Ecotoxicology and Environmental Safety 264 (2023) 115408

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

journal homepage: www.elsevier.com/locate/ecoenv

A systematic study of the competitive sorption of per- and polyfluoroalkyl substances (PFAS) on colloidal activated carbon

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ARTICLE INFO

Edited by Dr G Liu

Keywords:
PFAS
CAC
Contamination
Remediation
Groundwater
Soil
Sorption

ABSTRACT

Treatment of environmental media contaminated with per- and polyfluoroalkyl substances (PFAS) is crucial to mitigate mounting health risks associated with exposure. Colloidal activated carbon (CAC) has shown promise in treating contaminated soils, but understanding the interaction among PFAS during sorption is necessary for optimal remediation. This study investigated the extent to which PFAS of varying chain lengths and functional groups compete for sorption to CAC. Batch tests were conducted with natural soil and spiked water, using CAC at 0.2% w/w to remove seven PFAS with individual starting concentrations up to 0.05 mmol L^{-1}. PFAS sorption to CAC was evaluated in three systems: a composite mixture of all studied compounds, a binary-solute system, and a single-solute system. The sorption experiments exhibited strong PFAS affinity to CAC, with removal rates between 41% and 100%, and solid/liquid partition coefficients (K_d) between 10 and 10^4 L kg^{-1}. Differences were noticed among the various spiking mixtures, based on perfluorocarbon chain length, functional group, and the starting PFAS concentrations. Competition effects were detected when PFAS were in a multi-solute system, with an average 10% drop in removal, which can evidently become more relevant at higher concentrations, due to the observed non-linearity of the sorption process. The PFAS most vulnerable to competition effects in multi-solute systems were the short-chain perfluoropentanoic acid (PFPeA) and perfluorobutane sulfonic acid (PFBS), with an up to 25% reduction in removal. In bi-solute systems, perfluorooctane sulfonamide (FOSA) dominated over its ionisable counterparts, i.e. perfluorooctane sulfonic acid (PFOS) and perfluorononanoic acid (PFNA), indicating the importance of hydrophobic effects or layer formation in the sorption process. These results underscore the importance of considering competition in PFAS sorption processes when designing and implementing remediation techniques for PFAS-contaminated media.

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) comprise a broad group of emerging contaminants which have been extensively used in various commercial products and industries since the 1940s (Glüge et al., 2020). Serious health risks linked to PFAS exposure have been reported in the past decade, including alterations in immune and thyroid function, various cancer types, kidney and liver disease, and reproductive issues, while the toxicological profile of several PFAS is still uncertain (Fenton et al., 2021; Ojo et al., 2021). At the same time, their omnipresence in various environmental media (Zhao et al., 2012) and in biota (Åkerblom et al., 2017; Campo et al., 2016) has been well-documented, emphasising the need for active treatment strategies.

Although an increasing variety of technologies for the treatment of contaminated media exists, they often face challenges due to the recalcitrance of PFAS against degradation (Kissa, 2001). Even when degradation is feasible, for instance, through thermal treatment at temperatures > 1000 °C (Winchell et al., 2021), it can lead to the creation of by-products, including short-chain PFAS (Singh et al., 2019), which can be problematic due to their higher mobility (Li et al., 2020).

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https://doi.org/10.1016/j.ecoenv.2023.115408
Received 13 March 2023; Received in revised form 30 July 2023; Accepted 24 August 2023

Regarding soil treatment, another challenge is the strong adherence of PFAS to soils, which are the primary recipients and significant sinks of contamination (Brusseau et al., 2020; Sörengård et al., 2022). Specifically, PFAS tend to form bonds with soil particles, either due to hydrophobic interactions between the carbon tail and the soil organic matter or due to electrostatic interactions between the clay particles and the polar head group (Higgins and Luthy, 2006). Simultaneously, PFAS typically have a high solubility, which can lead to long groundwater plumes that are difficult to eliminate (Ross et al., 2018).

Considering the limitations of degradation and removal techniques, sorption methods have instead been in focus, aiming to contain PFAS and prevent their leaching from contaminated media into water sources (Darlington et al., 2018). Adsorption to activated carbons is effective both for the treatment of contaminated waters (Arias Espana et al., 2015) and soils (Mahinroosta and Senevirathna, 2020), with reported long-term effectiveness (Navarro et al., 2023). Utilising activated carbons for PFAS treatment comes with additional benefits, such as low operational costs (Høisæter et al., 2021; Mahinroosta and Senevirathna, 2020; Ross et al., 2018) and their ability to reduce PFAS uptake in biota (Bolan et al., 2021). Different types of activated carbon can be used in various matrices for PFAS treatment, such as granular activated carbon (GAC), powdered activated carbon (PAC), and carbon nanotubes (CNTs), with GAC being most commonly applied (Arias Espana et al., 2015; Darlington et al., 2018). One innovative material is colloidal activated carbon (CAC) which comprises a suspension of 1–2 μm carbon particles, often in combination with polymers, which makes it ideal for soil and groundwater treatment operations (McGregor, 2018).

The effectiveness of using CAC for soil and groundwater remediation has been recently demonstrated both in the laboratory (Navarro et al., 2023; Niarchos et al., 2022; Sorengard et al., 2019) and in the field (McGregor, 2020; Niarchos et al., 2023). When it comes to optimising immobilisation as a treatment technique, the solution chemistry, as well as the intrinsic properties of PFAS, are relevant. It has been well-established that sorption of PFAS to soils and activated carbons increases with increasing carbon chain length due to higher hydrophobicity (Ahrens and Bundschuh, 2014; Campos Pereira et al., 2018; Du et al., 2014; Higgins and Luthy, 2006; Milinovic et al., 2015; Park et al., 2020; Sorengard et al., 2019). Additionally, the functional head group has shown to have an effect, with perfluorosulfonic acids (PFSA) exhibiting higher sorption affinity than perfluorocarboxylic acids (PFCA) of the same perfluorocarbon chain length (Higgins and Luthy, 2006; Li et al., 2019; McCleaf et al., 2017).

Another critical aspect to consider is that oftentimes, a mixture of numerous PFAS exists in the solution, and consequently, there can be competition among them for the available sorption sites. Kah et al. (2021) hypothesised that competition effects were responsible for the release of PFAS from carbonaceous sorbents after treatment. Xiao et al. (2011) discussed that long-chain PFAS could negatively influence the adsorption of shorter-chain ones onto kaolinite due to the higher hydrophobicity of the former. Maimaiti et al. (2018) and Wang et al. (2019) investigated competitive sorption of PFAS to anion-exchange (AIX) resins and also suggested that competitive sorption was closely related to the hydrophobicity and functional head groups of PFAS, with PFSA outcompeting PFCA. Brusseau and Van Glubt (2019) studied the competition between PFOA and PFTrDA and showed a significant increase in surface activity in the presence of high concentrations of PFTrDA, which can increase adsorption at fluid-fluid interfaces. Elucidating the competition effects is therefore crucial for understanding the limitations of the sorption processes and optimising the relevant treatment techniques. McCleaf et al. (2017) have shown competitive sorption to GAC and AIX with desorption of shorter chain PFAS and enhanced sorption of PFTeDA. While competitive sorption has been indicated for sorption of PFAS in several materials and competition effects have been hinted in field applications of CAC, a systematic investigation of such effects has not yet been conducted.

The objective of this research was therefore to elucidate how the presence of other PFAS in the aqueous solution affects the sorption to CAC for a given PFAS. Seven PFAS, alone and in different combinations, were studied. Experiments were conducted in batch shaking tests, with CAC-treated soil as the solid phase and PFAS dissolved individually (single-solute system), in binary mixtures (bi-solute system), or in a mixture of all seven studied compounds (multi-solute system). Additionally, the study aimed to define adsorption coefficients and to observe the linearity of the process within environmentally relevant concentration ranges.

2. Materials and methods

2.1. Chemicals and materials

Seven PFAS were included in the study as native standards: three PFCA (perfluoropentanoic acid (PFPeA), perfluoroheptanoic acid (PFHpA), perfluorononanoic acid (PFNA)), three PFSA (perfluorobutane sulfonic acid (PFBS), perfluorohexane sulfonic acid (PFHxS), perfluorooctane sulfonic acid (PFOS)), and one perfluoroalkane sulphonamide (FASA) (perfluorooctane sulfonamide (FOSA)). The choice of PFAS was aimed at covering a variety of chain lengths, while including pairs consisting of the same C-F chain length but different functional groups, allowing for an investigation of the effect of functional group in competition. Specifically, for the C_8 PFAS, the ionisable PFNA and PFOS were compared to the non-ionisable FOSA. More information on the studied PFAS and their basic physicochemical properties are shown in Table 1. Additionally, isotopically-labelled internal standards were used for quantitation of the target PFAS: perfluoro-($^{18}O_2$)-hexane sulfonic acid ($^{18}O_2$-PFHxS), perfluoro-($^{13}C_4$)-octane sulfonic acid ($^{13}C_4$-PFOS), perfluoro-($^{13}C_2$)-hexanoic acid ($^{13}C_2$-PFHxA), perfluoro-($^{13}C_5$)-nonanoic acid ($^{13}C_5$-PFNA). All native and mass-labelled standards were purchased from Wellington Laboratories and had a purity > 98%. Other chemicals, including HPLC-grade methanol (purity > 99.9%) and calcium chloride anhydrous ($CaCl_2$, purity > 99.99%), were purchased from Sigma Aldrich.

The soil used in the experiments was sampled from central Sweden (59°23′13.7″ N, 15°53′48.2″ E), and consisted mainly of silt and a low fraction of clay and sand (for more information, see Table S1 in Supporting Information (SI)). After sampling, the soil was freeze-dried, ground with a mortar and pestle and sieved to remove bulky particles

Table 1
Basic physicochemical properties of the target PFAS, including their critical micelle concentrations (CMC).

Compound[a]	Molecular weight [g mol^{-1}][b]	Water solubility log S_w[b] [mol L^{-1}]	Acid dissociation constant pK[a]	CMC[c,d] [mmol L^{-1}]
PFPeA (C=4 *)	263.04	-0.37	-0.10[a] – 0.8[e]	700[c]
PFHpA (C=6 *)	363.05	-1.9	-0.20[a] – 0.82[e]	130[c]
PFNA (C=8 *)	463.07	-3.6	-0.2[a] – 0.82[e]	9.1[c]
PFBS (C=4*)	299.09	-1.0	-3.9[b] – 0.14[b]	-
PFHxS (C=6 *)	399.11	-2.2	-3.5[b] – 0.14[b]	-
PFOS (C=8*)	499.12	-3.9	-3.4[b] – 0.14[b]	8.0[c]
FOSA (C=8*)	499.15	-5.1	6.6[b]	0.039[d]

[*] C refers to the number of perfluoroalkyl chain length

[a] Ionized form for PFPeA, PFHpA, PFNA, PFBS, PFHxS, PFOS and neutral form for FOSA.

[b] Ahrens et al. (2012), pK_a estimated by SPARC model (version v4.5) predictions (25 °C).

[c] Kissa (2001).

[d] Costanza et al. (2020), CMC for FOSA in synthetic groundwater.

[e] Wang et al. (2011), pK_a estimated by COSMOtherm model (v.C2.1, release 01.10) predictions (25 °C).

(>2 mm). Based on initial screening, the soil was low in organic carbon (0.6%) (Table S2 in SI) and background PFAS concentrations (<0.16 µg kg^{-1}) (Table S3 in SI). The CAC used in the experiments was provided by Regenesis (PlumeStop®) and consisted of 20% activated carbon in a suspension. The CAC had a specific surface area (SSA) of 900 m^2 g^{-1}, iodine number ≈ 1000 mg g^{-1}, particle size 1–2 µm, and ζ potential − 80 – − 2 mV at pH 7 and ionic strength of 1–500 mM (Regenesis, personal communication, 2022), while it did not include polymers, in contrast with the commercially available version of PlumeStop®.

2.2. Adsorption experiments

The sorption of PFAS to CAC was evaluated through batch shaking tests. Competition effects were investigated by spiking the aqueous phase in three different ways; PFAS as single solutes (single-solute system), PFAS in binary pairs of the same C-F chain length and different functional groups (bi-solute systems), and PFAS in a mixture of all the seven targeted PFAS (multi-solute system). The pairs of PFAS in the bi-solute systems were PFPeA and PFBS (C4), PFHpA and PFHxS (C6), PFNA and PFOS (C8), PFNA and FOSA (C8), and PFOS and FOSA (C8). PFAS in single-solute systems were tested at five different starting concentrations (i.e. 0.002, 0.006, 0.015, 0.025, and 0.05 mmol L^{-1}). The concentration range was chosen to capture different environmentally relevant concentrations (Brusseau et al., 2020). For the multi-solute systems, the total PFAS concentrations were the same as in the single-solute; however, they were equally divided among the seven PFAS, resulting in individual concentrations of 0.0003, 0.0009, 0.0021, 0.0036, and 0.0071 mmol L^{-1}. The bi-solute systems were tested only at 0.025 mmol L^{-1} for each PFAS. All systems were evaluated by duplicate samples ($n = 2$), to evaluate the methodological error.

To conduct the experiments, 2.000 ± 0.003 g dry weight (dw) of soil were added to a 50 mL PP tube (Corning®), which was subsequently treated with 0.004 g of CAC, resulting in 0.2% weight for weight (w/w) CAC in the soil. The treatment concentration was in accordance with the manufacturer's recommendation, as it would correspond to injecting CAC at 0.1 g L^{-1} into the soil in up-scaled scenarios. The CAC-treated soil was homogenised by shaking, before being soaked with MilliQ® water and subsequently spiked with the appropriate PFAS mixtures and concentrations. The aqueous phase was also spiked with calcium chloride ($CaCl_2$) at 1 mM, as is typical in batch shaking tests (ISO, 2007). In total, 40 mL aqueous solution was prepared in 50 mL PP-centrifuge tubes, resulting in a liquid:solid ratio (L/S) of 20. Every sample, including blank samples, was agitated continuously in an end-over-end shaker for 14 days, which is reportedly sufficient for reaching equilibrium (Higgins and Luthy, 2006; Kupryianchyk et al., 2016).

2.3. PFAS analysis and quality control

On completion of the batch tests, all samples were centrifuged at 3000 rpm to separate the solid phase from the liquid phase. An aliquot of 500 µL of the supernatant was used for PFAS analysis after the addition of 100 µL internal standard (IS) and 400 µL HPLC-grade methanol and subsequent filtration through a 0.45 µm recycled cellulose (RC) filter (Sartorius®). The samples were analysed using ultra-performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS; Quantiva TSQ; Thermo Fischer Scientific, USA), injecting 10 µL on a BEH-C18 chromatographic column (1.7 µm, 2.1 mm × 50 mm, Waters) for separation. The UPLC-MS/MS analysis data were evaluated using TraceFinder™ (Thermo Fischer Scientific). PFAS concentrations were quantified using a nine-point calibration curve (0.01–100 ng mL^{-1}).

For quality control, duplicate negative blanks were prepared for the aqueous phase without soil ($n = 2$), the aqueous phase with soil ($n = 2$), and the soil with added CAC ($n = 2$). Method detection limits (MDL) were defined by using the concentrations found in negative blanks, as $MDL = mean_{blanks} + 3 * \sigma_{blanks}$, or by using the lowest point of a 9-point calibration curve (Table S4 in SI). The average recoveries of IS were 98% ± 11% (Table S5 in SI).

2.4. Data evaluation

The adsorption efficiency was determined by estimating the change in the retention of PFAS (%) by CAC. The removal of PFAS from the aqueous phase by adsorption to CAC was calculated by comparing the concentrations detected in the aqueous phase (C_w) with the nominal starting individual PFAS concentrations (C_{in}), according to *(1)*.

$$Removal = (1 - C_w/C_{in}) \quad x100\% \tag{1}$$

Solid-liquid partitioning coefficients (K_d, L kg^{-1}) were calculated as the distribution based on concentrations in the liquid and in the solid phase, according to *(2)*. The K_d values were first calculated based on specific concentrations (single-point K_d values). In some cases, and concentration ranges, linear isotherms could describe the data, but more often the sorption was non-linear, meaning that K_d was dependent on concentration.

$$K_d = C^*/C_w \tag{2}$$

where C^* is the individual PFAS concentration in the sorbed phase (including soil and carbon), calculated as the difference between the initial concentration and the concentration in the aqueous phase, and C_w is the concentration that was measured in the aqueous phase at equilibrium.

3. Results and discussion

3.1. Adsorption efficiency

Variations in the percent removal of PFAS from the aqueous phase were observed, contingent on whether PFAS were tested individually or in a composite mixture (Fig. 1). The removal efficiency was, on average 77% ± 7.8% in the single-solute system for all PFAS, compared to 67% ± 7.1% in the multi-solute system, suggesting the influence of competition effects on the sorption behaviour, while these effects varied for different PFAS. The removal rates for individual PFAS ranged between 99.8% (FOSA at $C_{w,ref} = 0.002$ mmol L^{-1}) and 41% (PFOS at $C_{w,ref} = 0.05$ mmol L^{-1}) for the single solute system, while for the multi solute system the removal was between 99.8% (FOSA at $C_{w,ref} = 0.0003$ mmol L^{-1}) and 44% (PFOS at $C_{w,ref} = 0.007$ mmol L^{-1}). In addition, the highest removal, on average, was found for FOSA (97%), PFPeA (87%), and PFHpA (87%) in the single-solute system, and FOSA (99%), PFHpA (73%), and PFOS (69%) in the multi-solute system. It is important to consider that a certain overestimation of the removal rates is expected, especially for long-chain PFAS, due to losses on container walls (Zenobio et al., 2022).

Since the initial concentration ranges were different between single- and multi-solute systems, a more accurate comparison was performed for the PFAS concentration of 0.002 and 0.006 mmol L^{-1}, respectively. When comparing these concentrations for individual PFAS between the two systems, the removal was, on average, 10% higher in the single-solute compared to the multi-solute system. Specifically, for the lower C_{in} (0.002 mmol L^{-1}), the removal was 8.2% ($p = 0.093$) higher in the single-solute system, while for the higher C_{in} (0.006 mmol L^{-1}), the same figure was 12% ($p = 0.027$), indicating that competition effects can become significant at higher concentrations. The biggest contrast between the multi- and single-solute systems was noticed for the short-chain PFPeA and PFBS, showing a reduction in removal efficiency of 25% and 24%, respectively. This suggests that short-chain PFAS were more susceptible to competition in the multi-solute system, likely due to the higher affinity of long-chain PFAS for CAC, which could outcompete their short-chain homologues during sorption, as has been observed in previous studies (Niarchos et al., 2022; Sorengard et al., 2019). Alternatively, the weaker electrostatic interactions of shorter-chain PFAS

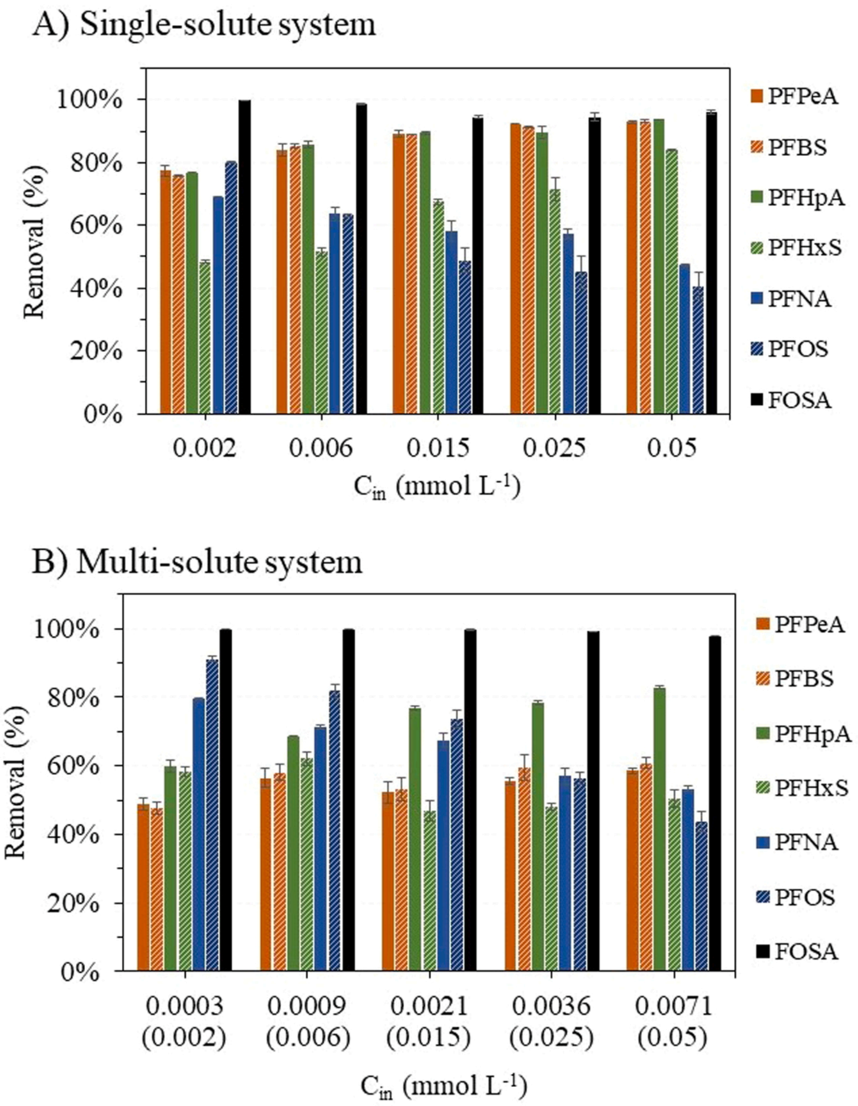

Fig. 1. Removal efficiency (%) for the target PFAS in a A) single-solute system, where PFAS were spiked individually, and in a B) multi-solute system spiked with all seven targeted PFAS, each having a different starting concentration (C_{in}). The values in parentheses on the horizontal axis of the multi-solute system correspond to the total PFAS concentrations for that system. Error bars represent the standard deviation of duplicate samples.

compared to the hydrophobic interactions that dominate sorption of longer-chain PFAS may also contribute to the differences in sorption behaviour.

Regarding differences based on perfluorocarbon chain length, higher removal rates were found for long-chain PFAS at low concentrations in the multi-solute compared to the single-solute system, supporting findings from other PFAS sorption studies (Campos Pereira et al., 2018; Hansen et al., 2010; Kupryianchyk et al., 2016; Sörengård et al., 2020). However, these results were not corroborated by the single-solute system, which, apart from FOSA, exhibited increased removal for short-chain PFAS and sometimes higher than their long-chain homologues. For instance, PFHpA had a higher removal than its long-chain homologue PFNA in the single-solute system at the highest concentration (94% vs 47%, respectively, at $C_{in} = 0.05$ mmol L^{-1}). This observation hints at the possibility that a portion of the adsorption sites may be reserved for specific PFAS due to the presence of steric effects, which has been previously documented in studies involving C_3-C_7 perfluorocarbon PFAS (Guelfo and Higgins, 2013; Sorengard et al., 2019).

Regarding differences among functional groups, the only tested FASA exhibited the highest removal of all investigated PFAS. Specifically, FOSA has a much higher pK_a value (6.6) than the rest of the PFAS (Table 1) and is therefore expected to be present in its neutral form within the studied pH range (≈7), therefore, the strong sorption of FOSA can be attributed to hydrophobicity, rather than electrostatic effects. Additionally, FOSA seemed to be relatively unaffected by the presence of other PFAS in solution (Fig. 1 B), showing resilience to competition. In contrast, stronger competition effects were observed between PFCA and PFSA in the multi-solute system, with the former exhibiting higher removal rates on average than the latter. This finding was unexpected, given that PFSA are known to have higher hydrophobicity, as the hydrophobic moiety constitutes a slightly larger part of the molecule (Higgins and Luthy, 2006). However, it is possible that the effect of hydrophobicity is concentration dependent, as at lower concentrations, the more hydrophobic PFAS dominated, but this shifted with increasing C_{in}.

Regarding the effect of C_{in} on sorption, it has been suggested that saturation of sorption sites can result in decreased removal at higher concentrations (Maizel et al., 2021; Niarchos et al., 2022); however, this phenomenon was not consistently corroborated in all cases and the PFAS removal demonstrated varying dependencies on starting concentrations. For short-chain PFAS, the removal was directly correlated with C_{in}, while for long-chain compounds, the opposite trend was noticed in both systems (see Table S6 in the SI). It is worth noting that starting concentrations can influence the formation of micelles and, consequently, PFAS sorption. The concentrations tested in this study are generally below the CMC of most PFAS (Table 1), except for FOSA, suggesting that the presence of FOSA in the mixture could potentially lead to increased adsorption through multi-layer formation. However, hemi-micelles can also form at concentrations tens to thousands of times lower than the CMC (Johnson et al., 2007); therefore, these factors may explain the unexpected sorption behaviours observed, particularly for PFAS that show increased removal at higher concentrations.

3.2. Competition in bi-solute systems

A more detailed understanding of competition effects based on functional group was obtained through bi-solute batch tests, comparing pairs of PFAS with the same chain length but different functional groups. The studied PFAS pairs included FOSA vs PFOS, FOSA vs PFNA, PFOS vs PFNA, PFHpA vs PFHxS, and PFPeA vs PFBS, representing compounds with the same perfluoroalkyl chain length but different functional groups. Differences between sorbed concentrations in single- and bi-solute systems were observed, with the functional group exhibiting an influence on the sorption for certain PFAS (Fig. 2). It is important to consider that the bi-solute systems occurred at double the total PFAS concentration compared to the single-solute ones, which could have a bearing on the sorption behaviour.

The differences between functional groups were more noticeable for the long-chain PFAS (C=8) but less for the short-chain PFPeA and PFBS. Both PFOS and PFNA exhibited lower sorbed concentrations in the bi-solute system compared to the corresponding concentrations in the single-solute system. In addition, PFOS showed a weaker sorption when it was in the solution with FOSA, with a 43% decrease of sorption in the bi-solute system. The observation that predominantly neutral molecules can exhibit stronger sorption than their ionisable C_8 counterparts (PFNA and PFOS), aligns well with the pattern of the multi-solute system, and indicates the importance of hydrophobic interactions for long-chain PFAS, which is likely the primary driving force for FOSA, rather than

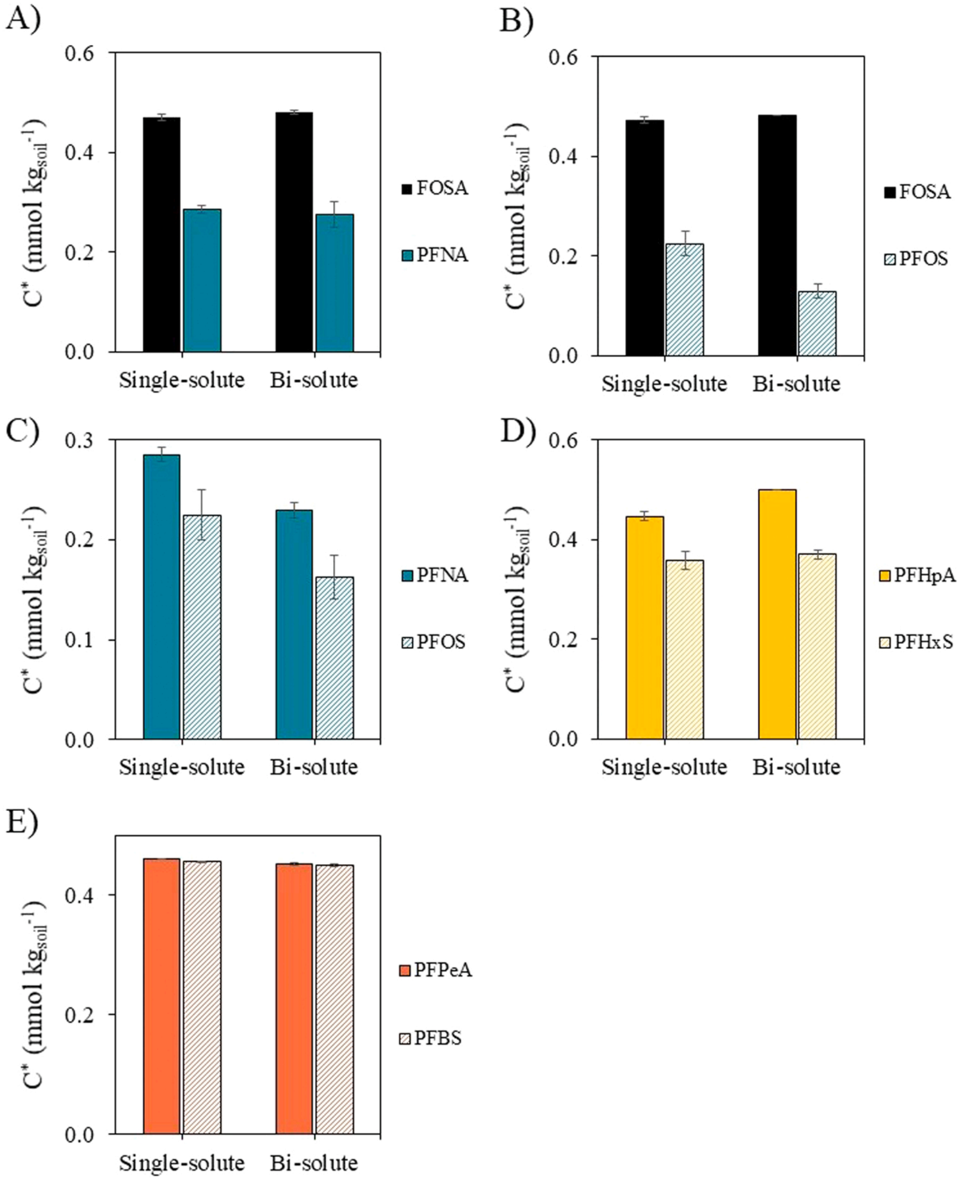

Fig. 2. Sorbed concentrations in treated soil in single- and bi-solute systems for the five studied PFAS pairs: A) FOSA vs PFNA, B) FOSA vs PFOS, C) PFNA vs PFOS, D) PFHpA vs PFHxS, E) PFPeA vs PFBS. The starting concentration was 0.025 mmol L^{-1} for individual PFAS, resulting in a total concentration of 0.05 mmol L^{-1} for the bi-solute system (i.e. double the total concentration used in the single-solute system). The error bars indicate the standard deviation of duplicate samples.

electrostatic interactions. This finding aligns well with other studies that also emphasize the significance of hydrophobic interactions (Cai et al., 2022; Miao et al., 2017; Sorengard et al., 2019). Synergistic effects were not suggested from the bi-solute system sorption, apart from PFHpA, which had a low increase of C* in the bi-solute system.

3.3. Isotherms and partitioning coefficients

To better understand the affinity of the solutes for the sorbent at different concentrations, the sorbed concentration (C*) was plotted as a function of equilibrium concentration in the aqueous phase (C_{eq}) for each PFAS, using five different concentrations, for both the single- and

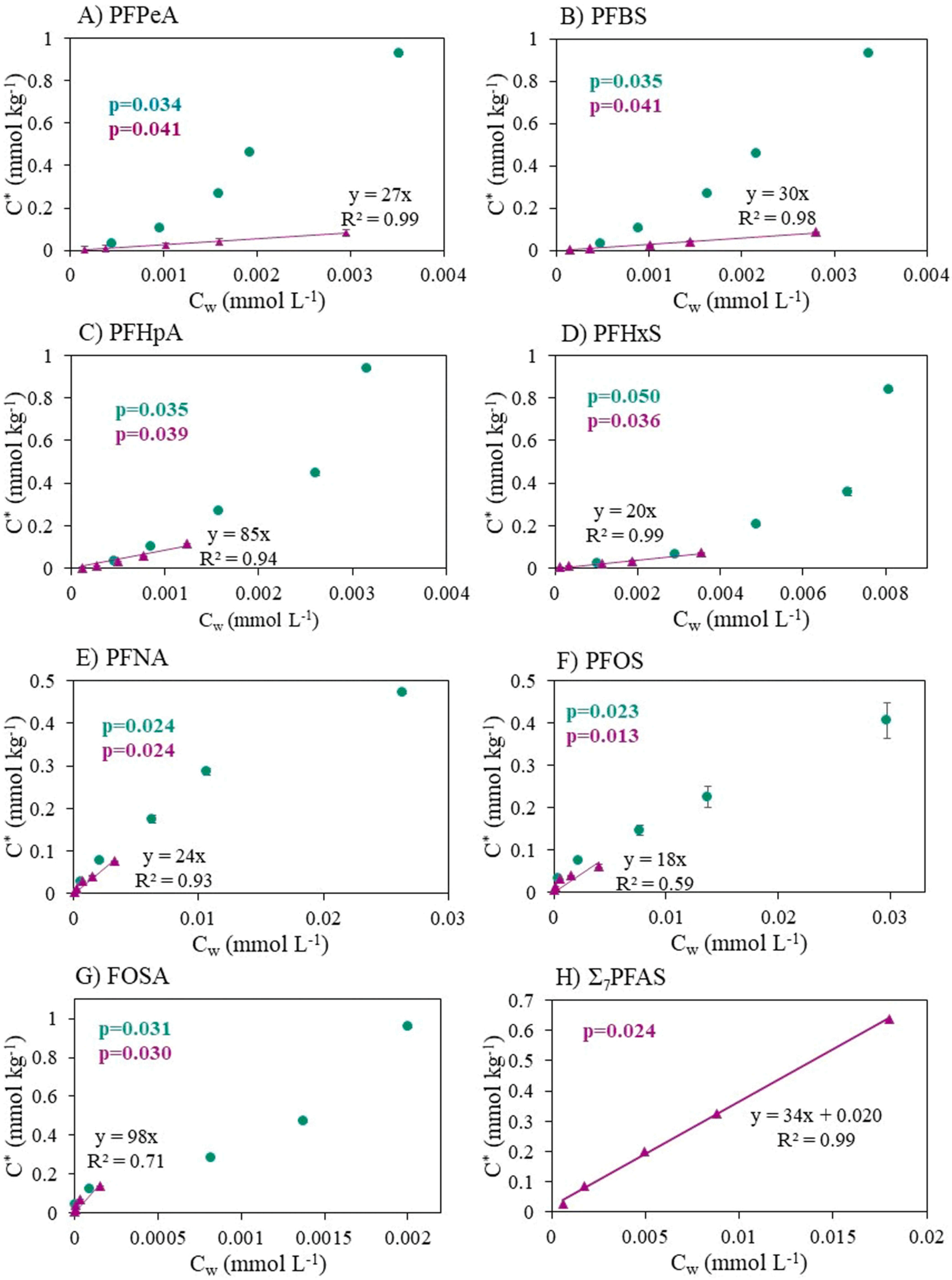

Fig. 3. Distribution isotherms between sorbed concentrations in the treated soil (C*) and individual PFAS dissolved concentrations (C_w) of A) PFPeA, B) PFBS, C) PFHpA, D) PFHxS, E) PFNA, F) PFOS, G) FOSA, and H) $\sum_7$PFAS are shown for both single-solute (●) and multi-solute (▲) systems. The linear fit is displayed for multi-solute systems. Each data point represents the average of duplicate data and the error bars indicate the standard deviation.

the multi-solute systems (Fig. 3). In the case of PFPeA and PFBS, the shortest of the tested PFAS, the sorption was notably stronger in the single-solute system compared to the multi-solute system (Fig. 3A, B), suggesting that these two PFAS face competition from other PFAS present in the system, leading to reduced adsorption. Conversely, for PFHpA, PFHxS, PFNA, and PFOS, the isotherms of the multi- and single-solute systems had similar slopes (Fig. 3C-F), indicating low competition.

In the multi-solute system, PFBS, PFPeA, PFHxS, and the $\sum_7$PFAS exhibited linear sorption behaviour within the range of tested concentrations, with a Pearson's correlation of $R^2 > 0.98$ (Fig. 3). Conversely, non-linear behaviour was observed for all PFAS in the single-solute system, where higher concentration ranges were tested. This non-linear trend in single-solute sorption was statistically significant, with p values ranging from $2.2 * 10^{-5}$ to $8.2 * 10^{-4}$. Additionally, in some cases, (e.g., PFNA and PFOS in single-solute systems), the distribution shifted towards the aqueous phase (lower K_d – see also Fig. 4) at higher concentrations, while in other cases (e.g., PFPeA, PFHpA, PFBS, PFHxS in single-solute systems), the distribution shifted towards the sorbed phase (higher K_d – see also Fig. 4) at higher concentrations. This suggests that sorption is somehow enhanced at higher concentrations, potentially triggered by layer- or hemi-micelle formation (Johnson et al., 2007). Why the non-linear trend is different for different PFAS in the single solute systems is not clear, however, this may indicate that different size molecules interact differently with the porous surface of CAC. A similar contrasting non-linear sorption behaviour for different PFAS was observed by Deng et al. (2012) for PFAS sorption to single-walled carbon nanotubes.

The partitioning coefficients, showed a pattern similar to the isotherms, with K_d values ranging between 10 and 10^4 L kg^{-1} (Fig. 4), comparable to values reported in the literature for CAC-treated soil (Niarchos et al., 2022; Sorengard et al., 2019). In the multi-solute system, K_d values were significantly lower than in the single-solute system for all PFAS at similar concentrations; on average for all PFAS, this difference in K_d was 0.19 ± 0.19 log units lower at $C_{in} = 0.002$ mmol L^{-1} ($p = 0.043$) and 0.3 ± 0.2 log units lower at $C_{in} = 0.006$ mmol L^{-1} ($p = 0.016$) (see also Fig. S1 at SI). Considering the observed correlation between C_{in} and the non-linearity of the isotherms, it is possible that such differences could become more relevant at higher individual PFAS concentrations, however, this remains to be elucidated further.

It is noteworthy that there was a significant correlation between sorption strength and the starting PFAS concentration for all PFAS in both systems ($p < 0.0008$). Specifically, the long-chain PFNA, PFOS, and FOSA exhibited comparatively lower K_d values at higher concentrations (up to 1.3 log units decrease in K_d), while for PFAS with $C < 7$ in

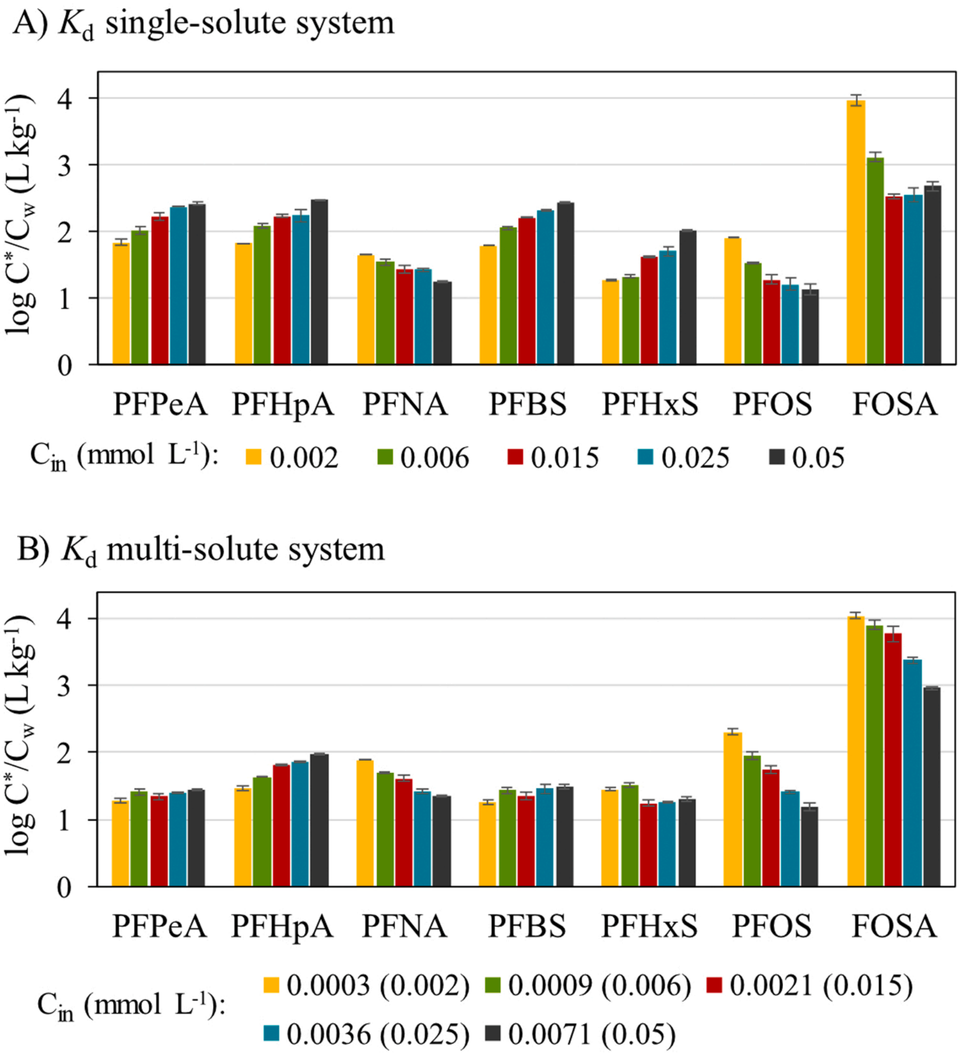

Fig. 4. Treated soil-water partitioning coefficients (K_d values) for PFAS in A) the single-solute system and B) the multi-solute system. C^* refers to the sorbed concentration, C_w to the dissolved concentration at equilibrium, and C_{in} to the starting concentrations. The values in parentheses in B) represent the $\sum_7$PFAS concentrations in the multi-solute system.

their perfluorocarbon chain, the K_d increased at higher concentrations by up to 0.7 log units. Additionally, strong affinity of FOSA to CAC was observed, which had the highest K_d values in both systems (Fig. 4). The strong affinity of FOSA to CAC has been corroborated by Sorengard et al. (2019), further supporting the importance of hydrophobic interactions during CAC sorption. In the single-solute system, PFOS and PFNA had low K_d values compared to other PFAS, however, the aforementioned trends were still noticeable.

4. Conclusions

This study examined the competition among seven PFAS during sorption on CAC-treated soil, revealing stronger sorption during individual compound testing compared to PFAS composite mixtures, thus indicating the presence of competition effects. Based on a systematic analysis, these effects varied based on perfluorocarbon chain length, functional group, as well as the starting concentrations.

In the multi-solute system, PFAS removal due to CAC sorption was 8–12% lower than in the single-solute system on average for all PFAS, with competition becoming more pronounced at higher concentrations. Notably, short-chain PFAS were more vulnerable to competition, showing a reduction of up to 25% in removal when present in the solution with other PFAS. Competition was also evident when observing C^* as function of C_w, with clear reduction in sorption strength for the short-chain PFPeA and PFBS in multi-solute systems. Non-linear behaviour became more pronounced at higher concentrations, indicating an increasing relevance of competition effects at those elevated concentrations. Overall, the starting concentrations significantly influenced the sorption behaviour, with short-chain PFAS displaying increased sorption at higher concentrations, while long-chain PFAS exhibited the opposite trend.

PFAS pairs were tested in the bi-solute experiments, which indicated significant competition among different functional groups for long-chain PFAS. PFOS and PFNA appeared to be the most vulnerable to competition effects in the bi-solute systems, while FOSA dominated over its ionisable counterparts. The strong sorption of the primarily neutral FOSA compared to the other PFAS indicated the dominance of hydrophobic effects over electrostatic ones in the adsorption process. Synergistic effects were also observed but did not reach a significant level to affect sorption. However, it is plausible that such effects could become more prominent at higher concentrations, potentially due to micelle formation. To explore this further, investigations at concentrations higher than those tested in this study would be necessary.

Overall, the results highlight the complexity of interactions among PFAS during sorption to CAC, which can vary depending on their intrinsic properties. Such interactions should be taken into careful consideration during treatment operations, based on the PFAS fingerprint involved. It should be noted that the results of this study focus on treatment with CAC, and thus may differ with other materials, governed by different adsorption mechanisms. However, the competitive effects identified here could also have implications on the PFAS mobility in the environment and bioaccumulation potential. It is also important to consider that this study used only one soil that was dominated by silt and had low organic carbon content; hence the behaviour in other soils might differ. Lastly, competitive and possibly synergistic effects can arise not only among different PFAS but also with other substances present in the solution. Future studies should therefore prioritise further elucidating competition effects, including interactions with hydrocarbon surfactants or dissolved organic carbon, which are commonly found at PFAS-impacted sites.

CRediT authorship contribution statement

Georgios Niarchos: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Project administration, Software, Supervision, Validation, Visualization, Writing – original draft. **Linnea Georgii**: Methodology, Writing – review & editing. **Lutz Ahrens**: Methodology, Resources, Supervision, Writing – review & editing. **Dan Berggren Kleja**: Supervision, Writing – review & editing. **Fritjof Fagerlund**: Data curation, Funding acquisition, Methodology, Supervision, Writing – review & editing.

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.

Data Availability

Data will be made available on request.

Acknowledgements

This work was financially supported by TUFFO – a research and innovation program on contaminated sites managed by the Swedish Geotechnical Institute (SGI) – through the StopPFAS project (1.1-1708-0501).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ecoenv.2023.115408.

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