in the negative blank samples ($n = 2$) were below the respective MDLs. The recovery of the ISs (mean ± standard deviation) was on average 89 ± 12% and the relative errors between duplicates were generally <20%. Positive control blanks were prepared in duplicate using similar pH values, background ionic strength (10 mM $NaNO_3$) and dissolved organic carbon (DOC) levels (DOC from the same soil sample as used throughout the study) as obtained in the main sorption experiment. With the exception of the C_8–C_{11} and C_{13} PFCAs, recoveries in the positive control blanks ranged from 79% (PFBS) to 103% (PFHxA, PFOA), on average, where a recovery of 100% corresponded to a reference spike in Milli-Q water ($n = 2$) (Table S4 in the Supporting Information). As for the C_8–C_{11} PFCAs, average positive blank recoveries were higher than 100%, i.e. 130% (PFNA)–166% (PFDA), which is likely attributed to smaller losses to PP tube walls in the DOC-containing blanks as compared to the reference spikes prepared with only Milli-Q water. As for the most long-chained PFAS (i.e. C_{13} PFTeDA) however, blank recoveries were low (on average, 15%), most likely due to analytical uncertainties. Applying a three-compartment equilibrium mass-balance (soil–water–PP tube) on the basis of the positive DOC-containing blanks indicated nevertheless that PP tube losses should not have influenced the results for PFTeDA in the sorption experiment to any significant extent, nor the results for any of the other compounds (data not shown). Thus, losses to PP tubes were assumed to be negligible in the sorption experiment.

2.5. Modeling of organic matter bulk net charge

Visual MINTEQ ver. 3.1 (Gustafsson, 2013), with the Stockholm Humic Model (SHM) (Gustafsson, 2001), was used to model the bulk net charge of SOM (Z^-, $mmol_c\ L^{-1}$) in the sorption experiment. Good performance of SHM for cation sorption has been demonstrated in previous modeling studies for soil from the same area (e.g. Gustafsson et al., 2014). A basic model assumption is that the sum of humic and fulvic acid constitute the proton and metal binding component of SOM, thus any contribution from the humin fraction is not explicitly accounted for. Thus, the bulk net charge of SOM is a function of the cation concentrations, solution pH, and the fraction of active humic and fulvic acid (Tipping and Woof, 1991; Löfgren et al., 2010). As an example, the net charge Z^- of humic and fulvic acids in a system with Ca^{2+} and Al^{3+} can be obtained from Eq. (1)

$$\left[Z^-\right] = \left[RO^-\right] - \left[ROCa^+\right] - \left[(RO)_2Al^+\right] \tag{1}$$

where RO^- is a deprotonated functional group (mainly carboxylic or phenolic), $ROCa^+$ represents a Ca^{2+} ion monodentately complexed by one functional group and $(RO)_2Al^+$ represents bidentate binding of an Al^{3+} ion by two functional groups. If additional cations are present, the surface net charge is still given as the sum of charge contributions from various species of SOM. Detailed information on the assumed complex configurations in the Stockholm Humic Model is discussed elsewhere (Gustafsson, 2001; Gustafsson and Kleja, 2005). Since $[RO^-]$ is usually greater than the sum of positive charge contributions, $[Z^-]$ will be a positive number as seen from Eq. (1). This number is henceforth referred to as the net (negative) charge.

The input to Visual MINTEQ was given as the geochemically active concentrations (Table S1 in the Supporting Information) (Gustafsson et al., 2014) along with measured pH, DOC and added concentrations of cations and NO_3^-, and simulated equilibrium concentrations of solid-phase organic complexes were obtained as output. Visual MINTEQ input and output data (Table S3 in the Supporting Information) along with modeling assumptions are described in the Supporting Information.

3. Results and discussion

3.1. Solid–liquid partitioning

Increasing binding strength with increasing perfluorocarbon chain length was observed for both PFSAs (C_4, C_6 and C_8) and PFCAs (C_3–C_{10}) (Figs. 1 and 2, Table 1) when accounting for the effect of pH and net charge on sorption. For the PFSAs and PFCAs, the increase in log K_{OC} per additional CF_2 moiety were 0.83 and 0.60 log units, respectively. Short-chained PFASs such as PFBA, PFPeA and PFBS were weakly sorbed (less than 10% on average), whereas long-chained PFASs (PFOS, FOSA, C_9–C_{11} and C_{13} PFCAs) were sorbed strongly (on average, 99–100%). The increased sorption with increased PFCA chain length is in agreement with previous results of Ahrens et al. (2010) and Higgins and Luthy (2006), who found suspended particulate matter and sediment partitioning coefficients to increase with 0.50–0.75 log units per CF_2 moiety. For the PFSAs, however, previous studies found an increase of 0.40–0.60 log units per CF_2 moiety, which is lower as compared to this study (Milinovic et al., 2015; Higgins and Luthy, 2006). The increased sorption upon increasing chain length is attributed to an increase in PFAS hydrophobicity with each CF_2 moiety. For the most long-chained PFASs (i.e. PFDoDA and PFTeDA), however, no increased sorption was observed upon increasing perfluorocarbon chain length (Fig. 2), which is in agreement with what was observed by Zhang et al. (2013). This observation might be explained by possible strong binding of the most long-chained PFCAs to DOC, which would decrease their observed K_{OC} values. Such an effect of DOC on sorption has for example been shown by Enell et al. (2016) with regard to high-molecular polycyclic aromatic compounds (PACs). Alternatively, the more or less equal average sorption among the C_9–C_{11} and C_{13} PFCAs could be attributed to steric hindrances originating from the increased rigidity reported for PFCA perfluorocarbon chains longer than C_{10} (Ellis et al., 2004).

PFSAs of a given perfluorocarbon chain length were sorbed more strongly than the corresponding PFCAs, with the exception of the analogs PFPeA and PFBS (Fig. 2), meaning that the presence of a sulfonate functional head group led to stronger sorption (by 0.72 log units, on average) than the presence of a carboxylic head group. This is in agreement with what was found in earlier research (Higgins and Luthy, 2006; Ahrens et al., 2009, 2010). Furthermore, the presence of an uncharged sulfonamide head group appeared to favor sorption, as FOSA was sorbed more strongly than its anionic analogs PFNA and PFOS, by, on average, 1.91 and 0.53 log units, respectively. This agrees with the order of sediment sorption observed by Ahrens et al. (2010, 2011).

3.2. Impact of pH and cations on sorption

Sorption increased with decreasing pH ($p \leq 0.05$) for 10 of 14 PFASs, i.e. for PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTeDA, FOSA and PFOS (Fig. 1). For these 10 PFASs, the mean decrease in log K_{OC} value per unit pH ($\Delta\log K_{OC}/\Delta pH$) was 0.32 ± 0.11 log units (Fig. S4a and Table S7 in the Supporting Information), which again is similar to that of 0.37 log units found by Higgins and Luthy (2006). Furthermore, the regressed log K_{OC}–pH slopes became somewhat steeper with increasing perfluorocarbon chain length and were calculated to decrease 0.04 log units per unit pH per CF_2 moiety ($p \leq 0.05$) (Fig. S4a, Supporting Information). Within the PFCA class, the Pearson r^2 values for the log K_{OC}–pH relationship increased consistently with perfluorocarbon chain length from C_3 PFBA ($r^2 = 0$) to C_8 PFNA ($r^2 = 0.68$). After a lower r^2 value for C_9 PFDA ($r^2 = 0.44$) the r^2 values for the C_{10}–C_{11} and C_{13} PFCAs were again higher ($r^2 = 0.76$–0.83) (Fig. 4). As for the PFSAs, however, sorption was poorly predicted by the pH value (Fig. 1, Fig. S3 and Table S8 in the Supporting Information).

For PFASs with intermediate chain length (i.e. C_5–C_8 PFCAs and PFHxS) the log K_{OC} increased with the addition of cations to the soil in the following order: Al^{3+} (2 mM) > Ca^{2+} (5 mM) > Ca^{2+} (3 mM) = Na^+ (10 mM) (paired Student's *t*-test, Fig. 1, Table S9 in the Supporting Information). Moreover, for the C_5–C_8 PFCAs, the effects on sorption due to different cation treatments were more pronounced at higher pH as compared to lower pH values. These effects are consistent with the observations of Higgins and Luthy (2006) and Zhang et al. (2013) (effect of $Ca^{2+} > Na^+$), and Wang et al. (2015) ($Al^{3+} > Ca^{2+} > Na^+$). Except for stronger sorption in the Al^{3+} treatment, there was no clear effect of either the pH value or added cations for two of the three shortest PFASs, i.e. PFBA (C_3) and PFBS (C_4). By contrast, for the most long-chained PFASs (i.e. C_9–C_{11} and C_{13} PFCAs, PFOS and FOSA), there were few statistically significant effects of the added cations on the observed sorption (Table S9, Supporting Information). In other words, the strong effects of added cations that were seen for the PFASs of intermediate length were not seen for the substances with the longest chain lengths.

3.3. Impact of modeled SOM bulk net charge on sorption

The calculated SOM bulk net charge increased with increasing pH (Fig. 3), with the largest relative increase for the Na^+ (10 mM) treatment and the smallest for the Ca^{2+} (5 mM) treatment, while the Ca^{2+} (3 mM) treatment showed intermediate behavior. The Al^{3+} (2 mM) treatment yielded the lowest bulk net charge at pH < 5 due to strong complexation with humic and fulvic acid.

For 11 of the 14 investigated PFASs (i.e. PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTeDA, FOSA, PFHxS and PFOS) sorption increased with decreased SOM net negative charge ($p \leq 0.05$) (Fig. 1), with a mean decrease of 1.41 ± 0.40 log units for log K_{OC} per log unit $mol_c\ g^{-1}$ (Fig. S4b and Table S8 in the Supporting Information). For the three most short-chained PFASs (i.e. PFBA, PFPeA and PFBS), however, no significant relationship was found (Fig. 1). For PFHxS, addition of Al^{3+} resulted in an increase of sorption of ≥1 log unit as compared to the other cation treatments (Fig. 1), which was larger than expected with respect to the simulated net charge (Fig. 1). The reason for this is not known. For example, it is not likely that sorption increased as a result of Al^{3+} bridging between the sulfonate head group and the sorbent, due to the significant electron-withdrawing properties (low nucleophilicity) of organofluorine sulfonate groups (Lawrance, 1986).

The relationship between PFAS sorption and the SOM bulk net charge can be compared to the relationship with the pH value (Fig. 4, Fig. S3 in the Supporting Information). For short-chained

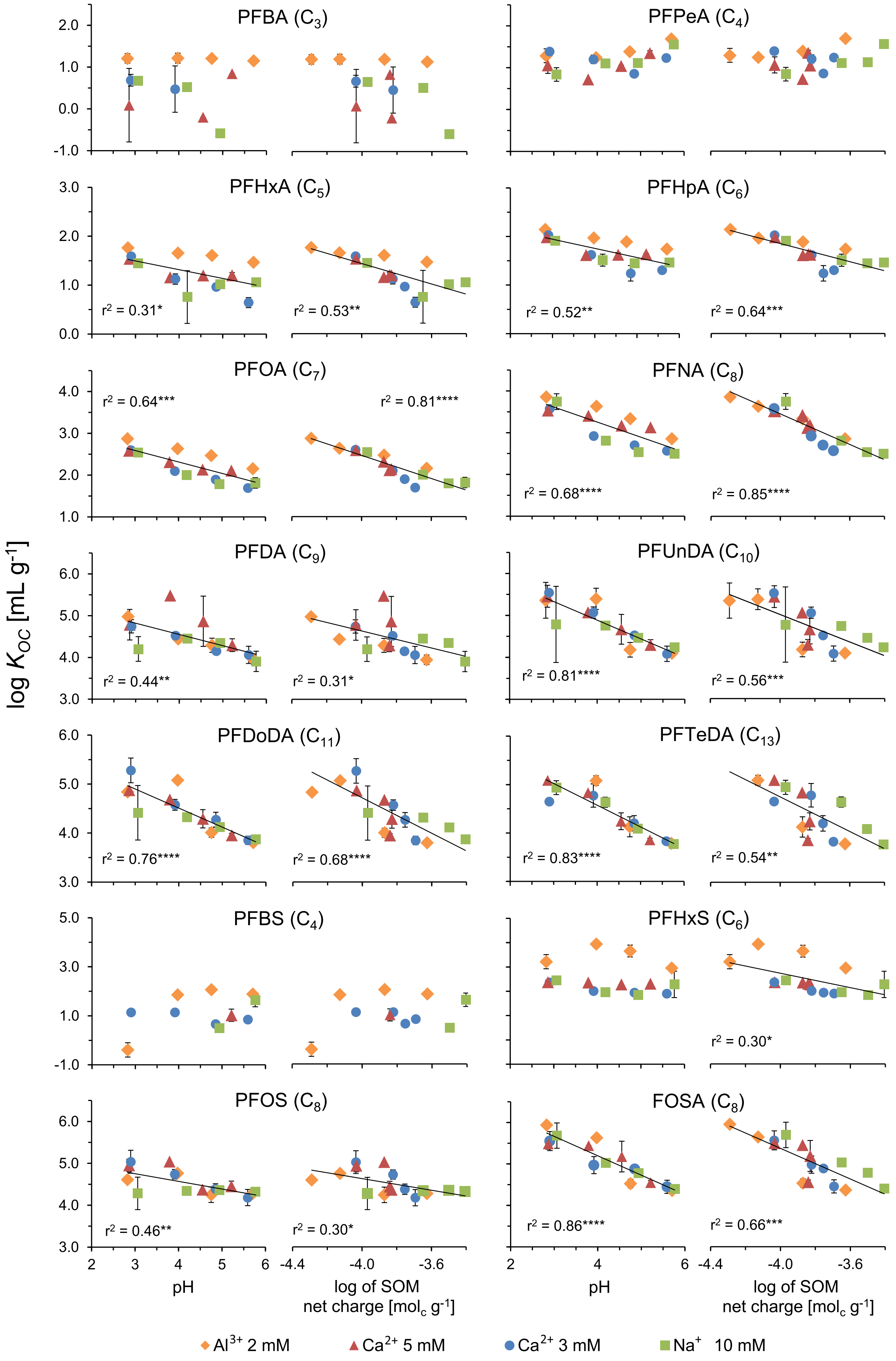

Fig. 1. Effect of pH and simulated SOM bulk net charge on log K_{OC} for the 14 target PFASs in the treatments with Al^{3+} (2 mM), Ca^{2+} (5 mM), Ca^{2+} (3 mM) and Na^{+} (10 mM) in the soil sorption experiment. Each data point represents the average of duplicates. log K_{OC} values of 0, 1, 2, 3, 4 and 5 correspond to sorbed fractions of 0.5, 4.5, 33.1, 83.6, 98.1 and 99.8%, respectively. $^{*}p \le 0.5$, $^{**}p \le 0.01$, $^{***}p \le 0.001$, $^{****}p \le 0.0001$.

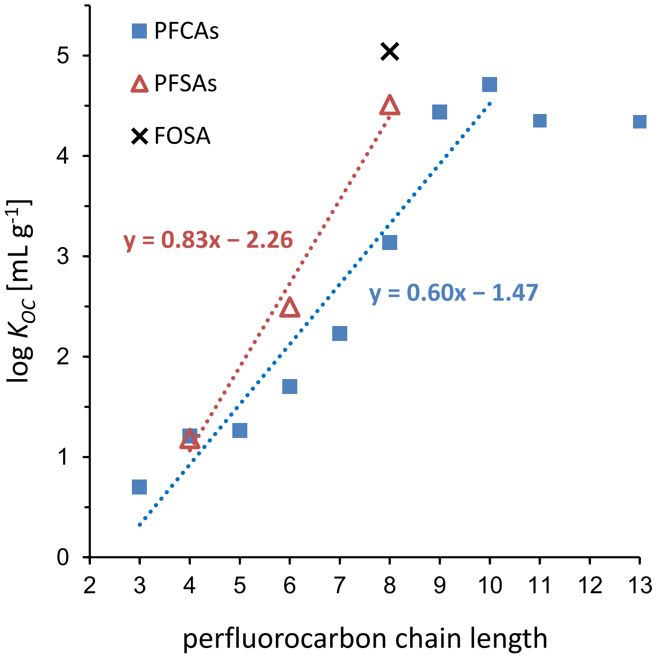

Fig. 2. Relationship between log K_{OC} [mL g^{-1}] and perfluorocarbon chain length for C_3–C_{10} PFCAs ($p \leq 0.05$), FOSA, and C_4, C_6 and C_8 PFSAs ($p \leq 0.05$) in the sorption experiment. Each data point represents the average log K_{OC} ($n = 31$). PFDoDA (C_{11}) and PFTeDA (C_{13}) were excluded from the PFCA regression fit.

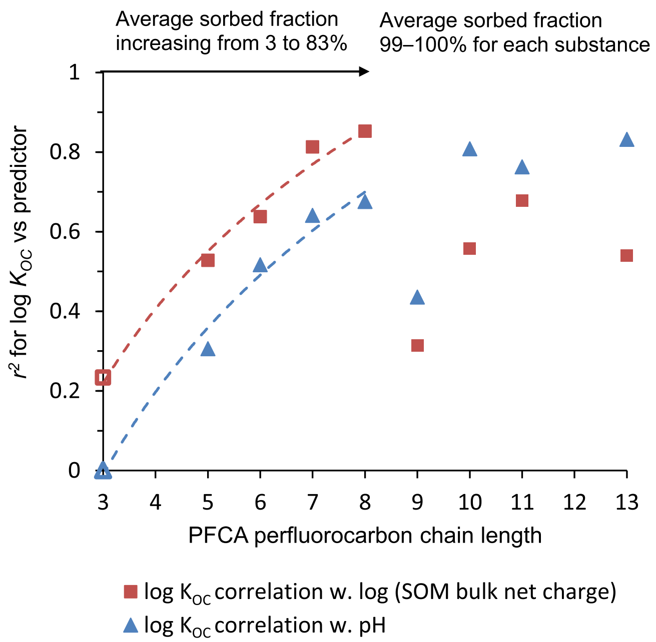

Fig. 4. The Pearson r^2 value for SOM bulk net charge vs. log K_{OC} and pH vs. log K_{OC} as influenced by the PFCA perfluorocarbon chain length (C_4 PFPeA excluded). Closed markers represent significant correlations ($p \leq 0.05$) and open markers non-significant relationships ($p > 0.05$).

PFASs (with the exception of PFPeA), and also for C_7–C_8 PFCAs and PFHxS, the relationship with the SOM bulk net charge was stronger and provides a better basis for a model able to predict the effects of both pH and cations on PFAS sorption. For the sorption of the most long-chained PFASs, however (i.e. C_9–C_{11} and C_{13} PFCAs, PFOS and FOSA), the relationship with the SOM bulk net charge was weaker than that with pH alone. This reflects the fact that the added cations, even though they influenced the SOM bulk net charge as a consequence of their binding, did not alter the PFAS sorption to any large extent. Our hypothesis that the SOM bulk net charge would be a better sorption predictor than pH was thus verified for C_3 and C_5–C_8 PFCAs and PFHxS, whereas the pH value alone was observed to be the better sorption predictor for C_9–C_{11} and C_{13} PFCAs, PFOS and FOSA (Fig. 4, Fig. S3 in the Supporting Information). As regards the PFASs for which sorption was better predicted by the SOM bulk net charge, the sorbed fractions ranged, on average, from 3% (PFBA) to 83% (PFNA), whereas for those PFASs for which sorption was better predicted by the pH value alone, sorption ranged, on average, between 99% and 100%.

For the most long-chained PFASs, the observation that pH alone was a better predictor of sorption than the SOM bulk net charge suggests that these PFASs may have had a high affinity for a SOM fraction that did not bind cations such as Ca^{2+} and Al^{3+} to any larger extent, although it possessed pH-dependent charge. A likely candidate is the humin fraction, which is known to be the most important SOM fraction for the sorption of other hydrophobic organic compounds (Gunasekara and Xing, 2003) including PFOS (Zhang et al., 2015). At low pH the degree of dissociation and the number of weak acids of humin is quite small compared to that of HA and FA (López et al., 2012; Cooke et al., 2008; Chang et al., 2014). This explains why a model for SOM bulk net charge, with parameters derived for only HA and FA, may be able to describe the acid-base characteristics of organic soils, including the soil used here, reasonably well as long as low pH is maintained (Gustafsson et al., 2014; Gustafsson and Kleja, 2005; Cooke et al., 2008). It may be hypothesized that the low net charge under low-pH conditions makes the humin fraction a relatively poor sorbent for cations as compared to HA and FA. Thus, the ability of humin to bind HOCs would remain largely unaltered upon cation additions, in accordance with what was observed for the most long-chained PFASs. The high sorption capacity of humin towards HOCs is attributed to its highly condensed aliphatic and aromatic domains (Gunasekara

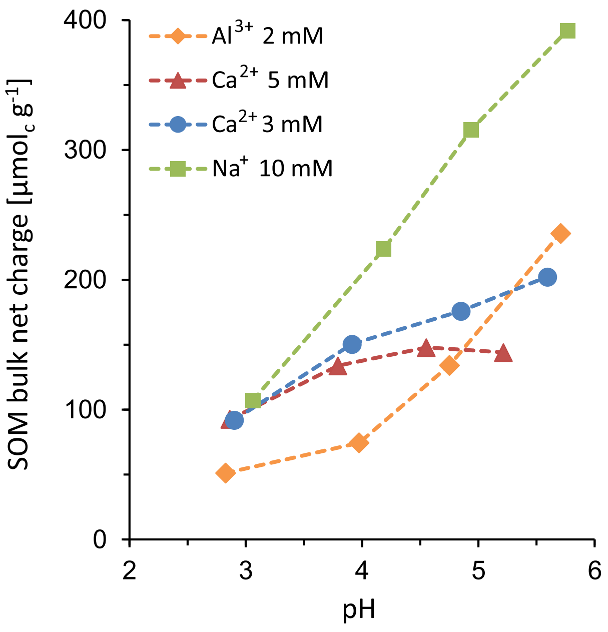

Fig. 3. Calculated SOM bulk net charge as a function of pH and cation treatment in the sorption experiment. Stated cation concentrations are additions of the respective nitrate (NO_3^-) salts. Dashed lines connect the points and are included for clarity.

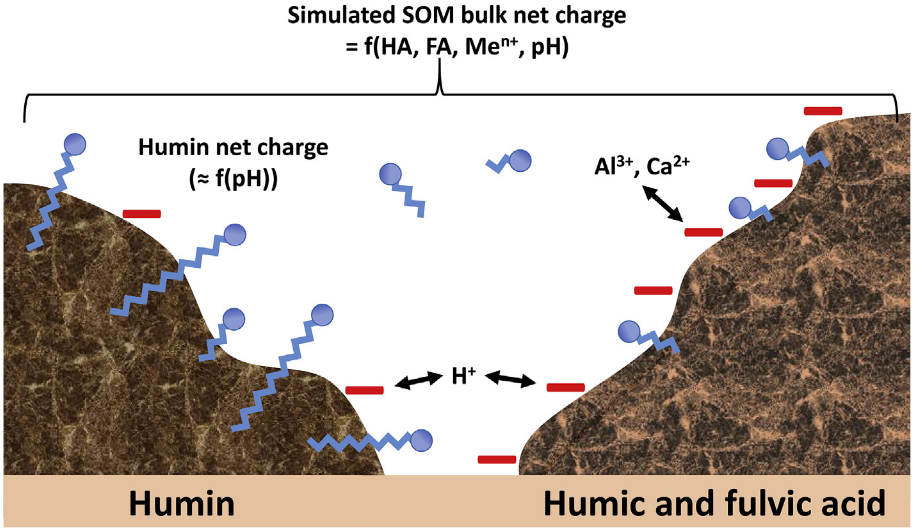

Fig. 5. Conceptual model for the observed PFAS SOM sorption, in which the PFASs (i.e. C_9–C_{11} and C_{13} PFCAs, PFOS and FOSA) with a strong SOM sorption (≥99%) are preferentially bound to the humin fraction, whereas the PFASs (i.e. C_3 and C_5–C_8 PFCAs and PFHxS) with a weaker SOM sorption are hypothesized to also bind to humic and fulvic acid.

and Xing, 2003; Chen et al., 2007), and thus it is suggested that these domains also bind the longer-chained, relatively more hydrophobic, PFASs.

3.4. Conceptual model

The results shown in Figs. 1 and 4 suggest that the interaction mechanisms between PFASs and SOM may be different depending on PFAS chain length, as conceptually described in Fig. 5. For the majority of the long-chain PFASs (i.e. C_9–C_{11} and C_{13} PFCAs, PFOS and FOSA), the pH-dependent sorption in combination with the small effect of cations other than H^+, suggests that the mechanism is similar to that of other hydrophobic organic compounds, i.e. these PFASs interact preferentially with the most highly condensed domains of the humin fraction, which carry a relatively low – although pH-dependent – net charge and do not bind other cations to any large extent. The extent of sorption of the most long-chained PFASs is poorly predicted by the SOM bulk net charge, simply because the latter does not provide a good representation of the net charge of the highly condensed humin fraction. It can be hypothesized that the most long-chained PFASs may penetrate (limited penetration, as suggested by Higgins and Luthy (2007), or full absorption) into the bulk solid organic phase of the humin fraction. For PFASs of shorter chain length (i.e. C_3 and C_5–C_8 PFCAs and PFHxS), penetration into the condensed domains may be less efficient due to the charge of the head group. This makes preferential sorption to the humin fraction less likely, and instead these PFASs may bind to HAs and FAs as well. This, however, makes sorption increasingly dependent on the sorption of cations such as Ca^{2+} and Al^{3+}, as they interact more strongly with HA and FA, causing a reduction in the SOM net charge, which in turn favors PFAS sorption.

HOCs preferentially sorbed to SOM humin-like fractions may be expected to exhibit sorption isotherms with a higher degree of nonlinearity as compared to compounds bound to less condensed, humic-type, carbon domains, and in addition their sorption may be less reversible (with pronounced sorption–desorption hysteresis) (Huang et al., 1997). Such sorption/desorption behavior has been observed for PFOS in previous studies (Wei et al., 2017; Qian et al., 2017; Milinovic et al., 2015) which may further support the suggestion of preferential PFOS binding to the humin fraction (c.f. Zhang et al., 2015). However, for PFOA, sorption isotherms are linear and the sorption more reversible as compared to that of PFOS (Miao et al., 2017; Milinovic et al., 2015). This may, in agreement with the conceptual model presented here, suggest that PFOA does not exhibit the same preferential affinity for humin and may also bind to humic and fulvic acid.

4. Conclusions

In this study we investigated the effect of the solution pH and SOM bulk net charge on PFAS sorption to an organic soil. The sorption was inversely related to both pH and to SOM bulk net charge, with SOM bulk net charge being more important for mainly short-chained PFASs, while the pH value alone was more important for the majority of the long-chained PFASs since cations had less effect on sorption for the latter group. This suggests that many long-chained PFASs are preferentially bound to the humin fraction of SOM, whereas shorter PFASs may also bind to the humic and fulvic acids. To further explore the role of humin for PFAS sorption to SOM, more knowledge on humin surface chemistry is essential. Of particular importance would be the development of a geochemical surface complexation model with the ability to simulate the acid-base and cation binding characteristics of humin.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.chemosphere.2018.05.012.

References

Ahrens, L., 2011. Polyfluoroalkyl compounds in the aquatic environment: a review of their occurrence and fate. J. Environ. Monit. 13, 20–31. https://doi.org/10.1039/c0em00373e.

Ahrens, L., Norström, K., Viktor, T., Palm Cousins, A., Josefsson, S., 2015. Stockholm

Arlanda Airport as a source of per- and polyfluoroalkyl substances to water, sediment and fish. Chemosphere 129, 33–38. https://doi.org/10.1016/j.chemosphere.2014.03.136.

Ahrens, L., Taniyasu, S., Yeung, L.W., Yamashita, N., Lam, P.K., Ebinghaus, R., 2010. Distribution of polyfluoroalkyl compounds in water, suspended particulate matter and sediment from Tokyo Bay, Japan. Chemosphere 79 (3), 266–272. https://doi.org/10.1016/j.chemosphere.2010.01.045.

Ahrens, L., Yamashita, N., Yeung, L.W.Y., Taniyasu, S., Horii, Y., Lam, P.K.S., Ebinghaus, R., 2009. Partitioning behavior of per- and polyfluoroalkyl compounds between pore water and sediment in two sediment cores from Tokyo Bay. Jpn. Environ. Sci. Technol 43 (18), 6969–6975. https://doi.org/10.1021/es901213s.

Ahrens, L., Yeung, L.W.Y., Taniyasu, S., Lam, P.K.S., Yamashita, N., 2011. Partitioning of perfluorooctanoate (PFOA), perfluorooctane sulfonate (PFOS) and perfluorooctane sulfonamide (PFOSA) between water and sediment. Chemosphere 85 (5), 731–737. https://doi.org/10.1016/j.chemosphere.2011.06.046.

Apelberg, B.J., Witter, F.R., Herbstman, J.B., Calafat, A.M., Halden, R.U., Needham, L.L., Goldman, L.R., 2007. Cord serum concentrations of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in relation to weight and size at birth. Environ. Health Perspect. 115 (11), 1670–1676. https://doi.org/10.1289/ehp.10334.

Barzen-Hanson, K.A., Davis, S.E., Kleber, M., Field, J.A., 2017. Sorption of fluorotelomer sulfonates, fluorotelomer sulfonamido betaines, and a fluorotelomer sulfonamido amine in national foam aqueous film-forming foam to soil. Environ. Sci. Technol. 51 (21), 12394–12404. https://doi.org/10.1021/acs.est.7b03452.

Chang, R.R., Mylotte, R., Hayes, M.H.B., McInerney, R., Tzou, Y.M., 2014. A comparison of the compositional differences between humic fractions isolated by the IHSS and exhaustive extraction procedures. Naturwissenschaften 101 (3), 197–209. https://doi.org/10.1007/s00114-013-1140-4.

Chen, D., Xing, B., Xie, W., 2007. Sorption of phenantrene, naphthalene and *o*-xylene by soil organic matter fractions. Geoderma 139 (3–4), 329–335. https://doi.org/10.1016/j.geoderma.2007.02.011.

Chen, H., Chen, S., Quan, X., Zhao, Y., Zhao, H., 2009. Sorption of perfluorooctane sulfonate (PFOS) on oil and oil-derived black carbon: influence of solution pH and $[Ca^{2+}]$. Chemosphere 77 (10), 1406–1411. https://doi.org/10.1016/j.chemosphere.2009.09.008.

Chen, W., Wang, H., Gao, Q., Chen, Y., Li, S., Yang, Y., Werner, D., Tao, S., Wang, X., 2017. Association of 16 priority polycyclic aromatic hydrocarbons with humic acid and humin fractions in a peat soil and implications for their long-term retention. Environ. Pollut. 230, 882–890. https://doi.org/10.1016/j.envpol.2017.07.038.

Conder, J.M., Hoke, R.A., De Wolf, W., Russel, M.H., Buck, R.C., 2008. Are PFCAs bioaccumulative? A critical review and comparison with regulatory criteria and persistent lipophilic compounds. Environ. Sci. Technol. 42, 995–1003. https://doi.org/10.1021/es070895g.

Cooke, J.D., Tipping, E., Hamilton-Taylor, J., 2008. Proton interactions with soil organic matter: the importance of aggregation and the weak acids of humin. Eur. J. Soil Sci. 59 (6), 1111–1121. https://doi.org/10.1111/j.1365-2389.2008.01071.x.

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. https://doi.org/10.1016/j.envint.2016.04.044.

Ellis, D.A., Denkenberger, K.A., Burrow, T.E., Mabury, S.A., 2004. The use of ^{19}F NMR to interpret the structural properties of perfluorocarboxylate acids: a possible correlation with their environmental disposition. J. Phys. Chem. A 108 (46), 10099–10106. https://doi.org/10.1021/jp049372a.

Enell, A., Lundstedt, S., Arp, H.P.H., Josefsson, S., Cornelissen, G., Wik, O., Kleja, D.B., 2016. Combining leaching and passive sampling to measure the mobility and distribution between porewater, DOC, and colloids of native oxy-PAHs, N-PACs, and PAHs in historically contaminated soil. Environ. Sci. Technol. 50 (21), 11797–11805. https://doi.org/10.1021/acs.est.6b02774.

Giesy, J.P., Kannan, K., 2001. Global distribution of perfluorooctane sulfonate in wildlife. Environ. Sci. Technol. 35 (7), 1339–1342. https://doi.org/10.1021/es001834k.

Giesy, J.P., Naile, J.E., Khim, J.S., Jones, K.C., Newsted, J.L., 2010. Aquatic toxicology of perfluorinated chemicals. Rev. Environ. Contam. Toxicol. 202, 1–52. https://doi.org/10.1007/978-1-4419-1157-5_1.

Goss, K.-U., Bronner, G., 2006. What is so special about the sorption behavior of highly fluorinated compounds? J. Phys. Chem. A 110 (30), 9518–9522. https://doi.org/10.1021/jp062684o.

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. https://doi.org/10.1021/es3048043.

Gunasekara, A.S., Xing, B., 2003. Sorption and desorption of naphthalene by soil organic matter: importance of aromatic and aliphatic components. J. Environ. Qual. 32 (1), 240–246. https://doi.org/10.2134/jeq2003.2400.

Gustafsson, J.P., 2001. Modeling the acid–base properties and metal complexation of humic substances with the Stockholm humic model. J. Colloid Interface Sci. 244 (1), 102–112. https://doi.org/10.1006/jcis.2001.7871.

Gustafsson, J.P., 2013. Visual MINTEQ – a free equilibrium speciation model [Internet document]. KTH Vis. MINTEQ. URL. http://vminteq.lwr.kth.se/. (Accessed 8 June 2015). Version 3.1. Compiled in Visual Basic 2012, 2013.

Gustafsson, J.P., Kleja, D.B., 2005. Modeling salt-dependent proton binding by organic soils with the NICA-Donnan and Stockholm Humic models. Environ. Sci. Technol. 39 (14), 5372–5377. https://doi.org/10.1021/es0503332.

Gustafsson, J.P., Persson, I., Kleja, D.B., van Schaik, J.W.J., 2007. Binding of iron(III) to organic soils: EXAFS spectroscopy and chemical equilibrium modeling. Environ. Sci. Technol. 41 (4), 1232–1237. https://doi.org/10.1021/es0615730.

Gustafsson, J.P., Persson, I., Oromieh, A.G., van Schaik, J.W.J., Sjostedt, C., Kleja, D.B., 2014. Chromium(III) complexation to natural organic matter: mechanisms and modeling. Environ. Sci. Technol. 48 (3), 1753–1761. https://doi.org/10.1021/es404557e.

Gustafsson, J.P., van Schaik, J.W.J., 2003. Cation binding in a mor layer: batch experiments and modelling. Eur. J. Soil Sci. 54 (2), 295–310. https://doi.org/10.1046/j.1365-2389.2003.00526.x.

Han, W., Luo, L., Zhang, S., 2013. Adsorption of tetrabromobisphenol A on soils: contribution of soil components and influence of soil properties. Colloids Surf. A Physicochem. Eng. Asp. 428, 60–64. https://doi.org/10.1016/j.colsurfa.2013.03.040.

Higgins, C.P., Luthy, R.G., 2006. Sorption of perfluorinated surfactants on sediments. Environ. Sci. Technol. 40 (23), 7251–7256. https://doi.org/10.1021/es061000n.

Higgins, C.P., Luthy, R.G., 2007. Modeling sorption of anionic surfactants onto sediment materials: an a priori approach for perfluoroalkyl surfactants and linear alkylbenzene sulfonates. Environ. Sci. Technol. 41 (9), 3254–3261. https://doi.org/10.1021/es062449j.

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. https://doi.org/10.1021/es4018877.

Huang, W., Young, T.M., Schlautman, M.A., Yu, H., Weber, W.J., 1997. A distributed reactivity model for sorption by soils and sediments. 9. General isotherm nonlinearity and applicability of the dual reactive domain model. Environ. Sci. Technol. 31 (6), 1703–1710. https://doi.org/10.1021/es960677f.

Jafvert, C.T., 1990. Sorption of organic acid compounds to sediments: initial model development. Environ. Toxicol. Chem. 9 (10), 1259–1268. https://doi.org/10.1002/etc.5620091004.

Kang, S., Xing, B., 2005. Phenanthrene sorption to sequentially extracted soil humic acids and humins. Environ. Sci. Technol. 39 (1), 134–140. https://doi.org/10.1021/es0490828.

Kinniburgh, D.G., van Riemsdijk, W.H., Koopal, L.K., Borkovec, M., Benedetti, M.F., Avena, M.J., 1999. Ion binding to natural organic matter: competition, heterogeneity, stoichiometry and thermodynamic consistency. Colloids Surf. A Physicochem. Eng. Asp. 151 (1–2), 147–166. https://doi.org/10.1016/S0927-7757(98)00637-2.

Kohl, S.D., Rice, J.A., 1998. The binding of contaminants to humin: a mass balance. Chemosphere 36 (2), 251–261. https://doi.org/10.1016/S0045-6535(97)10005-4.

Labadie, P., Chevreuil, M., 2011. Partitioning behaviour of perfluorinated alkyl contaminants between water, sediment and fish in the Orge River (nearby Paris, France). Environ. Pollut. 159 (2), 391–397. https://doi.org/10.1016/j.envpol.2010.10.039.

Lawrance, G.A., 1986. Coordinated trifluoromethanesulfonate and fluorosulfate. Chem. Rev. 86 (1), 17–33. https://doi.org/10.1021/cr00071a002.

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. https://doi.org/10.1016/j.scitotenv.2018.01.167.

López, R., Gondar, D., Antelo, J., Fiol, S., Arce, F., 2012. Study of the acid-base properties of a peat soil and its humin and humic acid fractions. Eur. J. Soil Sci. 63 (4), 487–494. https://doi.org/10.1111/j.1365-2389.2012.01461.x.

Löfgren, S., Gustafsson, J.P., Bringmark, L., 2010. Decreasing DOC trends in soil solution along the hillslopes at two IM sites in southern Sweden — geochemical modeling of organic matter solubility during acidification recovery. Sci. Total Environ. 409 (1), 201–210. https://doi.org/10.1016/j.scitotenv.2010.09.023.

Milinovic, J., Lacorte, S., Vidal, M., Rigol, A., 2015. Sorption behaviour of perfluoroalkyl substances in soils. Sci. Total Environ. 511, 63–71. https://doi.org/10.1016/j.scitotenv.2014.12.017.

Miao, Y., Guo, X., Peng, D., Fan, T., Yang, C., 2017. Rates and equilibria of perfluorooctanoate (PFOA) sorption on soils from different regions of China. Ecotoxicol. Environ. Saf. 139, 102–108. https://doi.org/10.1016/j.ecoenv.2017.01.022.

Qian, J., Shen, M., Wang, P., Wang, C., Hou, J., Ao, Y., Liu, J., Li, K., 2017. Adsorption of perfluorooctane sulfonate on soils: effects of soil characteristics and phosphate competition. Chemosphere 168, 1383–1388. https://doi.org/10.1016/j.chemosphere.2016.11.114.

Steinle-Darling, E., Reinhard, M., 2008. Nanofiltration for trace organic contaminant removal: structure, solution, and membrane fouling effects on the rejection of perfluorochemicals. Environ. Sci. Technol. 42 (14), 5292–5297. https://doi.org/10.1021/es703207s.

Tipping, E., Woof, C., 1991. The distribution of humic substances between the solid and aqueous phases of acid organic soils; a description based on humic heterogeneity and charge-dependent sorption equilibria. Eur. J. Soil Sci. 42 (3), 437–448. https://doi.org/10.1111/j.1365-2389.1991.tb00421.x.

Wang, F., Shih, K., Ma, R., Li, X.Y., 2015. Influence of cations on the partition behavior of perfluoroheptanoate (PFHpA) and perfluorohexanesulfonate (PFHxS) on wastewater sludge. Chemosphere 131, 178–183. https://doi.org/10.1016/j.chemosphere.2015.03.024.

Wei, C., Song, X., Wang, Q., Hu, Z., 2017. Sorption kinetics, isotherms and mechanisms of PFOS on soils with different physicochemical properties. Ecotoxicol. Environ. Saf. 142, 40–50. https://doi.org/10.1016/j.ecoenv.2017.03.040.

Yeung, L.W.Y., So, M.K., Jiang, G., Taniyasu, S., Yamashita, N., Song, M., Wu, Y., Li, J., Giesy, J.P., Guruge, K.S., Lam, P.K.S., 2006. Perfluorooctanesulfonate and related fluorochemicals in human blood samples from China. Environ. Sci. Technol. 40, 715–720. https://doi.org/10.1021/es052067y.

Zareitalabad, P., Siemens, J., Hamer, M., Amelung, W., 2013. Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) in surface waters, sediments, soils and wastewater – a review on concentrations and distribution coefficients. Chemosphere 91, 725–732. https://doi.org/10.1016/j.chemosphere.2013.02.024.

Zhang, C., Yan, H., Li, F., Hu, X., Zhou, Q., 2013. Sorption of short- and long-chain perfluoroalkyl surfactants on sewage sludges. J. Hazard Mater. 260, 689–699. https://doi.org/10.1016/j.jhazmat.2013.06.022.

Zhang, R., Yan, W., Jing, C., 2015. Experimental and molecular dynamic simulation study of perfluorooctane sulfonate adsorption on soil and sediment components. J. Environ. Sci. 29, 131–138. https://doi.org/10.1016/j.jes.2014.11.001.

Zhao, L., Zhang, Y., Fang, S., Zhu, L., Liu, Z., 2014. Comparative sorption and desorption behaviors of PFHxS and PFOS on sequentially extracted humic substances. J. Environ. Sci. 26 (12), 2517–2525. https://doi.org/10.1016/j.jes.2014.04.009.