Binding of per- and polyfluoroalkyl substances (PFASs) by organic soil materials with different structural composition – Charge- and concentration-dependent sorption behavior

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HIGHLIGHTS

- Sorption to *Sphagnum* peat was generally stronger than to Spodosol Oe soil.
- Sorption pH dependency increased with perfluorocarbon chain length up to C_{10}.
- ^{13}C NMR spectroscopy suggested sorption contributions from carbohydrates (O-alkyls).
- Sorption non-linearity was more pronounced onto Spodosol Oe material.

GRAPHICAL ABSTRACT
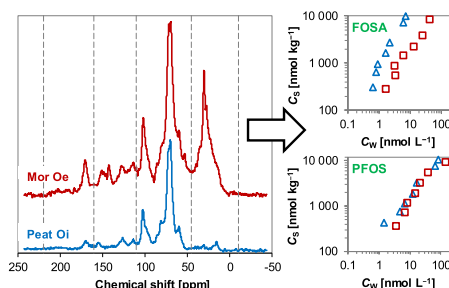
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ABSTRACT

The charge- and concentration-dependent sorption behavior of a range of per- and polyfluoroalkyl substances (PFASs) was studied for three organic soil samples with different organic matter quality, one Spodosol Oe horizon (Mor Oe) and two *Sphagnum* peats with different degrees of decomposition (Peat Oi and Peat Oe). Sorption to the two peat materials was, on average, four times stronger compared to that onto the Mor Oe material. In particular, longer-chained PFASs were more strongly bound by the two peats as compared to the Mor Oe sample. The combined results of batch sorption experiments and ^{13}C NMR spectroscopy suggested sorption to be positively related to the content of carbohydrates (i.e., O-alkyl carbon). Sorption of all PFAS subclasses was inversely related to the pH value in all soils, with the largest pH effects being observed for perfluoroalkyl carboxylates (PFCAs) with C_{10} and C_{11} perfluorocarbon chain lengths. Experimentally determined sorption isotherms onto the poorly humified Peat Oi did not deviate significantly from linearity for most substances, while for the Mor Oe horizon, sorption nonlinearity was generally more pronounced. This work should prove useful in assessing PFAS sorption and leaching in organic soil horizons within environmental risk assessment.

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1. Introduction

An increased mechanistic understanding of sorption of per- and polyfluoroalkyl substances (PFASs) to soil organic matter (SOM) is essential to more accurately assess their environmental binding, leaching and risks. Previous research has indicated that SOM is the dominant sorbent of PFASs in soils, which explains why the organic matter content is often found to be the main factor controlling PFAS sorption (e.g. Higgins and Luthy, 2006; Milinovic et al., 2015; Oliver et al., 2020). However, not only the abundance of SOM, but also its chemical properties, such as its net charge (Campos Pereira et al., 2018; Higgins and Luthy, 2007; Zhi and Liu, 2019) and structural composition (Zhao et al., 2014; Zhi and Liu, 2018) may influence PFAS sorption. Studies on isolated fractions of organic matter and soils rich in organic matter show marked pH-dependent binding, with increasing affinity at decreasing pH (Zhao et al., 2014; Campos Pereira et al., 2018). This is due to protonation of functional groups resulting in a decreased net negative charge of the organic matter, which, in turn, results in a lower repulsion between the negatively charged PFASs and the organic material (Higgins and Luthy, 2006). Also charge neutralization due to metal binding seems to enhance PFAS binding (Higgins and Luthy, 2006; Campos Pereira et al., 2018).

The quality of organic matter depends on its origin, and is further altered by the process of decomposition (humification). A powerful tool to investigate the chemical environment of the carbon atom is ^{13}C nuclear magnetic resonance (^{13}C NMR) spectroscopy, which has been applied widely in various aspects of environmental chemistry (e.g. Kögel-Knabner, 1997, 2002; Simpson et al., 2012; Prietzel et al., 2018). Cross-polarisation magic-angle-spinning (CP-MAS) techniques further enable the acquisition of high-resolution solid-state ^{13}C NMR spectra of SOM (Baldock et al., 1997). Previous research that combined investigations of PFAS binding onto SOM with the application of ^{13}C NMR spectroscopy includes the work of Zhao et al. (2014), who removed the 'humic substances' of a Chinese peat soil using alkaline reagents prior to sorption experiments. The authors found sorption of perfluorooctane sulfonate (PFOS) and perfluorohexane sulfonate (PFHxS) onto the treated peat to be stronger as compared to that onto two sequentially isolated humic acid fractions from the same soil. Structural characterization using ^{13}C NMR indicated that the PFAS binding strength seemed to be positively related to SOM aliphaticity and increased content of carbohydrates, but inversely related to the contents of aromatic C and to phenolic and carboxylic moieties (Zhao et al., 2014). However, Oliver et al. (2020) found no relationship between sorption of PFOS, perfluorooctanoate (PFOA) or PFHxS and any specific types of organic matter structures determined by ^{13}C NMR spectroscopy in an investigation of coastal sediments in Australia. The variation in sorption strength seemed to originate primarily from the variation in the organic C content itself and not from the variation in SOM quality. In addition, the binding of several PFAS compounds to soils is still poorly known. For example, as regards the PFOS precursor EtFOSA, which is still extensively used as an insecticide in South America (i.e. Sulfluramid) (Zabaleta et al., 2018; Nascimento et al., 2018), no published sorption data for soils has been found in the peer-reviewed literature. Thus, further studies are needed to clarify the binding strength for PFASs in soils and the link to SOM quality.

Hence, the overall objective of the present study was to investigate the sorption behavior of several legacy and precursor PFASs (including *N*-ethyl perfluorooctane sulfonamide (EtFOSA/Sulfluramid) and 6:2 and 8:2 fluorotelomer sulfonates (6:2 and 8:2 FTSAs)) in three types of organic soil horizons: a Spodosol Oe (Mor Oe), and two *Sphagnum* peats having different degrees of decomposition. Specific objectives were (i) to investigate the charge- and concentration-dependent sorption behavior of different PFAS subclasses, and (ii) to relate the sorption behavior to structural properties of the organic matter as determined by chemical extractions and ^{13}C NMR spectroscopy.

2. Materials and methods

2.1. Soil characteristics

Two surface horizon *Sphagnum* peat soils of low (Oi) and moderate (Oe) degree of humification, respectively, were sampled at depths of 5–25 cm from a Sphagnofibrist (Soil Survey Staff, 2014). Photos of the sampling site located in central Sweden (WGS84: 59°46′25.2″N 14°58′15.4″E) are provided in the Supplementary Materials, Fig. S1-Fig. S3. *Sphagnum fuscum* was the dominant species in both peat samples. The peat (Oi) exhibited a low degree of humification (decomposition) and had a value between H$_2$ and H$_3$ on the von Post scale (von Post and Granlund, 1926), whereas the peat material with a somewhat more pronounced humification (Oe) had a value between H$_4$ and H$_5$. Peat soil from this site has previously been used in studies on proton binding to SOM (Gustafsson and Berggren Kleja, 2005). The organic mor (Oe) layer (10 cm thickness) was sampled from a nearby Spodosol developed in glacial till, which was dominated by Scots Pine (*Pinus sylvestris*) vegetation (Fig. S3 in the SI). The two peat soils and the Spodosol mor layer (Oe) are hereafter referred to as Peat Oi, Peat Oe, and Mor Oe, respectively.

After collection, the samples were sieved (<2 mm), homogenized and stored at +5 °C in their field-moist state until further use. A portion of each sample was air-dried for the purpose of soil chemical characterisation (Table S1, Supplementary materials), determination of total organic carbon (accredited method EN 13137), and ^{13}C NMR spectroscopy as described below.

2.2. PFAS standards

PFAS native standards were purchased from Sigma Aldrich. A stock mixture of 14 PFASs, i.e. C$_6$–C$_{11}$ and C$_{13}$ PFCAs, C$_4$, C$_6$ and C$_8$ perfluoroalkyl sulfonates (PFSAs), perfluorooctane sulfonamide (FOSA), *N*-ethyl perfluorooctane sulfonamide (EtFOSA/Sulfluramid), and 6:2 and 8:2 FTSAs, was prepared in methanol of analytical grade (LiChrosolv, Merck, Germany). Mass-labeled internal standards (ISs), i.e. ^{13}C$_2$-PFHxA, ^{13}C$_4$-PFOA, ^{13}C$_5$-PFNA, ^{13}C$_2$-PFDA, ^{13}C$_2$-PFUnDA, ^{13}C$_2$-PFDoDA, ^{13}C$_2$-PFTeDA, ^{18}O$_2$-PFHxS, ^{13}C$_4$-PFOS, ^{13}C$_8$-FOSA, d$_3$-*N*-EtFOSA, ^{13}C$_2$-6:2 FTSA and ^{13}C$_2$-8:2 FTSA (>98% purity, Wellington Laboratories, Guelph, ON), were included for analytical quantification and quality control. Native PFASs and internal standards are summarized in Table S2.

2.3. Sorption experiments

2.3.1. pH and salt dependence of PFAS sorption

The pH-dependent sorption of PFASs onto the three soils was evaluated in batch mode after additions of dissolved nitrate (NO$_3^-$) salts of Al^{3+}, Ca^{2+} or Na$^+$ (Section S1 and Table S3 in the Supplementary materials). All experiments were conducted with field-moist, sieved samples. 1.00 g dry weight (dw) soil was added to 50 mL polypropylene (PP) centrifuge tubes (Corning™ Falcon®) in duplicate sets and suspended in a total solution volume of 40 mL (Table S3). Varying volumes of sodium hydroxide (NaOH, prepared the same day) or nitric acid (HNO$_3$) were added to reach pH values of approximately 3, 4, 5 and 6. This resulted in a total of 24 samples per soil, excluding duplicate negative controls for which no PFASs were spiked to the soil suspensions (10 mM NaNO$_3$). Dissolved nitrate salts of Al^{3+}, Ca^{2+} and Na$^+$ were added to the suspensions to yield initial aqueous concentrations of 2.0 mM Al^{3+}, 5.0 mM Ca^{2+} or 10 mM Na$^+$. Additional sodium nitrate (NaNO$_3$) was added to the Na$^+$ and Al^{3+} treatments to ensure similar NO$_3^-$ background concentrations (~10 mM) in all suspensions. Finally, 50 μL of a PFAS stock mixture dissolved in methanol was added to each suspension to yield initial aqueous concentrations of individual PFASs of, on average, 30 nM (i.e. 1.2 nmol g^{-1} dw soil), with some exceptions (see Table S4). Soil suspensions and controls were equilibrated using an end-over-end

shaker at 20 °C for 7 days, which has been shown to be sufficient to reach equilibrium for PFASs in research involving organic soils (Zhao et al., 2014; Zhi and Liu, 2018). Following equilibration, suspensions were centrifuged for 20 min at 2100 *g* prior to analysis of aqueous PFAS concentrations (section 2.5). The pH was measured in the supernatant of subsamples using a GK2401C Red-Rod combined pH electrode (Radiometer Analytical). Dissolved organic carbon (DOC) was determined for unspiked (i.e. methanol-free) suspension replicates (Table S5) using a TOC-V CPH analyzer (Shimadzu).

Addition of biocides such as sodium azide (NaN₃) was avoided, to keep the ionic strength as close to natural as possible, while at the same time varying the cationic composition. Recent findings indicate that the PFAS precursors (i.e., EtFOSA, 6:2 FTSA and 8:2 FTSA) might degrade in biologically active soil systems (Zabaleta et al., 2018; Chen et al., 2019). Soil microcosm experiments indicated biodegradation rates of EtFOSA (Zabaleta et al., 2018) and 6:2 FTSA (Chen et al., 2019) corresponding to losses of about 10% following 7 days of incubation. However, our soils were all nutrient-poor (C/N > 50), low in pH (4.0–4.7) (Table S1), and originated from either recalcitrant Pine/*Ericaceae* (Mor Oe) or *Sphagnum* peat (Peat Oi and Oe) litter (Wallenstein et al., 2013; Wiedermann et al., 2017), indicating a low potential microbial activity, and thereby also a low degradation potential for the PFAS precursors.

2.3.1.1. Modeling of net surface charge of soils. For the pH-dependent sorption experiment, the net surface charge of the soils at equilibrium was modeled. For this, the Stockholm Humic Model (Gustafsson, 2001) was employed (software: Visual MINTEQ v.3.1; Gustafsson, 2020), as described previously (Campos Pereira et al., 2018). Furthermore, to ensure that the added Al³⁺ (2 mM) did not form precipitates in the experiment, all solution compositions in the model output were confirmed to be undersaturated with respect to possible Al(OH)₃ soil phases.

2.3.2. Sorption isotherms

Multi-solute sorption isotherms were derived for the two soils that were the most different in terms of quality and the origin of their SOM, i. e., Peat Oi and Mor Oe. Samples were prepared in duplicate by suspending 0.75 g dw soil in 30 mL solution of 10 mM NaNO₃. Different amounts of PFAS stock mixture were added to the suspensions in order to produce initial concentrations of individual PFASs ranging from, on average, 7–200 nM (i.e., from 0.3 to 8 nmol g⁻¹ dw soil). The suspensions were equilibrated by end-over-end shaking for 7 days prior to phase separation (2100 *g*, 20 min). The pH value was measured in the equilibrated supernatants after samples were taken out for analysis of PFASs, and was 3.5 and 3.7 for Mor Oe and Peat Oi, respectively.

2.4. ¹³C NMR spectroscopy

Air-dried, finely ground portions of all soils were subjected to ¹³C CP-MAS NMR spectroscopy (Bruker DSX 200 spectrometer, Billerica/USA). The samples were spun at 6.8 kHz in a 7 mm zirconium dioxide rotor, using a recycle delay of 1 s. 3000 scans per sample were aquired. As reference for the chemical shifts, tetramethylsilane was equated with 0 ppm. Spectra were phase-adjusted and baseline-corrected prior to integration over the C regions given in Table 1. In addition, the spectra were integrated according to Nelson and Baldock (2005) to allow the application of their molecular mixing model to convert the NMR spectra into the following compound classes: carbohydrates, protein, lignin, lipid and carbonyl.

2.5. PFAS analysis

For quantification of aqueous PFAS concentrations, sample aliquots of 500 μL were transferred to 1.5 mL Eppendorf tubes together with 400 μL of methanol and 100 μL of an IS stock mixture (50 ng mL⁻¹ for each

Table 1
¹³C NMR-derived soil carbon characteristics.

Integrated C domains	Chemical shift region (ppm)	Peat Oi	Peat Oe	Mor Oe
Alkyl C [%]	−10–45	2.9	15	25
O-alkyl C [%]	45–119	78	68	52
Aromatic C [%]	110–160	13	12	16
Carboxyl/carbonyl/amide C [%]	160–220	6.3	6.2	6.9
Alkyl C to O-alkyl C ratio[a]		0.04	0.22	0.48
C chemistry from molecular mixing model[b]				
Carbohydrate [%]		72	61	42
Protein [%]		2.4	5.1	4.6
Lignin [%]		20	22	30
Lipid [%]		0.0	9.6	21
Carbonyl [%]		5.3	3.3	2.9

[a] Alkyl C to O-alkyl C ratio = Alkyl (0–45 ppm)/O-alkyl (45–110 ppm) (Baldock et al., 1997).

[b] Model and associated integrations of chemical shifts: Baldock et al. (2004) and Nelson and Baldock (2005).

IS) prepared in methanol. Prior to analysis, the samples were vortexed and filtered through a 0.45 μm syringe filter (Minisart® hydrophilic regenerated cellulose, Sartorius™, Germany; recoveries tested by Lath et al., 2019, and Sörengård et al., 2020) into 1.7 mL PP analysis vials. PFAS concentrations were measured with direct injection into a Dionex UltiMate 3000 ultra-high performance liquid chromatography (UPLC) system (Thermo Fisher Scientific, MA, USA) coupled to a triple quadrupole tandem mass (MS/MS) spectrometer (TSQ Quantiva, Thermo Fisher Scientific). LC-MS/MS parameters and conditions for PFAS analysis are provided elsewhere (Franke et al., 2021). All peak integrations were checked manually. Aqueous limits of quantification (LoQs) ranged from 0.01 ng mL⁻¹ (FOSA) to 0.5 ng mL⁻¹ (PFHpA), with the majority of the LoQs being ≤0.05 ng mL⁻¹. For information on quality assurance and control, see Section S2, and Tables S6 and S7.

2.6. Data treatment

The sorption of PFAS to SOM can be expressed by:

$$K_d = \frac{C_s}{C_w} \tag{1}$$

where C_S is the concentration of the individual PFAS sorbed to the soil (nmol kg⁻¹ dw) and C_W its concentration in the aqueous phase (nmol L⁻¹) upon equilibration, while K_d is the solid-solution distribution coefficient (L kg⁻¹ dw). C_S was obtained from the difference between added concentrations and concentrations found in the solution phase. Commonly, the distribution coefficient is normalized to the fraction of organic carbon (f_{OC}):

$$K_{OC} = \frac{K_d}{f_{OC}} \tag{2}$$

where K_{OC} has the unit L kg⁻¹ OC. As all three soils consisted essentially of pure organic matter (f_{OC} = 0.45–0.54, ash contents ≤2.9%), all measured sorption was attributed to the organic carbon content (f_{OC}) of the soils, and any binding to mineral phases was hence assumed to be negligible. The logarithms of the K_{OC} values (i.e. log K_{OC}) were in general normally distributed, as confirmed with the Shapiro-Wilk test (α = 0.05). Thus, whenever the average sorption is referred to henceforth, this should be interpreted as the arithmetic average of the log K_{OC} value. For the analysis of the data of the pH-dependent sorption experiment, a generalized linear mixed model (GLMM) was derived, see Section S3, Supplementary materials.

2.7. Fitting of sorption isotherms

The sorption isotherms were fitted to the linear (Eq. (1)) as well as to the Freundlich equation (Eq. (3)):

$$C_S = K_F \cdot C_W^{\ n} \tag{3}$$

where the empirical n value indicates the degree of nonlinearity ($n \approx 1$ corresponds to a linear isotherm) and K_F is the specific Freundlich sorption coefficient [$nmol^{1-n}$ L^n kg^{-1} soil]. The K_F and n parameters were fitted to the isotherm data using the Microsoft Excel™ Solver

function (nonlinear generalized reduced gradient method) to minimize the residual root-mean-square error (RMSE) of the fit (Kinniburgh, 1986).

Finally, to enable comparisons between isotherms, K_F values were converted to concentration-specific K_{OC} values ($K_{OC}*$) using Eq. (4) (Mejia-Avendaño et al., 2020):

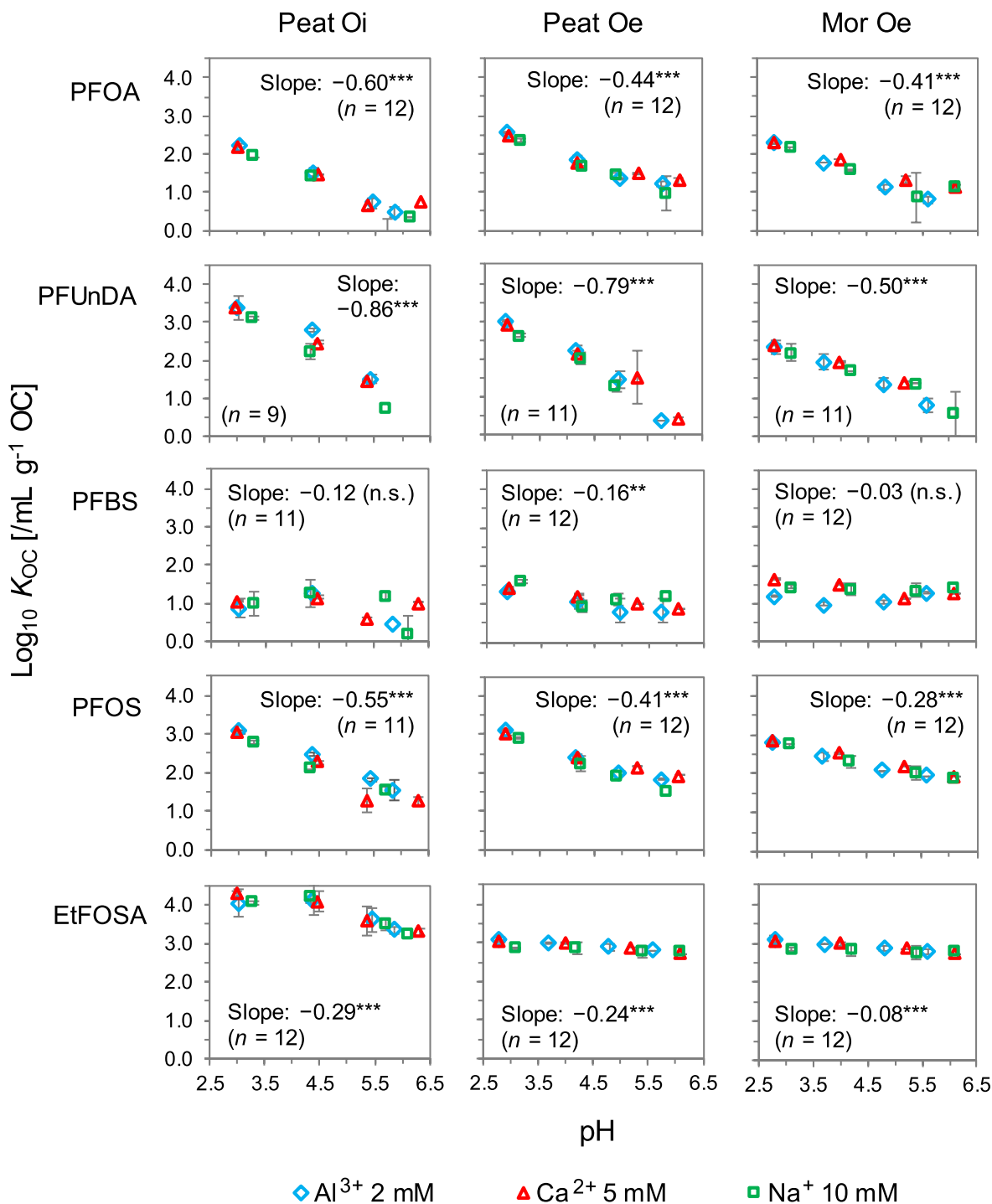$$K_{OC}^{\ *} = \frac{K_F \cdot C_W^{\ n-1}}{f_{OC}} \tag{4}$$

Fig. 1. pH-dependent sorption ($\log_{10} K_{OC}$) of selected PFASs as affected by additions Al^{3+} or Ca^{2+}. Error bars represent the standard deviation ($n = 2$). **$p \leq 0.01$, ***$p \leq 0.001$, n.s.: non-significant relationship ($\alpha = 0.05$). Data for the other analyzed PFASs are provided in Fig. S6 and Table S8, Supplementary Materials.

3. Results and discussion

3.1. pH- and charge dependent sorption to the different organic soils

For all three soils, sorption was inversely related to the pH value ($p <$ 0.05) for all PFASs except for the short-chained PFBS (Fig. 1, Table S8, Table S9). Calculated across all PFASs, the log K_{OC} value decreased with, on average, 0.38 ± 0.20 log units per unit pH. This value is in agreement with the value obtained in our previous work (Campos Pereira et al., 2018) for a Spodosol mor layer similar to Mor Oe (Δlog K_{OC} per pH unit $= -0.32 \pm 0.11$ L kg^{-1} OC) and with that reported by Higgins and Luthy (2006) for sorption of PFASs onto a sediment material (Δlog K_{OC} per pH unit $= -0.37$ L kg^{-1} OC). As none of the analyzed PFASs change their aqueous speciation within the studied pH range of 3–6 (Rayne and Forest, 2009a, 2010; Barzen-Hanson et al., 2017), the pH-dependent sorption was attributed to a decreasing SOM net negative charge upon a decrease in pH (Table S10, Figs. S4–S5).

Similar to our previous work (Campos Pereira et al., 2018), we varied the solution composition, with some suspensions containing Al^{3+} or Ca^{2+} rather than Na^{+}, to investigate the extent to which the net charge of the SOM governs the pH dependency. The Al^{3+} and Ca^{2+} ions form complexes with organic matter, thus decreasing its net negative charge. However, under the conditions of the experiments the cation-induced effects on SOM net charge obtained were relatively minor, as compared to the pH-induced effect on the net charge (Figs. S4–S5), i.e., the relationships between calculated log SOM net charge and log K_{OC} were very similar to the ones between pH and log K_{OC} (Figs. S6 and S7). Accordingly, based on the current data set it was difficult to draw any conclusions on the effect of cationic composition on PFAS binding.

As regards the magnitude of the effect of pH on sorption, the pH dependence (i.e. the regressed slope Δlog K_{OC} per unit pH) varied depending on the substance in question (Fig. 2). For the C$_4$, C$_6$ and C$_8$ PFSAs and for the C$_7$ and C$_{10}$ PFCAs, the pH dependence became more pronounced (i.e. the slope became more negative) as the perfluorocarbon chain length increased. Previous studies reported similar observations of an increa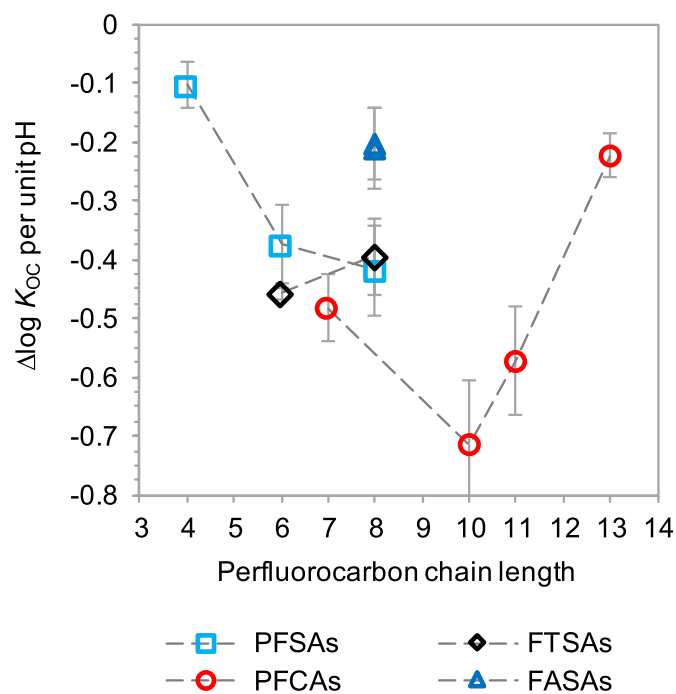sed pH dependency of PFAS sorption with increasing chain length (e.g. Campos Pereira et al., 2018; Campos-Pereira et al., 2020). This is consistent with the presence of charge interactions between the perfluorocarbon backbone and the sorbent (c.f. Johnson et al., 2007; Xiao et al., 2011), which may be explained by the excess negative charge ($\delta-$) present on the electronegative fluorine atoms. For PFOS, this excess charge has been calculated to be -0.11 ± 0.02 to -0.27 ± 0.01 elementary charge units per fluorine atom (Erkoç and Erkoç, 2001; Xiao et al., 2011; Johnson et al., 2007). However, the PFCAs with the longest chain lengths reached a maximum pH dependency for C$_{10}$ PFUnDA in all three soils (average Δlog K_{OC} per unit pH $\pm$ SD $= -0.72 \pm 19$ log units, $n = 3$ soils), which then decreased again for the more long-chained C$_{11}$ PFDoDA and C$_{13}$ PFTeDA. A possible explanation for the observed maxima in the sorption pH dependence of the PFCAs is that the larger hydrophobicity of PFDoDA, and in particular PFTeDA, stabilized the sorption to some extent, which may have made it less sensitive to changes in pH as compared to that of shorter-chained PFCAs and other PFASs.

For a few of the analyzed PFASs in the present study, i.e. 6:2 FTSA, 8:2 FTSA and EtFOSA, the pH-dependent sorption behavior has previously been described only to a limited extent in the literature. Here, the binding of 6:2 FTSA and 8:2 FTSA decreased with, on average, 0.46 and 0.39 log units per unit pH, respectively. These decreases were larger as compared to those previously reported, i.e. 0.08–0.17 log units per pH unit (Nguyen et al., 2020; Barzen-Hanson et al., 2017; Zhi and Liu, 2019). As for EtFOSA, its average sorption decrease across soils was 0.20 log K_{OC} units per pH unit (Figs. 1 and 2), which was essentially identical to that of the other investigated non-ionized PFAS (i.e., FOSA) (Fig. 2 and Fig. S6b), having the same number of fluorinated carbons. This suggests that, for the C$_8$ fluoroalkyl sulfonamides (FASAs), the pH dependency was governed by charge interactions between the perfluorocarbon backbone and the sorbent.

3.2. Sorption isotherms

The Mor Oe soil exhibited more or less nonlinear sorption isotherms for 8 out of 13 analyzed PFASs with fitted Freundlich exponent n values lower than 0.75 (Fig. 3, Table S11, Figs. S8–S9). For the Peat Oi soil, the exponent $n \pm$ SD of the fitted Freundlich isotherm was, on average, 0.85 ± 0.21 across 12 analyzed PFAS. Thus, sorption onto Peat Oi was generally linear or close to linear, as for this soil, the 95% confidence interval of the exponent n included the value 1.0 for all PFASs except PFDoDA. Only a few studies with sorption isotherm data for organic soils have been published up to date (i.e., Zhi and Liu, 2018; Zhi and Liu, 2019; Milinovic et al., 2015). The data for the peat soil DUBLIN (Milinovic et al., 2015) and Pahokee peat IHSS standard (Zhi and Liu, 2018, 2019) showed linear sorption isotherms for PFOS as well as for PFOA (Freundlich n values for PFOS: 0.82–0.9; n values for PFOA 0.83–1.05), which agrees with our observation that there is a more or less linear sorption behaviour for these PFASs onto peat. As for the binding strength, the calculated concentration-specific log K_{OC}* values (mL g^{-1} OC) for PFOS and PFOA were slightly lower than those determined previously for PFAS sorption to peat. For example, the log K_{OC} values for PFOS at pH:s between 4.6 and 5.3 ranged from 2.59 to 2.88 in three previous studies (Milinovic et al., 2015; Zhao et al., 2014; Zhi and Liu, 2018), while in the current study, a log K_{OC}* value of 2.58 was obtained for Peat Oi at pH 3.7 (Table S11), at similar concentrations (i.e., $C_W \sim$ 10 nmol L^{-1}). For PFOA, the corresponding log K_{OC} values were 1.99 and 2.23 in the studies of Milinovic et al. (2015) and Zhi and Liu (2018), respectively, while the log K_{OC}* was 1.80 for Peat Oi in the current study. Also in comparison with our previous study (Campos Pereira et al., 2018), the log K_{OC} values were generally lower. The reasons for this are unclear, although both structural differences between samples as well as differences in the methodological approach may be involved. The more or less linear sorption onto Peat Oi suggests that this material was fairly homogeneous in terms of "binding sites" for PFASs, which may be due to the fact that the substrate was made up entirely of
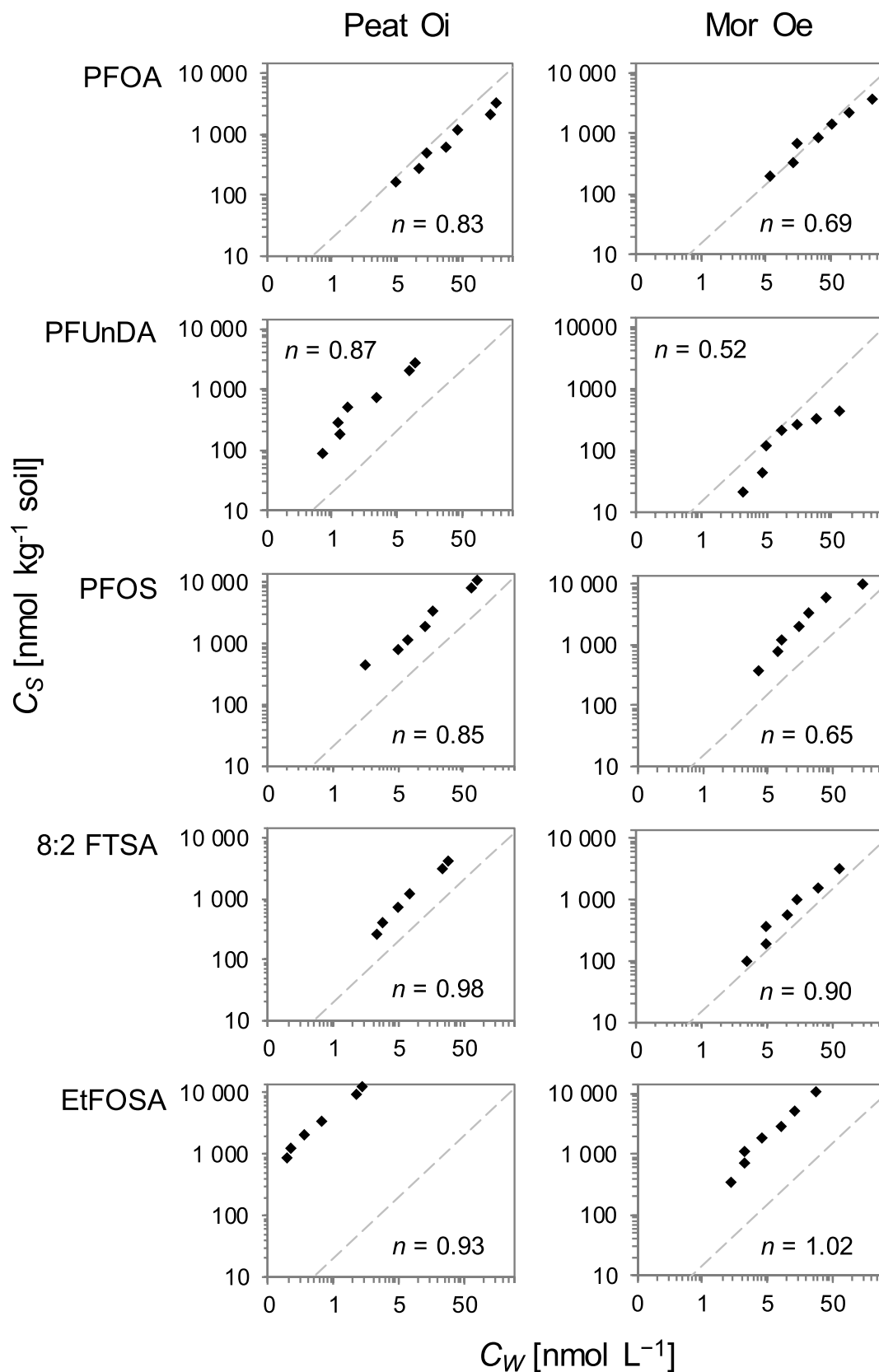

Fig. 2. Regressed slopes of Δlog$_{10}$ K_{OC} (mL g^{-1} OC) per unit pH as a function of the length of the perfluorinated carbon chain for various PFAS subclasses. Error bars represent the standard error of the mean ($n = 3$ soils).

Fig. 3. Sorption isotherms for soils Peat Oi and Mor Oe. n is the fitted exponent of the Freundlich sorption isotherm. The dashed line indicates 50% binding. Each data point corresponds to duplicate samples. Experimental conditions: background electrolyte 10 mM $NaNO_3$, pH 3.5–3.7. Data for the other analyzed PFASs are given in the Supplementary data section (Figs. S10–S11 and Table S12).

Sphagnum fuscum with a low degree of alteration through decomposition. It also suggests that these binding sites were far from being saturated with PFAS. The more pronounced sorption nonlinearity in Mor Oe suggested that factors such as sorbate–sorbate (i.e. PFAS–PFAS) interactions and/or binding site heterogeneity influenced the sorption behaviour in this soil. The SOM of Mor Oe was derived from multiple litter sources and had been subjected to a more pronounced decomposition. Notably, the higher general affinity for PFASs of the Peat Oi sample compared to the Mor Oe sample was consistent over the studied concentration range (Fig. 3 and Figs. S8–S9). The log $K_{OC}*$ values for the Peat Oi and Mor Oe samples normalized at $C_W = 10$ nmol L^{-1} (Fig. S10) largely agree with the data from the pH-dependent sorption test (Fig. 4). Across all analyzed PFASs, K_{OC} values were between −0.27 (PFHxS) and 1.70 (PFDoDA) log units larger in Peat Oi as compared to those in Mor Oe, with an average difference of 0.59 log units in sorption strength between the soils.

3.3. Effect of PFAS structural features on sorption to SOM

In agreement with previous studies, the average sorption onto SOM increased with increasing length of the perfluorocarbon chain within the homologue groups of PFCAs, PFSAs and FTSAs (Fig. 4) (e.g. Higgins and Luthy, 2006; Milinovic et al., 2015; Campos Pereira et al., 2018). For the partitioning shown in Fig. 4, the aqueous concentration C_W after equilibration was, on average, 17 ± 15 nM, i.e. C_W ranged from 0.61 nM (PFTeDA) to 52 nM (PFBS). Exceptions (* in Fig. 3) are the partitioning coefficients for PFHpA, PFNA and PFDA, which, because of incorrect mass balances in the pH-dependent sorption experiment, were calculated from their respective sorption isotherm at a C_W of 10 nM (pH = 3.5–3.7). For the PFCA and PFSA subclasses, the increase in sorption per additional CF_2 moiety were 0.13 ± 0.12 and 0.30 ± 0.06 log K_{OC} units, respectively, which is slightly lower as compared to previously reported values for PFCAs (Guelfo and Higgins, 2013; Higgins and Luthy, 2006) and PFSAs (Milinovic et al., 2015; Higgins and Luthy, 2006). These differences may be due both to differences in the studied substrates, and in the compounds included in the regressions. For example, we covered most PFCAs having chain lengths between C_6 and C_{13}, while, e.g.

Higgins and Luthy (2006) covered PFCAs with chain lengths between C_7 and C_{10}. However, for the FTSAs, the Δlog K_{OC} values per additional CF_2 moiety observed in the present study (0.49 ± 0.13) were similar to those of Barzen-Hanson et al. (2017) for soils with lower organic carbon contents (0.10–7.7%). As for the role of PFAS head group type in the sorption behavior, the overall binding of the C_8 analogs onto SOM decreased in the order of EtFOSA > FOSA > 8:2 FTSA ≈ PFOS > PFNA (Table S12). Hence, the presence of an uncharged (*N*-ethyl) sulfonamide functional group (Rayne and Forest, 2009b) favored sorption over the presence of an anionic sulfonate or carboxylate head group, in agreement with previous work on sorption of anionic and neutral chemicals including PFASs (e.g. Nguyen et al., 2020). The similar binding strengths of 8:2 FTSA and its perfluorinated analog PFOS indicated that the hydrogenated spacer group (–CH_2CH_2–) of 8:2 FTSA did not contribute to its sorption behavior in any of the soils (Fig. 3, Fig. S11). This agrees with previous reports on the similarity of FTSA and PFSA mobility and changes in sorption upon changes in solution chemistry (Zhi and Liu, 2019). However, 6:2 FTSA was generally bound somewhat less strongly as compared to its perfluorinated analog PFHxS (Fig. S11).

The binding strength of EtFOSA was similar (Mor Oe and Peat Oe) or higher (Peat Oi) than that of FOSA (Fig. 3). Hence, the addition of an ethyl group to the –SO_2-NH- head group appeared to have enhanced the binding strength in some soils. However, more research is needed to more accurately assess the fate and transport of EtFOSA in the terrestrial environment.

3.4. Sorption of PFASs to the different organic soil materials

The overall sorption by the peat materials was stronger as compared to that of the mor layer for the majority of the PFASs, i.e. for PFCAs with a perfluorocarbon chain length of C_6, C_8–C_{11} and C_{13}, the FASAs (i.e. FOSA and EtFOSA), and 8:2 FTSA (Figs. 3 and 4, Fig. S10 in SI). For these PFASs, the overall sorption tended to decrease in the order of Peat Oi > Peat Oe > Mor Oe ($p < 0.05$, generalized linear mixed model). Generally, the difference in sorption of a specific PFAS between peat and mor layer material increased with the length of the perfluorocarbon chain within the PFCA subclass, and with the size of the functional head group (EtFOSA > FOSA) among the FASAs (Fig. 4, Fig. S10).

The overall larger sorption of PFASs to Peat Oi and Peat Oe as compared to that of the Mor Oe may be due to several factors. One possible explanation could be that the surface charge density differed between the three soil materials. However, the surface charge properties of the soils were similar according to its respective titration curve (Fig. S4) and its calculated surface net charge (Fig. S5). This indicates that the overall quality of SOM was the soil property that caused the difference in sorption behavior (Table 1 and Fig. S12). The quality among the soils reflected the origin and the pedogenic alteration of their SOM. For example, as compared to the two peat soils, Mor Oe was characterized by larger amounts of phenolic moieties (142–160 ppm of chemical shift), lignin and lipid compounds, and by a higher alkyl C to O-alkyl C ratio, indicating a stronger decomposition of its SOM (Baldock et al., 1997; Prietzel et al., 2018) and/or a higher contribution of lignin-like or woody substrates (Hedges and Oades, 1997; Normand et al., 2017). Furthermore, the abundance of carbohydrates decreased distinctly in the order of Peat Oi (72%) > Peat Oe (61%) > Mor Oe (42%), which is in accordance with the overall order of sorption affinity of the soils. Thus, although our study was limited to a small number of soils, our results suggested that the overall sorption of the majority of PFASs (i.e., C_6, C_8–C_{11} and C_{13} PFCAs, FASAs and 8:2 FTSA) was positively related to carbohydrate (O-alkyl) content and inversely related to phenolic (aromatic) moieties. This is in agreement with the findings of Zhao et al. (2014), who found that the binding of PFOS and PFHxS to three organic fractions was positively related to their aliphatic content and inversely related to their aromatic content.
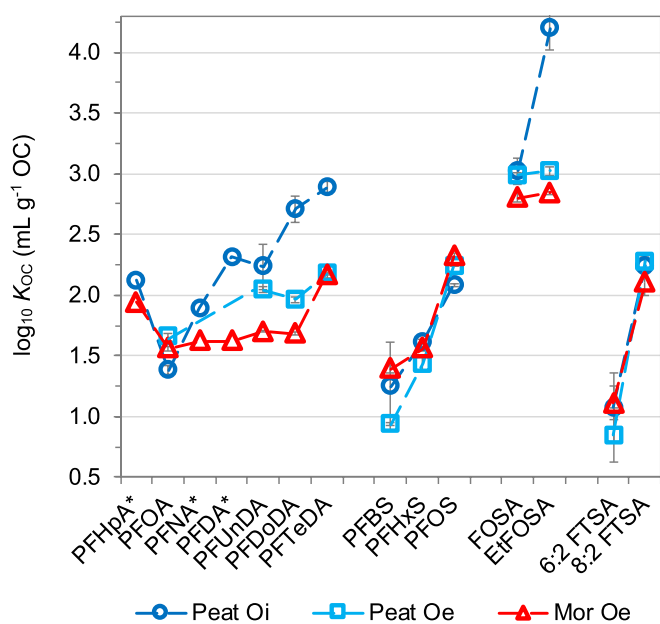

Fig. 4. Partitioning coefficients $\log_{10} K_{OC}$ (mL g^{-1} OC) at pH 4.2 ± 0.2, i.e. at pH values similar to the pH(H$_2$O) of the respective soil. See text for the meaning of the asterisk (*). Background electrolyte: 0.01 mol L^{-1} NaNO$_3$. Error bars represent the standard deviation ($n = 2$).

4. Conclusions

The pH-dependent binding of PFASs to the three organic soil materials could be related to changes in surface charge, assessed by geochemical modelling, which mainly was due to protonation of acidic functional groups. The pH/charge dependency increased as a function of perfluorocarbon chain length up to C_{10} (PFUnDA), probably due to increased charge interactions between the perfluorocarbon backbone and the substrate resulting from the negative charge ($\delta-$) present on the electronegative fluorine atoms. For more long-chained PFCAs, the hydrophobic effect caused by the perfluorocarbon chain possibly overrides this phenomenon, as a smaller pH/charge dependency was observed.

Sorption to the peat soils (Oi and Oe) was generally stronger as compared to that onto mor layer (Spodosol Oe) material. The three soils all had similar charge density properties, suggesting that the quality of SOM was the principal soil property explaining the different sorption behaviors of PFASs in this study. The carbohydrate content (O-alkyl C) was positively related to the overall binding. However, only three soils were included in our study and more research is needed to clarify the link between the quality of organic matter and its binding affinity for PFASs.

The two PFAS precursors 6:2 FTSA and 8:2 FTSA exhibited the same pH-dependent binding as their perfluorinated analogs PFHxS and PFOS, supporting the hypothesis that the perfluorocarbon chain length played an important role for the pH dependency. The binding strength was the same for 8:2 FTSA and PFOS, indicating that the hydrogenated spacer group ($-CH_2CH_2-$) of 8:2 FTSA did not contribute to its sorption behavior in any of the soils. For the shorter-chained 6:2 FTSA, inclusion of this group resulted in a slightly weaker sorption compared to PFHxS. Accordingly, the environmental behaviour of the two fluorotelomer sulfonates can be expected to be similar to that of their perfluorinated analogs.

Credit author statement

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.chemosphere.2022.134167.

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