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Differential Sorption of Short-Chain versus Long-Chain Anionic Per- and Poly-Fluoroalkyl Substances by Soils

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Abstract: The impact of chain length on the sorption of anionic PFAS by soils and sediments was investigated by aggregating and synthesizing data sets from the literature. Quantitative structure/property relationship (QSPR) analysis was applied to characterize the influence of molecular size and soil properties on sorption. The log of the organic carbon-normalized equilibrium sorption coefficient (K_{oc}) exhibited a biphasic relationship with molar volume, wherein the log K_{oc} values for the short-chain PFAS were generally greater than would be predicted using the QSPR correlation determined for the long-chain PFAS. This enhanced differential sorption is observed to different degrees for all studies, which are compiled and synthesized for the first time. The results reveal remarkable congruency across a wide array of soils comprising a large range of properties and indicate that the observed enhanced differential sorption of short-chain PFAS is a prevalent phenomenon. Aggregating the long-chain PFAS data for all soils and sediments with organic carbon contents > 1% produced a strong correlation, indicating that the resultant QSPR model can produce representative log K_{oc} values irrespective of the other properties of the medium. Silt+clay content was shown to be an important soil component for the short-chain PFAS for most soils, as well as the long-chain PFAS for soils with organic carbon contents < 1%. The results indicate that while the simple K_{oc} - f_{oc} approach may produce reasonable estimates of K_d values for long-chain anionic PFAS, particularly for soils and sediments with larger organic carbon contents, it is unlikely to do so for short-chain anionic PFAS.



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Keywords: PFCAs; PFSAs; PFOS; PFOA; retention; chain length

1. Introduction

Numerous field studies have demonstrated the presence of per- and poly-fluoroalkyl substances (PFAS) in soils and sediments across the globe, as reported in a recent meta-analysis [1]. A critical concern for sites with PFAS soil contamination is the potential for leaching through the vadose zone to groundwater and the subsequent impairment to groundwater quality, which may lead to possible risk of human exposure for downgradient end users. Understanding the retention and transport behavior of PFAS in soils and aquifer media is central to effective and accurate characterization and quantification of contamination and exposure risks.

Risks posed by soil contamination to groundwater quality are commonly assessed by the determination of soil screening levels (SSLs). The most widely used approach for determining SSLs for the soil-to-groundwater exposure pathway is the U.S. EPA's Dilution-Attenuation Factor model [2]. This model is based on the assumption that sorption by soil is the primary source of retention. Sorption is quantified through the use of the equilibrium sorption coefficient (K_d). The default method used to determine K_d values for organic contaminants is the K_{oc} - f_{oc} approach (i.e., $K_d = K_{oc}f_{oc}$), where K_{oc} is the organic carbon normalized sorption coefficient, and f_{oc} is the fraction of organic carbon [2]. This method is widely used for estimating K_d values for exposure assessments [3–5] and for modeling contaminant transport in soil and groundwater [6–8]. This approach is predicated on the assumption that sorption is mediated solely by the organic carbon fraction of the

soil and is governed by the hydrophobic interaction mechanism. Concomitantly, K_{oc} is generally assumed to be a function of and correlate to molecular properties that govern the hydrophobic interaction of the compounds, such as chain length in the case of PFAS. As recently noted, a critical question to address is whether or not this approach is representative of the retention and transport of PFAS [9,10].

PFAS are amphiphilic molecules containing fluoroalkyl groups of different chain lengths and structures. The chain length, which is commonly used as a surrogate term to represent molecular size, has been demonstrated to influence the distribution and fate of PFAS in the environment. For example, multiple field studies reporting PFAS soil concentrations have shown that the highest concentrations of longer-chain PFAS tend to be closer to the land surface, whereas the highest concentrations of shorter-chain PFAS typically reside at greater depths, indicating differential rates of retention and leaching as a function of chain length [1,11,12]. The impact of chain length on the sorption of PFAS by soils and sediments has been investigated in several laboratory studies. Greater sorption is typically observed for longer-chain PFAS, and in some cases, correlations have been reported between $\log K_d$ or $\log K_{oc}$ and chain length properties such as molecular weight [13], fluorinated carbon number [14–18], and molar volume [19]. However, the sorption of short-chain PFAS has been observed in some studies to deviate from the chain length correlations determined for long-chain PFAS [13,15,16,18]. These observations indicate that a singular chain length function may not be adequate for shorter-chain PFAS, which has significant implications for the estimation of sorption coefficients using the standard K_{oc} approach or other methods employing simple singular functions.

Interest in the transport and fate behavior of short-chain PFAS has heightened recently because of their use as replacements for long-chain legacy PFAS. Considerable concern exists over their use in part because of their anticipated greater mobility in the environment [20,21]. Hence, it is critical to investigate the sorption of short-chain PFAS and to determine the prevalence of the observed deviation from the chain length dependence measured for long-chain PFAS. This knowledge is needed to support robust site characterization, risk assessment, and mathematical modeling efforts.

The objective of this research is to conduct an assessment of the sorption of PFAS by soils and sediments, focused on examining observed differences between short-chain and long-chain constituents. Data sets comprising measured sorption of both long- and short-chain PFAS are aggregated and synthesized from the literature. The analysis is focused on anionic PFAS, the class for which the most data are available. Quantitative structure/property relationship (QSPR) analysis is applied to characterize the influence of molecular size and soil properties on sorption. A novel aspect of this work is the compilation and aggregation of all relevant data sets to examine integrated correlations of K_{oc} to chain length for both short-chain and long-chain PFAS. These analyses provide new insights into the influence of chain length and soil properties on PFAS sorption.

2. Methods

Standard search engines were used to identify relevant studies. The search was focused on identifying works that reported laboratory measurements of sorption for multiple long- and short-chain PFAS within the same study. Six studies were identified that matched the focus criterion. An additional 5 studies were identified that investigated the sorption of three or more long-chain, but no short-chain, PFAS. The 11 studies are listed in Table 1. All data sets were generated using some version of batch sorption methods described in the source works.

Table 1. Literature data sets and properties of the media used in the experiments.

Study	# Media	OC ^a (%)	Silt+Clay ^b (%)	pH	C ₀ ^c
<i>Studies reporting data for both long- and short-chain PFAS</i>					
[16] Guelfo and Higgins, 2013 ^d	3	0.8–4.5	10–67	5.2–7.8	5 nM
[17] McLachlan et al., 2019 ^e	2	0.4/0.93	0/29	5.2/5.7	5 µg/L
[18] Sorengard et al., 2019 ^f	10	0.4–22	4.6–65 ^e	5.0–7.7	low µg/L
[15] Gredelj et al., 2020 ^g	1	1.43	38/15	7.8	low µg/L
[13] Nguyen et al., 2020 ^h	10	0.08–4.9	6–83	6.2–7.7	low µg/L
[14] Fabregat-Palau et al., 2021 ⁱ	7	1.6–41	45.6–85.8	5.2–8.0	<70 µg/L
<i>Studies reporting data for only long-chain PFAS- 5 or more data points</i>					
[22] Higgins and Luthy, 2006 ^j	5	0.6–9.7	20–89	5.7–7.6	5 nM
[23] Chen et al., 2016 ^k	1	2.5	96	7.6	2.5 µg/L
[24] Campos-Pereira et al., 2023 ^l	6	1.1–3.1	14–96	4.6–8.2	low µg/L
<i>Studies reporting data for only long-chain PFAS- 3 data points</i>					
[25] Mejia-Avendaño et al., 2020 ^m	5	1.7–7.3	41–80	4.5–8.2	10 nM
[26] Oliver et al., 2020 ⁿ	15	1.1–11.2	7–68	6.2–7.7	low µg/L

^a Organic carbon content; ^b Silt and clay content; ^c Concentration used to determine K_d or K_{oc}; ^d K_{oc} determined from K_ds reported in their Table S8 and their reported OCs; ^e K_{oc} determined from K_ds reported in their Table S9 and their reported OC; ^f K_{oc} reported in their Figure S7B; ^g K_{oc} determined from K_ds reported in their Table S15 and their reported OC; ^h K_{oc} reported in their Table S7, K_{oc} for individual data sets determined from K_ds reported in their Table S6 and their report OCs and all data are for the native soil pH; ⁱ K_{oc} determined from K_ds reported in their Table 2 and their reported OCs; ^j K_{oc} reported in their Table 2; ^k K_{oc} reported in their Table 1; ^l K_{oc} reported in their Table A8 and all data are for the native soil pH; ^m K_{oc} reported in their Table S4; ⁿ K_{oc} reported in their Figure 4.

Three additional studies were identified that reported measurements of PFAS sorption by organic media, specifically humin [27] and peat [28,29]. These data are used to determine benchmark values for log K_{oc} under the assumption that soil organic carbon controls PFAS sorption for these organic-based media. Benchmarks are determined for those PFAS for which measurements are reported for at least three media each. Benchmarks are thus obtained for three PFAS, PFOS, PFOA, and PFHxS. The soil data will be compared to these benchmark values.

Acronyms for all PFAS included in the analyses are presented in Table 2. The standardized nomenclature for chain length is employed, wherein short-chain PFCAs and PFASs are defined as those with n < 7 and n < 6 fluorinated carbons, respectively [30]. The methods used for the QSPR analyses are those described in Brusseau [31]. Molar volume (V_m) is used as the molecular descriptor and has been used successfully in prior PFAS studies [19,31].

Table 2. PFAS acronyms.

PFAS
Perfluorobutanoate, PFBA
Perfluoropentanoate, PFPeA
Perfluorohexanoate, PFHxA
Perfluoroheptanoate, PFHpA
Perfluorooctanoate, PFOA

Table 2. *Cont.*

PFAS
Perfluorononanoate, PFNA
Perfluorodecanoate, PFDA
Perfluoroundecanoate, PFUnDA
Perfluorododecanoic acid, PFDoA
Perfluorobutanesulfonate, PFBS
Perfluoropentanesulfonate, PFPeS
Perfluorohexanesulfonate, PFHxS
Perfluoroheptanesulfonate, PFHpS
Perfluorooctanesulfonate, PFOS
Perfluorononanesulfonate, PFNS
Perfluorodecanesulfonate, PFDS

3. Results and Discussion

3.1. Data Sets

Data are aggregated from six batch-mode studies that examined the sorption of multiple long- and short-chain PFAS by soils. Additional data are aggregated from five studies that reported measurements for three or more long-chain PFAS. These 11 studies are identified in Table 1. The number of media included in each study varies from 1 to 15. Most studies used soils, whereas three reported data for surface water sediments [22,23,26]. The latter five data sets are used for specific analysis of chain length effects for sorption of long-chain PFAS by soils and sediments with OC > 1%. For the Oliver et al. study, only data for the 15 media with OC > 1% were used. The data set for Higgins and Luthy includes one medium with an OC < 1%. The inclusion of this single set of data has minimal impact, given the large number of total media included in the analyses. In total, the soils and sediments included in the analysis comprise a very wide range of properties (Table 1), with greatly different organic carbon contents (0.08–41%), silt+clay contents (0–96%), and pHs (4.5–8.2).

Variations in batch sorption methods were used between the studies. Sorbed mass was determined by the difference in initial and final solution concentrations for some and by measurement of both solution and sorbed concentrations for others. Some studies employed multi-point isotherms, whereas others conducted single-concentration measurements. Two studies measured desorption for synthetically aged soils [18,24].

The vast majority of the studies directly reported K_{oc} values, which were used as reported. The few remaining studies reported K_d values, from which K_{oc} values were calculated using the reported f_{oc} s. Several of the studies plotted $\log K_d$ and/or $\log K_{oc}$ values as a function of chain length properties. Notably, the mean values determined for all media employed in the respective studies were used for the data plotting and discussions reported in the source works. Data for individual media and sub-sets of media were not discussed in the source works but are examined herein to provide additional investigation into sorption processes.

As noted, some of the studies measured sorption isotherms. The results indicated that sorption was a function of concentration in some cases. Nonlinear sorption complicates the determination and comparison of K_d and K_{oc} values. This is especially true when comparing results from multiple studies that use different ranges of concentrations for the measurements. It is further complicated by the uncertainty associated with sorption measurements for those studies that employed single-concentration experiments, as the potential for nonlinear sorption is indeterminate. This issue was specifically dealt with herein by ensuring that K_d and K_{oc} values were determined for a consistent narrow range of concentration, specifically the low (primarily single-digit) $\mu\text{g/L}$ range (see Table 1).

3.2. QSPR Analyses of Integrated Data Sets

The combined data sets for the six studies with measured values for both long- and short-chain PFAS are presented in Figure 1 as log K_{oc} versus molar volume. The log K_{oc} values for the long-chain PFAS are observed to correlate well to molar volume, consistent with prior observations [19]. Conversely, the short-chain PFAS clearly deviate from the QSPR correlation determined for the long-chain PFAS (Figure 1), exhibiting greater magnitudes of sorption than would be predicted. This phenomenon will be referred to herein as enhanced differential sorption, given that different (greater) magnitudes of sorption are observed for the short-chain PFAS compared to that predicted with the long-chain QSPR correlation.

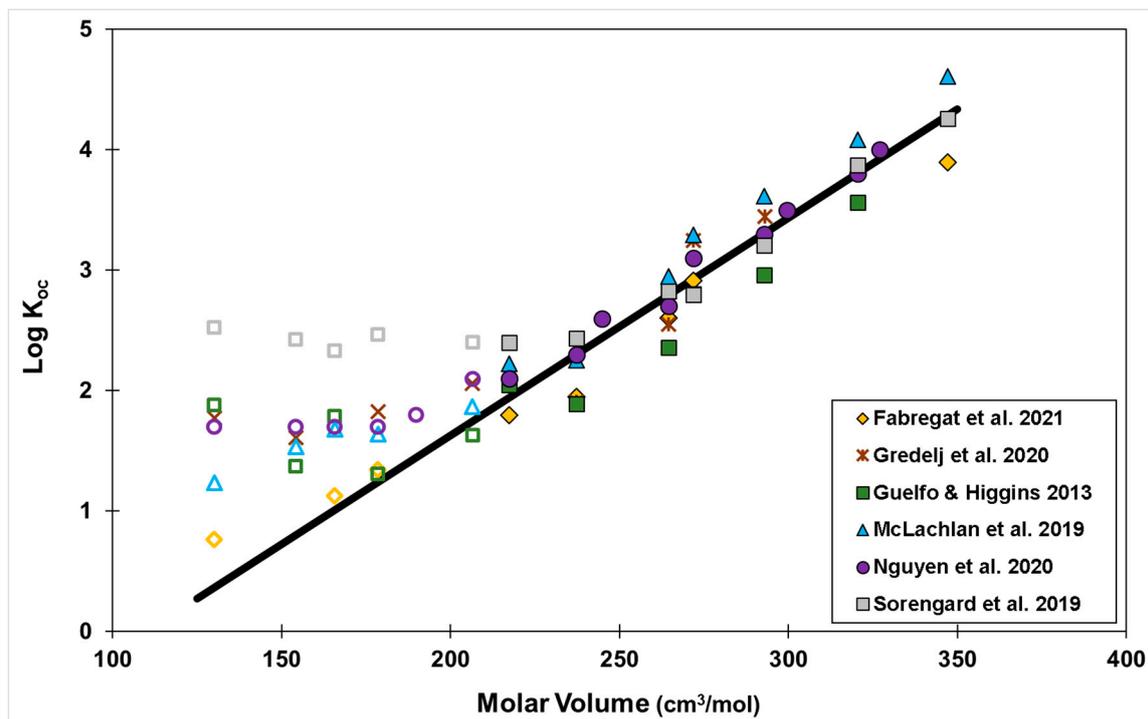


Figure 1. Correlation of log K_{oc} to molar volume for batch-measured sorption data for which both long-chain (filled symbols) and short-chain (open symbols) PFAS were included in the study. The QSPR correlation (solid black line; $\text{Log } K_{oc} = 0.018 (0.016\text{--}0.020) \times V_m - 2.0 (1.4\text{--}2.6)$, values in parentheses are 95% CIs, $r^2 = 0.89$) is determined only for the long-chain PFAS. The values reported for each study represent the means determined for all soils for those studies employing multiple soils. The plot was created in the present study using data reported in the cited works [13–18].

The results presented in Figure 1 represent the first time that these several data sets have been compiled, aggregated, and synthesized in one integrated analysis. The outcome reveals remarkable congruency across the multiple studies, especially considering that they employed a wide array of soils and different experiment methods. These results indicate that the observed enhanced differential sorption of the short-chain PFAS is a prevalent phenomenon.

The data presented in Figure 1 were parsed to produce a plot comparing log K_{oc} values for perfluorocarboxylic acids (PFCAs) versus perfluorosulfonic acids (PFSAs). The results are presented in Figure 2. No measurable differences are observed between the PFCAs and PFSAs for either short-chain or long-chain PFAS. The single QSPR correlation provides an excellent representation of the mean values for both long-chain PFCAs and long-chain PFSAs. In addition, the data-point means for the short-chain PFCAs and short-chain PFSAs are congruent. Individual plots comparing PFCAs and PFSAs were created for each of the six studies for which data are presented in Figures 1 and 2. No measurable differences are observed for five of the six studies, with small differences observed only

for the Guelfo and Higgins data set. Overall, these results indicate that the difference in headgroups had minimal impact on sorption and corresponding $\log K_{oc}$ values for the data sets reported herein.

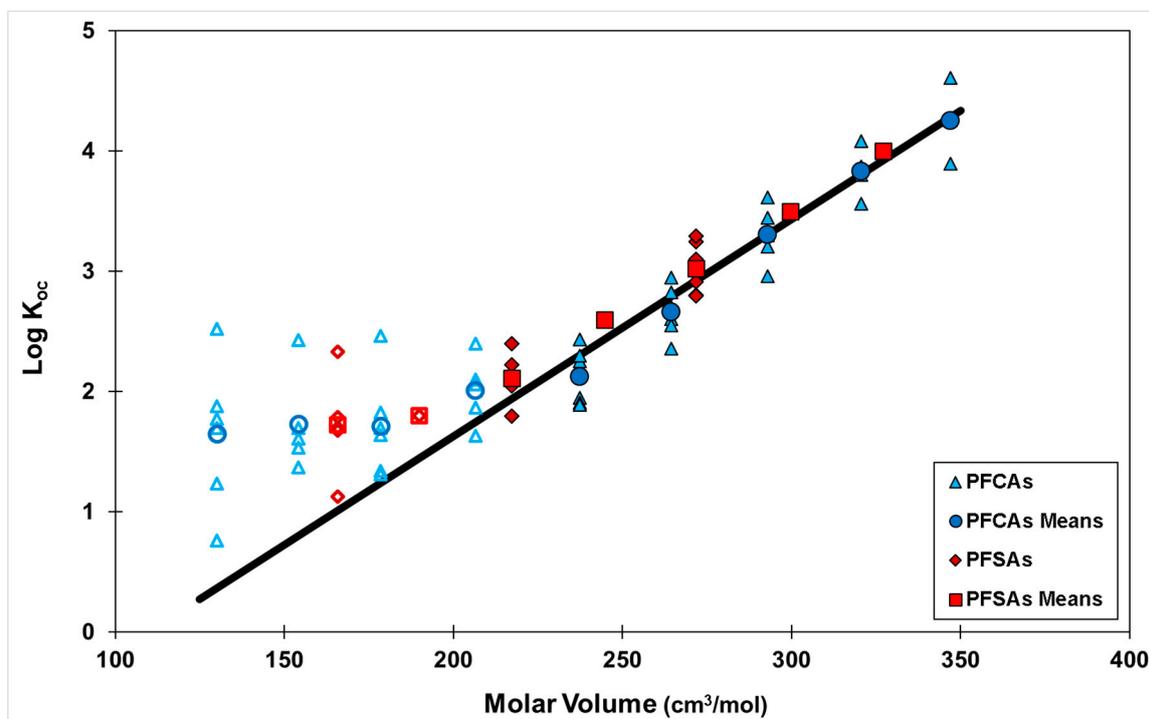


Figure 2. Correlation of $\log K_{oc}$ to molar volume for batch-measured sorption data presented in Figure 1 plotted as PFCAs versus PFSA for long-chain (filled symbols) and short-chain (open symbols) PFAS. The means represent the means of all values across the studies for each PFAS. The QSPR correlation (solid black line) is the same as that presented in Figure 1. The plot was created in the present study using data reported in the cited works (see Figure 1).

3.3. Influence of Soil Components

The sorption of long-chain anionic PFAS by soils has been demonstrated to be controlled by soil organic carbon in numerous studies, including several of the source works [13,16,18,22,25,26,32]. The K_{oc} values reported in or determined from the source studies are comparatively consistent for the long-chain PFAS, varying by approximately a factor of 3 (Figure 1). This is especially noteworthy considering the great range of soil properties across the studies and suggests that OC content is the primary soil component of importance for sorption of the long-chain PFAS. In contrast, the K_{oc} values vary by factors of up to almost two orders of magnitude for the short-chain PFAS. This suggests that inorganic soil components are much more important for the short-chain PFAS.

The impact of organic carbon content on PFAS sorption is further investigated by comparing the $\log K_{oc}-V_m$ functions for several individual soils from the Fabregat-Palau et al. and Nguyen et al. studies (Figure 3). The soils were selected to achieve a wide range of organic carbon contents while all having large (>45%) silt+clay contents. The $\log K_{oc}$ values for the long-chain PFAS are generally somewhat smaller for the soils with OC > 1% compared to those for the three soils with OC < 1%. This suggests that the silt+clay component provides a measurable contribution to the sorption of the long-chain PFAS for the low-OC soils.

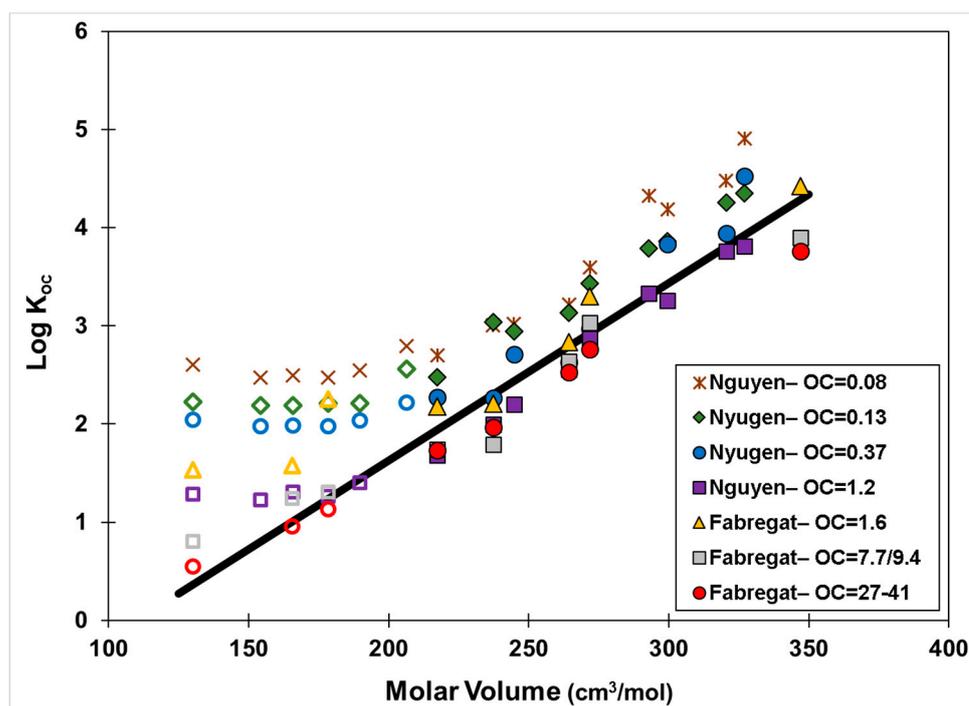


Figure 3. Correlation of $\log K_{oc}$ to molar volume for batch-measured sorption data for long-chain (filled symbols) and short-chain (open symbol) PFAS. Impact of organic carbon (OC) content for soils that have large (>45%) silt+clay contents. The QSPR correlation (solid black line) is the same as that presented in Figure 1. The plot was created in the present study using data reported in the cited works.

Similar to the results in Figure 1, the $\log K_{oc}$ values vary greatly across the range of soils for the individual short-chain PFAS (Figure 3). Interestingly, the magnitude of the deviation from the long-chain QSPR correlation appears to be a function of organic carbon content. Specifically, very large deviations are observed for the low-OC soils, whereas they deviate to a lesser extent for the soils with moderate OC (1–2%). The values deviate minimally or not at all for the soils with high (8–9%) and very high ($\geq 27\%$) organic carbon contents, respectively. These results suggest that enhanced differential sorption behavior for short-chain PFAS may be muted or absent for soils with very large organic carbon contents. This may result from a reduction or effective elimination of the sorption contributions from inorganic soil components when soil organic carbon content is very large.

Based on the results presented in Figure 3, a separate QSPR model is developed for the long-chain PFAS using only data for those media with OC contents > 1%. Three additional data sets from Table 1 are included in the plot, representing studies wherein only long-chain PFAS were used (with five or more PFAS included in the study). The results from the different studies are observed to be quite consistent (Figure 4). Weighted means of $\log K_{oc}$ values are determined for each PFAS using the data measured for the media with OC contents > 1%. These calculations include additional data from two studies that measured the sorption of three PFAS by multiple soils (Table 1). The means are weighted based on the number of soils or sediments included in each study for each specific PFAS, which are noted in the Figure caption.

Inspection of Figure 4 shows that the QSPR correlation determined for these data has a slightly lower intercept compared to the original QSPR correlation presented in Figure 1. This reflects the impact of the greater sorption measured for the soils with OC contents < 1% that was discussed previously. Notably, the QSPR correlation matches very well with the benchmark values reported for PFAS sorption by organic media (humins and peat). This further supports the contention that the sorption of the long-chain PFAS is controlled by soil organic carbon, particularly for the media with OC > 1%.

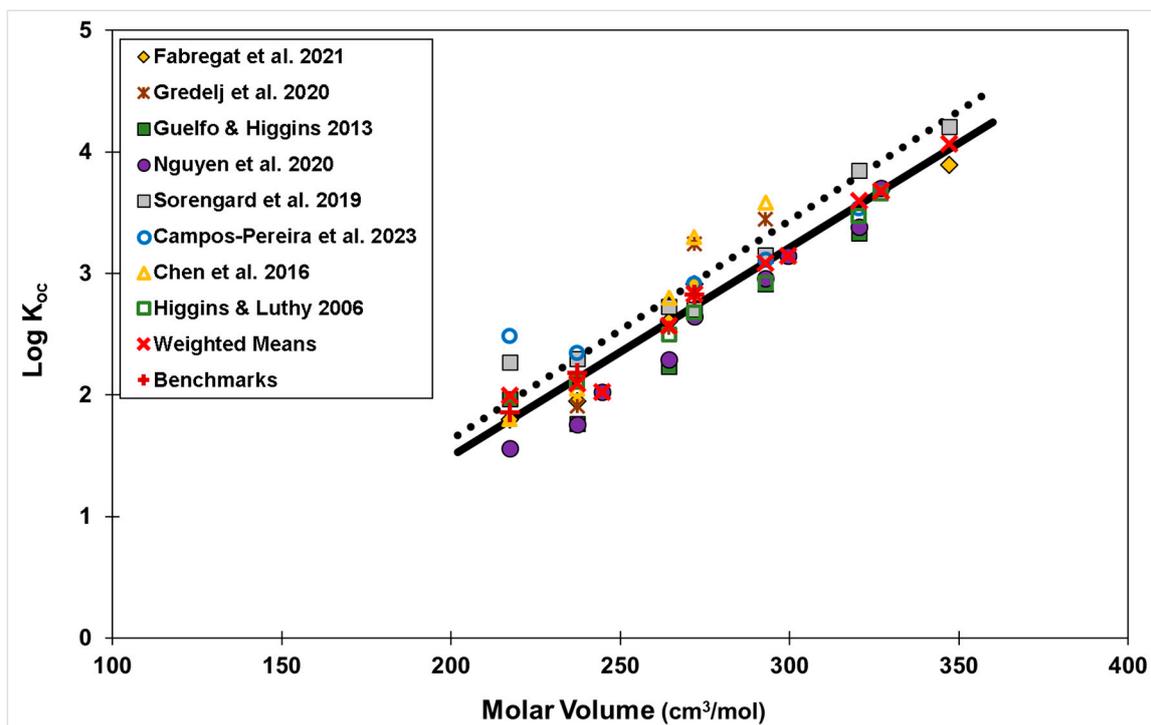


Figure 4. Correlation of $\log K_{oc}$ to molar volume for batch-measured sorption data for long-chain PFAS. Data included only for media with OC > 1%. The values reported for each study represent the means determined for all soils for those studies employing multiple soils. Data for media with OC < 1% that are included in Figure 1 are removed as follows: Guelfo and Higgins-1 soil, Nguyen et al.-7 soils, and Sorengard-1 soil. The QSPR correlation (solid black line; $\log K_{oc} = 0.017 (0.015\text{--}0.019) \times V_m - 1.9 (1.3\text{--}2.6)$, values in parentheses are 95% CIs, $r^2 = 0.98$) is determined for the weighted-mean values as described in the text. The benchmark values represent measurements for PFAS (PFHxS, PFOA, PFOS) sorption by humin and peat; values determined for 10 $\mu\text{g/L}$. The plot was created in the present study using data reported in the cited works [13–16,18,22–24].

The relative significance of silt and clay content is investigated by comparing data sets reported by Nguyen et al. [13] for two soils with very similar OC contents ($\sim 0.4\%$) but vastly different silt+clay contents. The $\log K_{oc}$ values for the long-chain PFAS are relatively similar between the two soils despite the vast difference in silt+clay contents of 6 vs. 51% (Figure 5). This indicates that organic carbon is the predominant soil component mediating sorption of the long-chain PFAS, consistent with the prior results. In contrast, the values differ greatly for the short-chain PFAS, with ~ 10 times larger values measured for the soil with high silt+clay content. In addition, there is a greater deviation of the short-chain PFAS from the long-chain QSPR correlation for the soil with the high silt+clay content. These results demonstrate that the silt+clay component has a much greater impact on the sorption of the short-chain PFAS compared to the long-chain PFAS.

All of the data sets presented herein represent sorption measured under conditions of the natural soil pHs to provide the most representative assessment. Some studies have investigated the impact of altered solution pHs on PFAS sorption to help evaluate operative sorption mechanisms [13,22]. The three cited studies all observed that K_d values generally increased at lower pHs, which for anionic PFAS was attributed to changes in the surface charge and/or hydrophobicity of the soil components. Two example data sets comparing $\log K_{oc}$ values for specific soils at two pHs are presented in Figure 6. Differences are observed, with the magnitude of the differences a function of the specific soil.

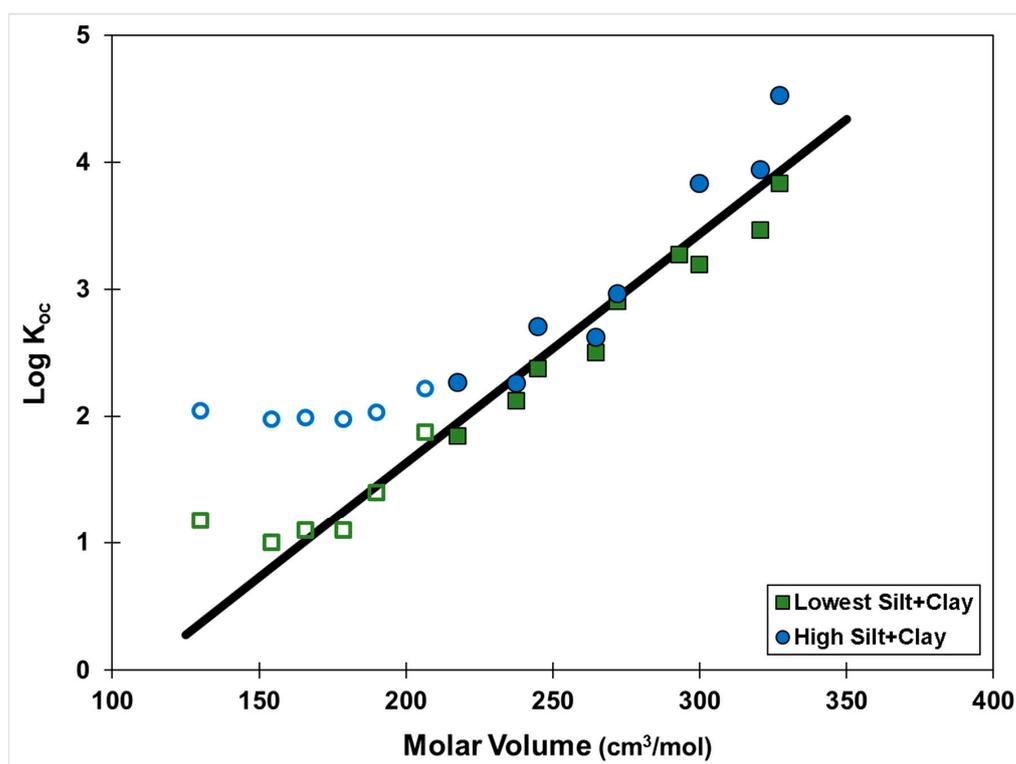


Figure 5. Correlation of $\log K_{oc}$ to molar volume for batch-measured sorption data for long-chain (filled symbols) and short-chain (open symbol) PFAS. Impact of silt+clay content for two soils with similar organic carbon contents ($\sim 0.4\%$). Lowest silt+clay = 6% (soil 8); highest silt+clay = 51% (soil 2). The correlation (solid black line) is the same as that presented in Figure 1. The plot was created in the present study using data reported by Nguyen et al. [13].

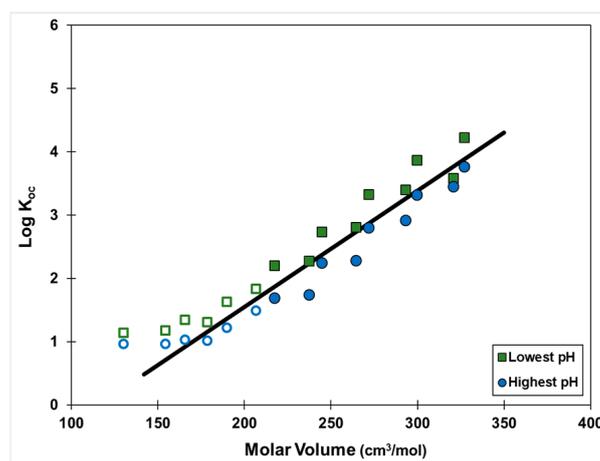
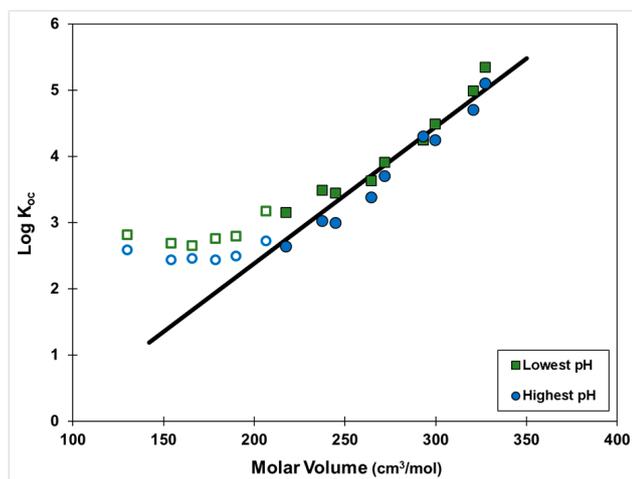


Figure 6. Correlation of $\log K_{oc}$ to molar volume for batch-measured sorption data for long-chain (filled symbols) and short-chain (open symbols) PFAS. Impact of pH (3.4 vs. 8.3) for two soils (left-soil 3 and right-soil 6). The plot was created in the present study using data reported by Nguyen et al. [13].

The magnitude of the differences observed in Figure 6 are not as great as those observed when comparing soils with different organic carbon or silt+clay contents in Figures 3 and 5, respectively. Examination of Figure 3 shows, for example, that $\log K_{oc}$ values range by an order of magnitude or more among the four soils from the Nguyen et al. study. The native soil pHs are relatively similar for these four soils, ranging between 6.2 and 7.7. Notably, the $\log K_{oc}$ values for the OC = 0.13 soil, which has a pH of 7.7, are almost

universally greater than those for the OC = 0.37 soil, which has a pH of 6.8. In addition, the native pHs for the Fabregat et al. soils range from 5.2 to 5.8, with one exception. Despite the fact that the soil pHs are significantly lower than those for the Nguyen soils, the $\log K_{oc}$ values for the Fabregat data are generally similar to the lower range of values measured for the Nguyen soils. Finally, it is important to note that the data sets presented in Figure 1 represent soils comprising a relatively wide range of pHs (Table 1). The magnitudes of variability in $\log K_{oc}$ values among each PFAS observed in Figure 1 are similar to those observed in Figure 2, for which the variability was demonstrated to be related to soil organic carbon content. In total, these results indicate that pH is of secondary importance compared to organic carbon and silt+clay contents for these soils.

3.4. Sorption Mechanisms

Strong correlations of $\log K_d$ or $\log K_{oc}$ to chain length properties are typically viewed as an indication that the hydrophobic interaction mechanism governs PFAS sorption [13,16,18,19,22]. The significance of the hydrophobic interaction mechanism for PFAS sorption was demonstrated by a comparison of the $\log K_{oc}$ - V_m function determined for the sorption of several PFAS to the corresponding functions determined for air–water interfacial adsorption and sorption by granular activated carbon [19]. The comparison is shown in Figure 7, wherein it is seen that the slopes of the three correlations are statistically identical.

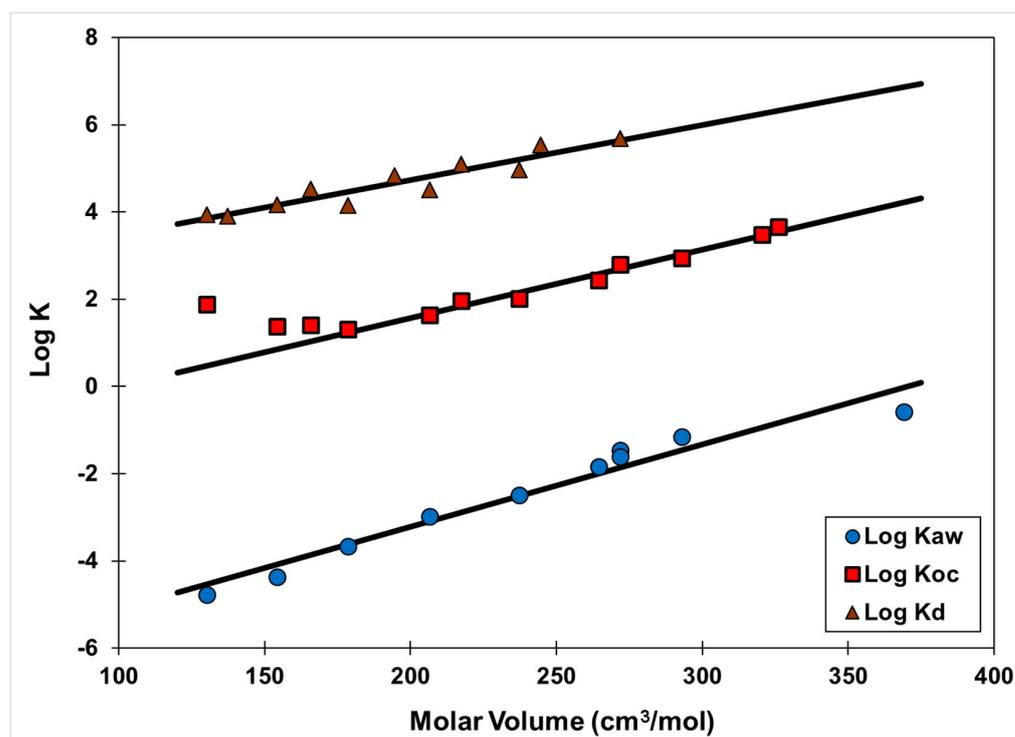


Figure 7. Correlations for $\log K_{aw}$ (air–water interfacial adsorption), $\log K_{oc}$ (sorption by soil), and $\log K_d$ (sorption by granular activated carbon, GAC) for several PFCAs and PFASs. Figure revised from Brusseau, 2019 [19] with $\log K_{aw}$ data from Brusseau and Van Glubt, 2021 [33]. Regression equation for adsorption by soils and sediments: $\log K_{oc} = 0.016$ (0.014–0.018) $\times V_m - 1.6$ (1.1–2.1), $r^2 = 0.98$. Regression equation for adsorption by GAC: $\log K_d = 0.013$ (0.009–0.016) $\times V_m - 2.2$ (1.6–2.9), $r^2 = 0.89$. Regression equation for adsorption at the air–water interface: $\log K_{aw} = 0.019$ (0.017–0.021) $\times V_m - 7.1$ (6.6–7.5), $r^2 = 0.95$. Values in parentheses are 95% confidence intervals.

Notably, the slopes of the PFAS sorption correlations in Figures 1 and 4 are statistically identical to the slope determined for PFAS air–water interfacial adsorption. It is well established that hydrophobic interaction is the driving force for the adsorption of surfactants, including PFAS, at the air–water interface. The similarity of the correlation

slopes determined for PFAS sorption to that determined for air–water interfacial adsorption, in combination with the results from the preceding sub-section demonstrating the predominant contribution of soil organic carbon, strongly indicates that the hydrophobic interaction mechanism is the primary process mediating sorption of the long-chain PFAS. It is likely that it also contributes to the sorption of the short-chain PFAS. For example, as discussed above with respect to Figure 3, $\log K_{oc}$ values measured for the short-chain PFAS were consistent with the correlation determined for the long-chain PFAS for soils with higher organic carbon contents.

Interestingly, singular QSPR functions match both long-chain and short-chain PFAS for air–water interfacial adsorption and GAC sorption in Figure 7. This is in contrast to the deviations observed for the soil sorption data in Figures 1 and 7. This disparity likely reflects the fact that soils are geochemically heterogeneous and the resultant involvement of additional sorption mechanisms, compared to the relative homogeneity of the air–water interface and GAC surface for which hydrophobic interaction is the predominant mechanism of adsorption [19]. This is consistent with the typical hypothesis that the enhanced differential sorption observed for the short-chain PFAS is due to additional sorption contributions, such as electrostatic interactions with inorganic soil components.

4. Conclusions

Batch-measured sorption data reported in the literature for short- and long-chain PFAS were compiled and synthesized to conduct an integrated investigation of chain length effects. The $\log K_d$ and $\log K_{oc}$ values exhibited a biphasic relationship with molar volume, with the magnitude of measured sorption for the short-chain PFAS generally significantly greater than would be predicted using the QSPR correlation developed for the long-chain PFAS. The results reveal remarkable congruency across the multiple studies employing a wide array of soils and indicate that the observed enhanced differential sorption of short-chain PFAS is likely a prevalent phenomenon.

The QSPR analyses indicated that organic carbon is the predominant soil component influencing the sorption of the long-chain PFAS, with hydrophobic interaction serving as the driving force. The analyses also indicated that the enhanced differential sorption of short-chain PFAS is a function of organic carbon and silt+clay contents and was minimal for soils with high organic carbon contents. In addition, $\log K_{oc}$ values were similar for long-chain PFAS sorption by two soils with similar organic carbon contents but greatly different silt+clay contents, whereas the $\log K_{oc}$ values varied greatly for the short-chain PFAS. These results demonstrate that sorption of short-chain PFAS is generally more sensitive to differences in the organic carbon and inorganic components of the soil. It should be noted that the PFAS examined in this study are all anionic and that the sorption of non-anionic PFAS may be more complex in some cases [13,25,34].

By definition, K_{oc} values represent the sorption contributions associated with organic carbon components of a soil or sediment. The enhanced K_{oc} values observed for the short-chain PFAS likely represent the contributions of additional soil components and associated sorption mechanisms. In such cases, the K_{oc} becomes an apparent, lumped parameter that represents the combined contributions of all sorption mechanisms and soil components. There are multiple options available for attempting to estimate K_d s when multiple sorption mechanisms and soil components are relevant. One approach is to use distributed-sorption models, wherein the contributions of each component are represented explicitly. This approach has been used in several studies for characterizing PFAS sorption [14,18,32,35]. A limiting factor for this approach is the need to measure additional soil properties, which are not always characterized or reported. Such models remain in the development and testing stage. Another approach is to use the standard K_{oc} - f_{oc} approach, with apparent K_{oc} values used for short-chain PFAS. While simplistic, this approach is readily available. It is limited by the availability of empirical data sets for short-chain PFAS. The data sets presented in the present study provide an initial source that needs supplementing with additional measurements.

Overall, the results reported herein suggest that the sorption of shorter-chain PFAS may be greater in some cases than anticipated and that estimates based on empirical or anecdotal observations of longer-chain PFAS may not be representative in those circumstances. This highlights the need to exercise caution in the application of the standard K_{oc-foc} approach for predicting K_d values, which may under-predict the sorption of short-chain PFAS in some cases. This has significant implications for conducting site characterizations, risk assessments, and mathematical modeling of PFAS transport in soils and groundwater.

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References

1. Brusseau, M.L.; Anderson, R.H.; Guo, B. PFAS concentrations in soils: Background levels versus contaminated sites. *Sci. Total Environ.* **2020**, *740*, 140017. [[CrossRef](#)]
2. EPA. *Soil Screening Guidance; User's Guide* Publ. 9355; Environmental Protection Agency: Washington, DC, USA, 1996.
3. ECETOC. Environmental Exposure Assessment of Ionisable Organic Compounds. Technical Report No. 123, European Centre for Ecotoxicology and Toxicology of Chemicals. 2013. Available online: <https://www.ecetoc.org/publication/tr-123-environmental-risk-assessment-of-ionisable-compounds/> (accessed on 3 August 2023).
4. OECD. *Considerations for Assessing the Risks of Combined Exposure to Multiple Chemicals*; Series on Testing and Assessment No. 296; Environment, Health and Safety Division, Environment Directorate: Paris, France, 2018.
5. van Leeuwen, C.J.; Vermeire, T.G. (Eds.) *Risk Assessment of Chemicals: An Introduction*, 2nd ed.; Springer: Dordrecht, The Netherlands, 2007.
6. Batu, V. *Applied Flow and Solute Transport Modeling in Aquifers*; Taylor & Francis: Boca Raton, FL, USA, 2006.
7. EPA. Guidance for Selecting Input Parameters in Modeling the Environmental Fate and Transport of Pesticides. Environmental Protection Agency. 2009. Available online: <https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/guidance-selecting-input-parameters-modeling#guidance> (accessed on 3 August 2023).
8. MECCS. *Technical Guidance on Contaminated Sites: Groundwater Protection Model*; Ministry of Environment and Climate Change Strategy: Victoria, BC, Canada, 2017.
9. Anderson, R.H. The Case for direct measures of soil-to-groundwater contaminant mass discharge at AFFF-impacted sites. *Environ. Sci. Technol.* **2021**, *55*, 6580–6583. [[CrossRef](#)] [[PubMed](#)]
10. Brusseau, M.L.; Guo, B. Revising the EPA dilution-attenuation soil screening model for PFAS. *J. Hazard. Mater. Lett.* **2023**, *4*, 100077. [[CrossRef](#)]
11. Baduel, C.; Mueller, J.; Rotander, A.; Corfield, J.; Gomez-Ramos, M. Discovery of novel per- and polyfluoroalkyl substances (PFASs) at a fire fighting training ground and preliminary investigation of their fate and mobility. *Chemosphere* **2017**, *185*, 1030–1038. [[CrossRef](#)]
12. Washington, J.; Yoo, H.; Ellington, J.; Jenkins, T.; Libelo, E. Concentrations, distribution, and persistence of perfluoroalkylates in sludge-applied soils near Decatur, Alabama, USA. *Environ. Sci. Technol.* **2010**, *44*, 8390–8396. [[CrossRef](#)] [[PubMed](#)]
13. Nguyen, T.M.H.; Braunig, J.; Thompson, K.; Thompson, J.; Kabiri, S.; Navarro, D.A.; Kookana, R.S.; Grimison, C.; Barnes, C.M.; Higgins, C.P.; et al. Influences of chemical properties, soil properties, and solution pH on soil-water partitioning coefficients of per- and polyfluoroalkyl substances (PFASs). *Environ. Sci. Technol.* **2020**, *54*, 15883–15892. [[CrossRef](#)] [[PubMed](#)]
14. Fabregat-Palau, J.; Vidal, M.; Rigol, A. Modelling the sorption behaviour of perfluoroalkyl carboxylates and perfluoroalkane sulfonates in soils. *Sci. Total Environ.* **2021**, *801*, 149343. [[CrossRef](#)]
15. Gredelj, A.; Nicoletto, C.; Valsecchi, S.; Ferrario, C.; Polesello, S.; Lava, R.; Zanon, F.; Barausse, A.; Palmeri, L.; Guidolin, L.; et al. Uptake and translocation of perfluoroalkyl acids (PFAA) in red chicory (*Cichorium intybus* L.) under various treatments with pre-contaminated soil and irrigation water. *Sci. Total Environ.* **2020**, *708*, 134766. [[CrossRef](#)] [[PubMed](#)]
16. Guelfo, J.L.; Higgins, C.P. Subsurface transport potential of perfluoroalkyl acids at aqueous film-forming foam (AFFF)-impacted sites. *Environ. Sci. Technol.* **2013**, *47*, 4164–4171. [[CrossRef](#)]
17. McLachlan, M.S.; Felizeter, S.; Klein, M.; Kotthoff, M.; de Voogt, P. Fate of a perfluoroalkyl acidmixture in an agricultural soil studied in lysimeters. *Chemosphere* **2019**, *223*, 180–187. [[CrossRef](#)]
18. Sorengard, M.; Kleja, D.B.; Ahrens, L. Stabilization of per- and polyfluoroalkyl substances (PFASs) with colloidal activated carbon (PlumeStop®) as a function of soil clay and organic matter content. *J. Environ. Manag.* **2019**, *249*, 109345. [[CrossRef](#)] [[PubMed](#)]
19. Brusseau, M.L. Estimating the relative magnitudes of adsorption to solid-water and air/oil-water interfaces for per-and polyfluoroalkyl substances. *Environ. Poll.* **2019**, *254*, 113102. [[CrossRef](#)] [[PubMed](#)]

20. Brendel, S.; Fetter, E.; Staude, C.; Vierke, L.; Biegel-Engler, A. Short-chain perfluoroalkyl acids: Environmental concerns and a regulatory strategy under REACH. *Environ. Sci. Eur.* **2018**, *30*, 9. [[CrossRef](#)] [[PubMed](#)]
21. Wang, Z.; Cousins, I.T.; Scheringer, M.; Hungerbuehler, K. Hazard assessment of fluorinated alternatives to long-chain perfluoroalkyl acids (PFAAs) and their precursors: Status quo, ongoing challenges and possible solutions. *Environ. Int.* **2015**, *75*, 172–179. [[CrossRef](#)]
22. Higgins, C.P.; Luthy, R.G. Sorption of perfluorinated surfactants on sediments. *Environ. Sci. Technol.* **2006**, *40*, 7251–7256. [[CrossRef](#)]
23. Chen, H.; Reinhard, M.; Nguyen, V.T.; Gin, Y.-H. Reversible and irreversible sorption of perfluorinated compounds (PFCs) by sediments of an urban reservoir. *Chemosphere* **2016**, *144*, 1747–1753. [[CrossRef](#)]
24. Campos-Pereira, H.; Kleja, D.B.; Ahrens, L.; Enell, A.; Kikuchi, H.; Pettersson, M.; Gustafsson, J.P. Effect of pH, surface charge and soil properties on the solid–solution partitioning of perfluoroalkyl substances (PFASs) in a wide range of temperate soils. *Chemosphere* **2023**, *321*, 138133. [[CrossRef](#)]
25. Mejia-Avendano, S.; Zhi, Y.; Yan, B.; Liu, J. Sorption of polyfluoroalkyl surfactants on surface soils: Effect of molecular structures, soil properties, and solution chemistry. *Environ. Sci. Technol.* **2020**, *54*, 1513–1521. [[CrossRef](#)]
26. Oliver, D.P.; Navarro, D.A.; Baldock, J.; Simpson, S.L.; Kookana, R.S. Sorption behaviour of per- and polyfluoroalkyl substances (PFASs) as affected by the properties of coastal estuarine sediments. *Sci. Total Environ.* **2020**, *720*, 137263. [[CrossRef](#)]
27. Zhao, L.; Zhang, Y.; Fang, S.; Zhu, L.; Liu, Z. Comparative sorption and desorption behaviors of PFHxS and PFOS on sequentially extracted humic substances. *J. Environ. Sci.* **2014**, *26*, 2517–2525. [[CrossRef](#)]
28. Campos-Pereira, H.; Makselon, J.; Kleja, D.B.; Prater, I.; Kogel-Knabner, I.; Ahrens, L.; Gustafsson, J.P. Binding of per- and polyfluoroalkyl substances (PFASs) by organic soil materials with different structural composition – Charge- and concentration-dependent sorption behavior. *Chemosphere* **2022**, *297*, 134167. [[CrossRef](#)] [[PubMed](#)]
29. Zhi, Y.; Liu, J. Sorption and desorption of anionic, cationic and zwitterionic polyfluoroalkyl substances by soil organic matter and pyrogenic carbonaceous materials. *Chem. Eng. J.* **2018**, *346*, 682–691. [[CrossRef](#)]
30. Buck, R.C.; Franklin, J.; Berger, U.; Conder, J.M.; Cousins, I.T.; de Voogt, P.; Jensen, A.A.; Kannan, K.; Mabury, S.A.; van Leeuwen, S.P. Perfluoroalkyl and polyfluoroalkyl substances in the environment: Terminology, classification, and origins. *Integr. Environ. Assess. Manag.* **2011**, *7*, 513–541. [[CrossRef](#)] [[PubMed](#)]
31. Brusseau, M.L. The influence of molecular structure on the adsorption of PFAS to fluid–fluid interfaces: Using QSPR to predict interfacial adsorption coefficients. *Water Res.* **2019**, *152*, 148–158. [[CrossRef](#)]
32. Milinovic, J.; Lacorte, S.; Vidal, M.; Rigol, A. Sorption behaviour of perfluoroalkyl substances in soils. *Sci. Total Environ.* **2015**, *511*, 63–71. [[CrossRef](#)]
33. Brusseau, M.L.; Van Glubt, S. The influence of molecular structure on PFAS adsorption at air–water interfaces in electrolyte solutions. *Chemosphere* **2021**, *281*, 130829. [[CrossRef](#)]
34. Xiao, F.; Jin, B.; Golovko, S.A.; Golovko, M.Y.; Xing, B. Sorption and desorption mechanisms of cationic and zwitterionic per- and polyfluoroalkyl substances in natural soils: Thermodynamics and hysteresis. *Environ. Sci. Technol.* **2019**, *53*, 11818–11827. [[CrossRef](#)]
35. Wang, Y.; Khan, N.; Huang, D.; Carroll, K.C.; Brusseau, M.L. Transport of PFOS in aquifer sediment: Transport behavior and a distributed-sorption model. *Sci. Total Environ.* **2021**, *779*, 146444. [[CrossRef](#)]

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