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Article

Influences of Chemical Properties, Soil Properties, and Solution pH on Soil−Water Partitioning Coefficients of Per- and Polyfluoroalkyl Substances (PFASs)

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Cite This: *Environ. Sci. Technol.* 2020, 54, 15883−15892

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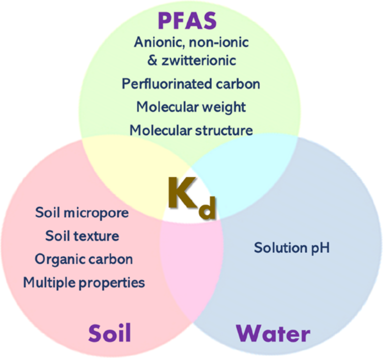
ABSTRACT: The aim of this study was to assess the soil−water partitioning behavior of a wider range of per- and polyfluoroalkyl substances (PFASs) onto soils covering diverse soil properties. The PFASs studied include perfluoroalkyl carboxylates (PFCAs), perfluoroalkane sulfonates (PFSAs), fluorotelomer sulfonates (FTSs), nonionic perfluoroalkane sulfonamides (FASAs), cyclic PFAS (PFEtCHxS), per- and polyfluoroalkyl ether acids (GenX, ADONA, 9Cl-PF3ONS), and three aqueous film-forming foam (AFFF)-related zwitterionic PFASs (AmPr-FHxSA, TAmPr-FHxSA, 6:2 FTSA-PrB). Soil−water partitioning coefficients (log K_d values) of the PFASs ranged from less than zero to approximately three, were chain-length-dependent, and were significantly linearly related to molecular weight (MW) for PFASs with MW > 350 g/mol ($R^2 = 0.94$, $p < 0.0001$). Across all soils, the K_d values of all short-chain PFASs (≤5 −CF2− moieties) were similar and varied less (<0.5 log units) compared to long-chain PFASs (>0.5 to 1.5 log units) and zwitterions AmPr- and TAmPr-FHxSA (∼1.5 to 2 log units). Multiple soil properties described sorption of PFASs better than any single property. The effects of soil properties on sorption were different for anionic, nonionic, and zwitterionic PFASs. Solution pH could change both PFAS speciation and soil chemistry affecting surface complexation and electrostatic processes. The K_d values of all PFASs increased when solution pH decreased from approximately eight to three. Short-chain PFASs were less sensitive to solution pH than long-chain PFASs. The results indicate the complex interactions of PFASs with soil surfaces and the need to consider both PFAS type and soil properties to describe mobility in the environment.



INTRODUCTION

Per- and polyfluoroalkyl substances (PFASs) are a broad range of artificial chemicals. PFASs have been widely used for many applications because they are persistent, water- and oil-repellent, and highly resistant to acids and high temperatures. One key application of PFASs is in aqueous film-forming foam (AFFF). AFFFs have been intensively used at numerous military installations across the world and released into the environment through various activities such as firefighting training and fire suppression.[1] This has led to widespread PFAS contamination of soils, groundwater, and many other environmental matrices.[2−5] Some PFASs (especially perfluoroalkyl acids, PFAAs) have been found in areas never exposed to, or distant from, anthropogenic activities.[6,7] In Australia, AFFFs have been used in all states/territories and essentially across the continent reflecting contamination across the full spectrum of potential soil types and environments.[8]

Understanding the fate of PFASs that enter the soil environment and their mobility from the soil to groundwater relies on understanding the sorption behavior of a given chemical to specific soils under given environmental conditions (i.e., pH and temperature).[9,10] The soil sorption coefficient—or K_d value—describes a widely used equilibrium partitioning coefficient of chemicals used to predict their mobility. A meta-analysis of an extensive dataset of published K_d values proposed that the soil organic carbon (OC) fraction alone could not adequately explain the sorption of several PFAAs onto soil,[9] consistent with some earlier laboratory studies on sediments.[10] Li et al.[9] suggested that the contributions of multiple soil properties must be considered. For example, changes in solution pH or exchangeable cations could affect the partitioning of PFASs.[11,12] In addition, the chemical properties of the particular PFAS could affect partitioning to soil. For example, shorter-chain PFAAs bind less strongly to soil than longer-chain PFAAs,[13,14] and there are indications

Received: August 25, 2020
Revised: October 31, 2020
Accepted: November 4, 2020
Published: November 28, 2020

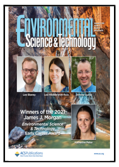
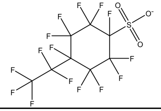
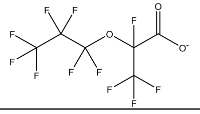
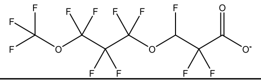
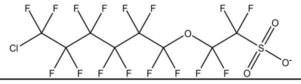
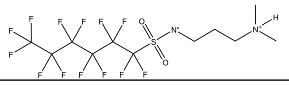
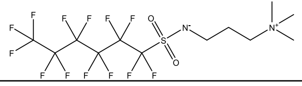
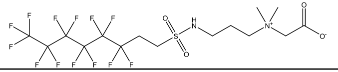


Table 1. PFASs Included in This Study[a]

PFAS subclass and structure	Number of perfluorinated carbons (or name)	Acronym	Formula	Mass	IS/SS
Perfluoroalkyl carboxylates (PFCAs) $C_nF_{2n+1}COO^-$	3	PFBA	$C_4F_7O_2^-$	213.03	$^{13}C_4$-PFBA
	4	PFPeA	$C_5F_9O_2^-$	263.04	$^{13}C_3$-PFPeA
	5	PFHxA	$C_6F_{11}O_2^-$	313.05	$^{13}C_2$-PFHxA
	6	PFHpA	$C_7F_{13}O_2^-$	363.05	$^{13}C_4$-PFHpA
	7	PFOA	$C_8F_{15}O_2^-$	413.06	$^{13}C_4$-PFOA
	8	PFNA	$C_9F_{17}O_2^-$	463.07	$^{13}C_5$-PFNA
	9	PFDA	$C_{10}F_{19}O_2^-$	513.08	$^{13}C_2$-PFDA
	10	PFUnDA	$C_{11}F_{21}O_2^-$	563.09	$^{13}C_2$-PFUnDA
	11	PFDoDA	$C_{12}F_{23}O_2^-$	613.09	$^{13}C_2$-PFDoDA
Perfluoroalkane sulfonates (PFSAs) $C_nF_{2n+1}SO_3^-$	4	L-PFBS	$C_4F_9O_3S^-$	299.09	$^{13}C_3$-PFBS
	5	L-PFPeS	$C_5F_{11}O_3S^-$	349.09	$^{13}C_3$-PFBS
	6	L-PFHxS	$C_6F_{13}O_3S^-$	399.1	$^{18}O_2$-PFHxS
	7	L-PFHpS	$C_7F_{15}O_3S^-$	449.11	$^{13}C_4$-PFOS
	8	L-PFOS	$C_8F_{17}O_3S^-$	499.12	$^{13}C_4$-PFOS
	9	L-PFNS	$C_9F_{19}O_3S^-$	549.13	$^{13}C_4$-PFOS
	10	L-PFDS	$C_{10}F_{21}O_3S^-$	599.13	$^{13}C_4$-PFOS
X:2 Fluorotelomer sulfonates (FTSs) $C_nF_{2n+1}CH_2CH_2SO_3^-$	4	4:2 FTS	$C_6H_4F_9O_3S^-$	327.14	$^{13}C_2$-4:2FTS
	6	6:2 FTS	$C_8H_4F_{13}O_3S^-$	427.16	$^{13}C_2$-6:2 FTS
	8	8:2 FTS	$C_{10}H_4F_{17}O_3S^-$	527.17	$^{13}C_2$-8:2 FTS
Perfluoroalkane sulfonamides (FASAs) C_nF_{2n+1} -SO_2NH^-	4	FBSA	$C_4HF_9NO_2S^-$	298.10	$^{18}O_2$-PFHxS
	6	FHxSA	$C_6HF_{13}NO_2S^-$	398.12	$^{13}C_8$-FOSA
	8	FOSA	$C_8HF_{17}NO_2S^-$	498.13	$^{13}C_8$-FOSA
Cyclohexane sulfonate (cyclic PFAS)	Potassium perfluoro-4-ethylcyclohexanesulfonate 	PFEtCHxS	$C_8F_{15}O_3S^-$	461.12	$^{13}C_4$-PFOA
Perfluoroalkyl ether carboxylic acid	Tetrafluoro-2-(heptafluoropropoxy)propanoate 	HFPO-DA (GenX)	$C_6F_{11}O_3^-$	329.05	$^{13}C_3$-HFPO-DA
Polyfluoroalkyl ether carboxylic acid	Sodium dodecafluoro-3H-4,8 dioxanonanoate 	ADONA	$C_7HF_{12}O_4^-$	377.06	$^{13}C_4$-PFOA
Chlorinated polyfluoroalkyl ether sulfonic acid	9-chlorohexadecafluoro-3-oxanonane-1-sulfonate 	9Cl-PF3ONS	$C_8ClF_{16}O_4S^-$	531.57	$^{13}C_4$-PFOS
N-dimethyl ammonio propyl perfluoroalkane sulfonamide (AmPr-FASA) (Zwitterion)	N-(3-dimethylaminopropan-1-yl)perfluoro-1-hexane-sulfonamide 	AmPr-FHxSA	$C_{11}H_{13}F_{13}N_2O_2S$	484.28	$^{13}C_8$-FOSA
N-trimethyl ammonio propyl perfluoroalkane sulfonamide (TAmPr-FASA) (Zwitterion)	N-[3-(perfluoro-1-hexanesulfonamido)propan-1-yl]-N,N,N-trimethylammonium 	TAmPr-FHxSA	$C_{12}H_{15}F_{13}N_2O_2S$	498.3	$^{13}C_8$-FOSA
X:2 fluorotelomer sulfonamido propyl betaine (Zwitterion)	N-(carboxymethyl)-N,N-dimethyl-N-[3-(1H,1H,2H,2H-perfluoro-1-octanesulfonamido)propan-1-yl]ammonium 	6:2 FTSA-PrB	$C_{15}H_{19}F_{13}N_2O_4S$	570.37	$^{13}C_4$-PFOS

[a] IS/SS: internal standard/surrogate standard. Surrogate standards were used for quantification of compounds without a matching IS.

that the molecular structure governs sorption behavior of cationic and zwitterionic PFASs.[11,15] However, to date, most studies have investigated a limited number of PFASs compared to the chemical complexity of most AFFFs.

AFFFs are formulated to meet the specifications of firefighting activities rather than to be composed of defined PFAS mixtures. Thus, the PFAS profile of AFFFs is much more complex than other sources, containing up to several dozen different PFAS classes, many of which are rarely analyzed.[16−18] Studies on the sorption behavior for PFASs have mainly focused on PFAAs.[9,10] Due to the concerns for bioaccumulation, the production of long-chain PFASs, especially PFASs containing eight or more perfluorinated carbons (CF_2 moieties), have been reduced and substituted.[19] Though not

Table 2. Soil Characteristics[a]

soil	BD (g/cm^3)	f_{oc} (%)	pH ($CaCl_2$)*	CEC ($cmol^+/kg$)	ESP (%)	sand (%)	silt (%)	clay (%)	micropore volume (cm^3/g)	soil texture	ASC order
S1	1.22	0.70	7.5	41.40	7.25	16.90	17.50	65.60	0.030	clay	vertosol
S2	1.59	0.37	6.8	7.10	0.00	48.90	27.00	24.20	0.011	sandy clay loam	sodosol
S3	1.66	0.08	6.2	8.00	3.03	51.44	10.17	38.38	0.010	sandy clay	kandosol
S4	1.47	0.25	7.7	4.80	6.25	46.00	37.00	17.00	0.005	loam	calcarosol
S5	1.38	2.23	7.4	29.60	2.40	39.80	7.70	52.50	0.044	clay	calcarosol
S6	0.82	4.90	7.7	21.63	0.00	70.00	11.00	19.00	0.010	sandy loam	calcarosol
S7	1.59	0.13	7.7	7.80	15.60	48.90	32.60	18.50	0.007	loam	kandosol
S8	1.58	0.40	7.5	2.28	0.00	93.00	1.00	5.00	0.006	sand	tenosol
S9	1.49	1.19	7.1	17.42	0.11	48.86	16.05	35.09	0.010	sandy clay	ferrosol
S10	1.44	0.17	6.4	16.54	1.53	29.38	13.90	56.71	0.018	clay	ferrosol

[a] BD: bulk density. f_{oc} organic carbon content. pH at equilibrium (see batch sorption experiment). CEC: cation exchange capacity. ESP: exchangeable sodium percentage. Sand, silt, clay: fraction of particle size sand (62.5−500 μm), silt (3.9−62.5 μm), clay (0.98−3.9 μm). ASC: Australian soil classification. Micropore: cumulative volume of micropores (<2 nm width). *Soil-to-water ratio is 1:10.

components of AFFF, per- and polyfluoroalkyl ether compounds have been increasingly detected at concentrations significantly higher than those of PFAAs in surface water (drinking water sources) in the United States, Europe, and China,[20−22] and recently in arctic waters.[23] Nevertheless, the study of the behavior of PFAS-replacement products such as GenX and ADONA (PFOA replacement) or 9Cl-PF3ONS (PFOS replacement used in China) in the soil environment are still limited.[22,24,25] In addition, little is known of the sorption of the cyclic PFAS (PFEtCHxS), which has been frequently detected in the environment.[24,26] Moreover, a recent study of Nickerson et al.[18] reported that the vast majority (97%) of the total PFAS mass in AFFF-affected source-zone soils was composed of cations and zwitterions, which have often been overlooked because of limited analytical resources. This raises the question as to whether studies focusing on AFFF-source zones, which have, to date, mostly focused on anionic PFASs, are underestimating the mass of PFASs at those sites. The zwitterionic PFASs such as AmPr-FHxSA, TAmPr-FHxSA, and 6:2 FTSA-PrB (formerly known as 6:2 FTAB) are often found in AFFF-source zones,[16,18,27] yet comprehensive study of their sorption behavior is still very limited.[11] Hence, there is a need to obtain systematic data for sorption coefficients from a greater variety of PFAS subclasses and understand how PFAS structure, soil properties, and environmental factors influence sorption behavior in a range of soils.

Thus, the aim of this study was to determine sorption coefficients for a wide range of PFASs including rarely studied replacement PFASs, cyclic PFAS (PFEtCHxS), AFFF-related zwitterionic PFASs (i.e., AmPr- and TAmPr-FHxSA, and 6:2 FTSA-PrB), and other PFASs frequently found at AFFF-impacted sites such as PFAAs, fluorotelomer sulfonates (FTSs), and nonionic perfluoroalkane sulfonamides (FASAs). Sorption was studied in 10 systematically selected soils representing a wide range of physicochemical properties. The influence of solution pH and PFAS properties (including chain length, hydrophobicity, molecular weight (MW), and structure) on sorption behavior was also investigated. To gain insights into the relevant PFAS sorption mechanisms, we further aimed to evaluate how specific and multiple soil properties relate to observed differences in sorption coefficients among PFASs.

■ MATERIALS AND METHODS

Chemicals and Soils. Thirty-four PFASs covering a variety of different PFAS classes (including three AFFF-related zwitterionic PFASs) were included in this study (see Supporting Information 1, SI-1). However, only 29 PFASs were detected in both soil and water phases for K_d calculation. The studied PFASs (≥98% purity) and isotopically labeled PFAS standards were purchased from Wellington Laboratories (Canada). Details of the reported PFASs in terms of the subclass, number of perfluorinated carbons, acronym, formula, molecular weight, and their respective isotopically labeled internal standard/surrogate standard for quantification are presented in Table 1. The K_d values for five other PFASs including PFTrDA, PFTeDA, L-PFDoDS, 11Cl-PFOUdS, and 10:2 FTS were not reported in the main text because their concentrations in the aqueous phase were lower than the limits of detection (LODs) for analysis.

Ten soils designated as S1−S10 were chosen to represent a wide range of soil properties based on criteria such as Brunauer−Emmett−Teller (N_2-BET) surface area (11−120 m^2/g), OC (0.08−4.9%), cation exchange capacity (CEC) (2.28−41.4 cmol/kg), texture (sand, silt, clay), and other soil physical characteristics (see Tables 2, S1, and SI-2).

Batch Sorption Experiment. The experiment followed the international standard procedure for testing adsorption of chemicals using a batch equilibrium method.[28] In detail, the aqueous phase was prepared with Milli-Q water containing 0.01 M $CaCl_2$ (as electrolyte) and 0.003 M NaN_3 (as a microbial inhibitor). Each soil was weighed 0.8 ± 0.005 g into 50 mL polypropylene centrifuge tube (Corning Sigma-Aldrich). Approximately 8 mL of aqueous phase was added into each soil tube. All batch reactors were set up in duplicate. All soil tubes were placed at a 45° angle on an orbital shaker and shaken at 200 rpm for 24 h for pH equilibration. To assess the effects of solution pH on sorption in each soil, the experiment was conducted at 3 levels of pH ranging from approximately 3 to 8 by adjusting pH of the aqueous phase using 2 M NaOH and 2 M HCl. Again, all of the soil tubes were shaken at 200 rpm for 24 h for pH equilibrium. The supernatant pH was rechecked and readjusted to within 0.1 pH unit of the target pH where required. The natural pH of the soils in the sorption electrolyte varied from 6.2 to 7.7. The average equilibrated pHs of adjusted pH tubes were 3.4 ± 0.1, 5.2 ± 0.1, and 8.3 ± 0.1 for all soils (Table S2). The three levels of pH were chosen based on an environmentally relevant soil pH range for Australia. In each pH-equilibrated soil tube, 28 μL of PFAS stock (in methanol) was spiked into the aqueous phase to result in an initial concentration of approximately 5 ng/mL for each of the PFASs in the soil−water suspension. The final volume of aqueous phase after spiking was 8 mL, leading to a soil-to-water ratio of 1:10. The soil tubes were vortexed for 30 s and shaken at 180 rpm for 5 days (120 h) for reaching sorption equilibrium. The equilibrium time was based on kinetic tests in previous research.[29−31] See SI-3 and SI-4 for more information of the batch sorption experiment, analysis, and data quality assurance.

Data Analysis. The K_d value was estimated by the ratio of the concentration of PFAS measured in the soil phase (C_s) and the concentration of the PFAS measured in the aqueous phase (C_w), as detailed below (eq 1). To avoid an overestimation of the soil concentration, C_w was corrected by subtracting the PFASs mass in the 0.5 mL entrained aqueous phase. Using measured concentrations is more robust as both solution and solid-phase observations are independent observations.

$$K_d(\text{mL/g}) = \frac{C_s(\text{ng/g})}{C_w(\text{ng/mL})} \qquad (1)$$

Multiple linear regression (MLR) and simple linear regression (SLR) models (see SI-5) for assessing the relationship between soil characteristics (regressors) and the sorption coefficient were conducted using R software (R version 3.6.2, 2019-12-12). In addition, the analysis of variance (ANOVA) and the simple linear regression model were conducted using GraphPad Prism version 8.3.1. ANOVA was applied for evaluating the statistically significant differences in the sorption coefficient (K_d) among PFAS groups following the confidence interval (CI) of 95%. The K_d values were presented as mean ± standard deviation.

RESULTS AND DISCUSSION

Carbon-Chain Length. The raw K_d values for the 29 PFASs in 10 soils are presented in the Supporting information (Table S6). For further information, the K_d values normalized to the OC fraction or K_{oc} data are also provided in Table S7. The minimum K_d values of the other five compounds including PFTrDA, PFTeDA, L-PFDoDS, 11Cl-PF3OUdS, and 10:2 FTS were estimated using the concentration of soil phase and the LODs for the aqueous phase (Table S8). The nondetection in the aqueous phase of those five compounds was assumed to be because they were very strongly bound to the soil phase. Other PFASs were classified into four groups based on structure and sorption data: shorter chain (number of perfluorinated C ≤ 5), longer chain (number of perfluorinated C ≥ 6), zwitterionic, and others. The classification of shorter-chain and longer-chain PFASs in this study was slightly different from that of Buck et al.[32] Buck et al. defined long-chain PFASs as those with more than seven and six perfluorinated C for PFCAs and PFSAs, respectively. The log K_d values (mL/g) ranged from approximately −0.7 to 2.7 log units for all PFASs (Figure 1). All short-chain PFASs (C3−C5) including the C4 FASA (FBSA) had similar K_d values (p = 0.97). This suggests that the carbon-chain (C-chain) length does not control sorption of these compounds to soil, and binding might be attributed more to the interaction of the ionic groups of the PFAS molecules with soil surfaces.[33] In addition, K_d values of shorter-chain PFASs were less affected by soil characteristics as they were less variable with soil type (by approximately 0.5 log units). This indicates that shorter-chain PFASs associate preferentially to the aqueous phase in soil and will be highly mobile. This was also apparent for GenX and ADONA.

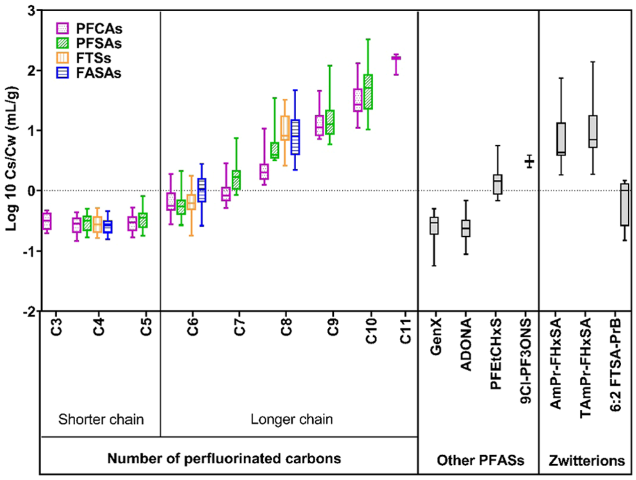


Figure 1. Box plots of logarithm (base 10) transformed K_d values for 29 PFASs in up to 10 soils as a function of perfluorinated C-chain length for PFCAs, PFSAs, FTSs, and FASAs (colored) together with other PFASs and zwitterions (gray). The boxes and whiskers represent median and minimum to maximum values, respectively; n = 3 for C11 PFCA, n = 2 for 9Cl-PF3ONS, n = 9 for zwitterions, and n = 10 for remaining compounds; n is the number of soils.

Conversely, K_d values of the longer-chain PFASs increased with the C-chain length (p < 0.001) by an average of 0.46−0.57 log units per each $-CF_2-$ moiety. This suggests that hydrophobicity is the main driving force for sorption, which agrees with most previous sorption studies.[9,12,13] Also, the longer the perfluorinated C-chain length (≥ C6), the greater the variation of K_d across soils (0.5 to ∼1.5 log units) (Figure 1), suggesting that hydrophobic effects and/or surface complexation with uncharged organic and mineral surfaces in soil could be the primary sorption mechanisms for longer-chain PFASs. This observation also applied to other longer-chain PFASs, the cyclic PFAS (PFEtCHxS), and zwitterions. For a perfluorinated C-chain length of eight but with different structures, K_d values increased in the following order: cyclic PFAS < PFCA < PFSA < FTS < FASA (p < 0.0001). This is because, at circumneutral pH, the SO_2NH_2 head group of FASAs could be partially uncharged.[34] As a result, this can possibly reduce the effect of electrostatic repulsion when C6 FASA (FHxSA) and/or C8 FASA (FOSA) molecules are close to negatively charged soil surfaces. This agrees partially with the results of Rodowa et al.[35] who studied the binding of PFASs in AFFF onto granular activated carbon. The stronger sorption (based on perfluoroalkyl carbon number) may be expected for FTSs due to their nonfluorinated carbons, and weaker sorption of the cyclic PFAS may be due to its smaller volume and molecular shape.[36] Notably, while all three zwitterions in our study had six perfluorinated carbons (Table 1), K_d values of FHxSA-derived compounds (AmPr- and TAmPr-FHxSA) were 1−2 orders of magnitude higher than those of 6:2 FTSA-PrB (zwitterion) and other C6 anionic compounds (Figure 1). This suggests that the functional groups play a substantial role in governing the sorption affinity of the zwitterions. The K_d values of AmPr- and TAmPr-FHxSA showed comparable values to C8 PFASs, indicating a high affinity for soils. This could explain why Nickerson and co-workers[18] recently reported that TAmPr-FHxSA was one of the dominant compounds remaining in soils in AFFF-contaminated zones.

The K_d values in this study are in good agreement in terms of both absolute values and range compared to those for the few compounds reported in the literature for laboratory-derived K_d values, where data are available (e.g., PFAAs, X:2 FTSs, and X:2 FTSA-PrB).[10,29] However, the K_d values are approximately 2-fold lower than those for field-derived K_d values for these same compounds.[10] It has been suggested that the differences between laboratory and field conditions is one reason for the differences in K_d values observed. Under field conditions, the temporal and spatial variability of pore water composition, the presence of additional retention processes (e.g., adsorption at the air−water interface), together with water flow could affect the K_d values observed.[37,38] In addition, the time of soil/PFAS contact in the field (field aging) is much longer than equilibration times generally used in the laboratory. If aging could occur as for some other persistent organic pollutants,[39] this would manifest in larger K_d values under field conditions. However, at least for PFOS, PFOA, and PFHxS, it has recently been demonstrated that aging in soil does not appear to reduce bioavailability markedly.[40]

Hydrophobicity. It is worth noting that the C18 column (end-capped) used for PFAS analysis separates compounds on the basis of hydrophobicity of the analytes. We noted a relationship between mean K_d values (across all soils) and retention time (RT) on the C18 chromatographic column (Figure 2). For short-chain PFASs, including PFASs ≤ C5, ADONA, and GenX, RTs were not related to K_d values. Within the same PFAS class, there was a good relationship between RT and mean K_d values of long-chain PFCAs and PFSAs. This agrees with Higgins and Luthy[12] who studied long-chain PFAAs and suggested that hydrophobicity is the predominant driving force controlling sorption. Moreover, although K_d values of nonionic FASAs seem to be significantly correlated with RT, they did not follow the trend of anionic PFASs. This further supports the presence of different sorption driving force(s).[34] In contrast, the RT values of zwitterion 6:2 FTSA-PrB (3.56 min), 9Cl-PF3ONS (3.6 min), PFNS (3.67 min), and PFDoDA (3.80 min) were close to each other, indicating similar hydrophobicity. However, the mean log K_d value of PFDoDA was 2, 1, and 0.5 orders of magnitude higher than those of 6:2 FTSA-PrB, 9Cl-PF3ONS, and PFNS, respectively. Moreover, the K_d values of 8:2 FTS and TAmPr-FHxSA were similar, but the RT of 8:2 FTS (3.04 min) was much earlier than TAmPr-FHxSA (5.38 min). Thus, the results suggest that hydrophobicity *per se* is not a reliable index for soil sorption behavior of PFASs unless they are long-chain PFAAs. This is in good agreement with previous studies[15,41] reporting that RT is an unreliable predictor for sorption of cationic and zwitterionic PFASs.

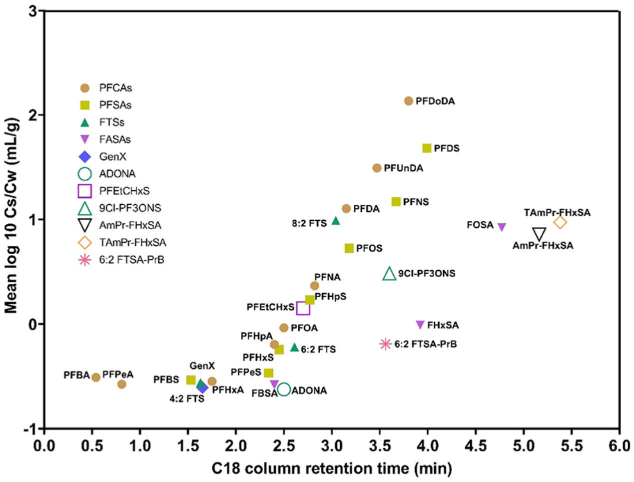


Figure 2. Mean logarithm (base 10) transformed K_d values of PFASs in 10 soils as a function of retention time on a C18 column.

Molecular Weight. For smaller PFASs (shorter-chain PFASs, GenX, and ADONA with molecular weight < 350 g/mol), there was no relationship between average K_d values (across soils) and molecular weight (MW). However, for larger PFASs (MW > 350 g/mol), there was a strongly linear and positive relationship between MW and average K_d values ($R^2 = 0.94$, $p < 0.0001$) (Figure 3). Larger molecules could have greater hydrophobicity due to the longer perfluoroalkyl chain. In addition, larger molecules may potentially enhance physical adherence of PFASs to soil surfaces through multiple contact points.[42] Large PFASs could theoretically adsorb to the soil mineral surface according to the multizone (multilayer) sorption model for surfactant-like or amphiphilic properties, which has been proposed by Kleber et al.[43] To be more specific, the first zone called contact zone where a single ligand exchange interaction could occur between the hydrophilic functional groups of the PFASs and the hydroxyl groups of soil material. Then, the second zone called the hydrophobic zone where the hydrophobic tails of the above molecules could bond to the hydrophobic portions of other amphiphilic molecules by entropic force. Finally, the third zone called the kinetic zone where the hydrophilic group of the molecules

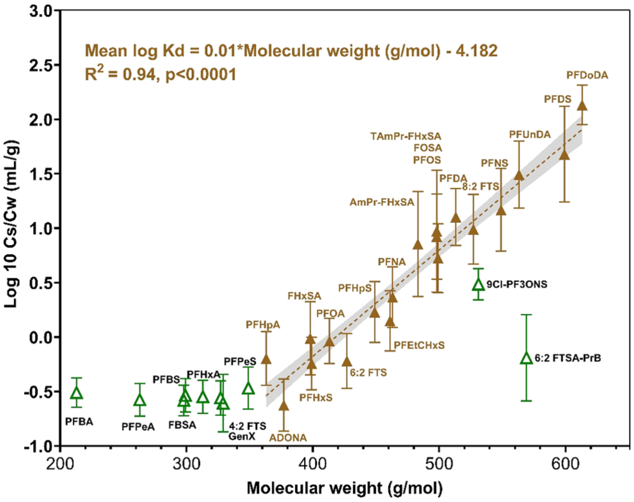


Figure 3. Logarithm (base 10) transformed K_d values (mean, SD) for 29 PFASs in up to 10 soils as a function of molecular weight. The solid brown triangles represent K_d of PFASs encompassing C6-C11 PFCA, PFSA, FTS, FASA, ADONA ($n = 10$), PFDoDA ($n = 2$), and two zwitterions including AmPr- and TAmPr-FHxSA ($n = 9$). The open green triangles represent C3-C5 PFCA, PFSA, FTS, FASA, and GenX ($n = 10$), 6:2 FTSA-PrB ($n = 9$), and 9Cl-PF3ONS ($n = 2$); n is the number of soils. The gray bar and the dashed line represent the simple linear regression of K_d values and MW, and the 95% CI, respectively. The data were grouped based on relationships between K_d values and MW.

on the second zone could theoretically interact with other molecules forming an outer region through loose hydrogen bonding or other interactions. Two larger MW compounds, 9Cl-PF3ONS and 6:2 FTSA-PrB, did not seem to fit the same relationship (Figure 3)—these two PFASs have particularly unique chemical structures that could heavily affect their sorption behavior, as will be discussed below. Maimaiti et al.[44] also reported that sorption increases with an increase in molecular size (e.g., K_d of PFCAs < K_d of PFSAs at the same perfluorinated chain length). In fact, for the same number of perfluorinated carbons (C6 and C8), molecular weight falls in the following order: PFCA < PFSA < FASA < FTS, while the order for K_d is PFCA < PFSA <FTS < FASA. This is because the SO_2NH_2 head group of FASAs might exhibit more nonionic sorbate interactions at circumneutral pH that has been discussed above.

Molecular Structure. The differences in terms of molecular structure among PFCAs, PFSAs, FTSs, and FASAs are because of their head group. The effect of the head group on K_d of these PFASs was discussed previously. Here, we will focus on compounds that have unique structures including alternative, cyclic, and zwitterionic PFASs. First, sorption coefficients of GenX and ADONA were lower than that of their predecessor PFOA and comparable to that of other shorter-chain PFASs (C3−C5) (Figure 1). This is in good agreement with previous laboratory batch sorption studies of Sun et al.,[22] the modeling approach of Gomis et al.,[25] and the field-based investigation of Joerss et al.[24] In detail, the substitution of $-CF_2-$ by an ether linkage $-O-$ in the structure of GenX (mono-ether) and ADONA (di-ether) results in a smaller MW compared to PFOA, which reduces the amount of energy needed for the formation of cavities among water molecules (or enhance hydrophilicity).[25] Similarly, 9Cl-PF3ONS, has an ether linkage that may lower its hydrophobicity compared to PFOS (C8). However, the replacement of one fluorine atom by one chlorine atom in the 9Cl-PF3ONS structure increases the MW and thus increases hydrophobicity (as discussed above) (Table 1 and Figure 3). As a result, 9Cl-PF3ONS had a similar K_d value to PFOS (Figure 3). Interestingly, we note that what we observed were different from what has been observed in biological systems, whereby the introduction of an ether linkage does not necessarily lower the affinity of these molecules for biomaterials such as albumin and biomembranes.[45,46] PFEtCHxS, another emerging PFAS similar to PFOS, has a total of eight perfluorinated carbons and a sulfonic acid functional group. However, owing to the cyclic structure, PFEtCHxS has a smaller MW compared to PFOS (Table 1), and thus its K_d value was lower than that of PFOS.

It is important to note that all three zwitterions in this study have the same number (six) of perfluorinated carbons (Table 1). Unlike other ionic PFASs, the K_d values for 6:2 FTSA-PrB were significantly lower than those of the other two zwitterions (AmPr-FHxSA and TAmPr-FHxSA), although its MW is significantly higher. This suggests that sorption of 6:2 FTSA-PrB is not affected by the perfluorinated carbon tail; thus, the sorption process(es) may be more hydrophilic in nature. At circumneutral pH, these zwitterions have one negative and one positive charge in their structures, resulting in a total net charge of zero. Hence, in this situation, the net charge may play little to no role in governing the sorption behavior of these zwitterions. Notably, while both AmPr- and TAmPr-FHxSA structures end with a positive charge, the 6:2 FTSA-PrB structure terminates with a negatively charged carboxylic head group. Soil organic matter might be generally deprotonated at pH values of 7 or above.[47] Carrasquillo et al.[48] reported that zwitterions with zero net charge but possessing a terminal negative charge could be repelled from negatively charged soil surfaces. As a result, this could reduce 6:2 FTSA-PrB sorption onto soil. This also agrees with Barzen-Hanson et al.[11] who reported the arrangement of electrical charge in zwitterion molecules governing their sorption behavior. More details on the relationship between soil properties and sorption of PFASs in this study will be discussed further below.

Effect of Soil Properties. The results for single linear regression (SLR) correlating a single soil property (Tables 2 and S1) to K_d values across all soils are presented in Table S9. Depending on the PFAS, some correlations were observed between K_d values and OC (for most of the anionic PFASs and C4, C8 FASA), K_d values and cation exchange capacity (CEC) and exchangeable calcium (Ca) (for some short-chain anionic PFASs), K_d values and soil pH (for zwitterions AmPr-FHxSA and TAmPr-FHxSA), and K_d values and soil texture (for 6:2 FTSA-PrB) ($p \leq 0.05$). Across all soils, the combinations of OC, silt-plus-clay content, and soil micropore volume in MLR models described well the sorption of anionic PFASs (Figure 4a). In contrast, the soil properties most strongly related to sorption of zwitterionic PFASs were sand (or silt-plus-clay) content, soil pH, CEC, and exchangeable sodium percentage (ESP) (Figure 4b). Interestingly, sorption of all nonionic PFASs showed weak to no relationship with soil properties (Figure 4a). Overall, MLR models explained more of the variation in the K_d values of anionic and zwitterionic PFASs than SLR models suggesting effects of multiple soil properties on sorption.[10,49,50] However, the effects of soil properties on K_d varied for different PFAS groups and perfluorinated chain lengths. Generally, multiple soil properties described the sorption of long-chain PFASs better than for short-chain PFASs (Figure 4 and Table S10). See SI-6 for a more detailed discussion on the effects of each soil property such as soil OC, silt-plus-clay content, and soil micropore volume on sorption.

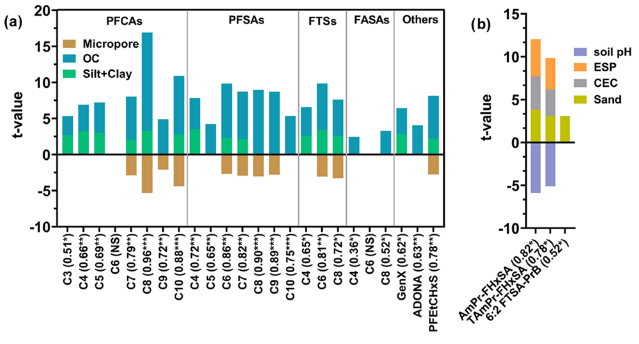


Figure 4. t-Values of significant soil properties ($p \leq 0.05$) of MLR models ($p \leq 0.05$) describing K_d values for (a) anionic and nonionic PFASs and (b) zwitterionic PFASs of the 10 soils. Data for C5 and C10 PFSA, C4 and C8 FASA, and ADONA were derived from single linear regression (SLR) ($p \leq 0.05$). No data points were available for C6 PFCA and FASA because of poor fits of the models in both SLR and MLR. The critical t-values were 2.31, 2.37, 2.45, and 2.57 for models consisting of 1, 2, 3, and 4 predictors, respectively. On the x-axis, the titles are "perfluorinated C-chain length (adjusted R^2 of the MLR, significance level)". The significant levels included not significant (NS) $p > 0.05$, $*p \leq 0.05$, $**p \leq 0.01$, and $***p \leq 0.001$. MLR models for C12 PFCA (PFDoDA) and 9Cl-PF3ONS were not computed because of the low number of soils ($n = 2$).

The K_d values of zwitterions showed big variations across soils, especially AmPr-FHxSA and TAmPr-FHxSA (~1.5 to 2 log units) (Figure 1). MLR results showed that the K_d values of zwitterionic AmPr- and TAmPr-FHxSA was dominantly and positively affected by soil charged sites, including ESP and CEC (Figure 4b). This suggested the dominant effect of electrostatic attraction/exclusion and/or cation exchange processes on sorption of these zwitterions, which agrees with previous studies on sorption of zwitterionic PFASs.[11,15] The molecular structure of zwitterions comprises both positive and negative charges making their sorption behavior different from other anionic and nonionic PFASs. For example, Xiao et al.[15] reported that the electrostatic potential of a zwitterion N-betaine propyl perfluorooctane amine—BPr-FOAd (formerly known as perfluorooctaneamido betaine, PFOAB—a PFOA precursor) was several orders of magnitude higher than that of PFOA. This also explained the significantly negative effect of soil pH on K_d values (Figure 4b) where the increase of pH could reduce the number of positive charge sites available.[51] The positive relationship with sand content (or negative to silt-plus-clay content) was unexpected. However, sorption of amphoteric surfactants on sandy materials such as sandstone and dolomite has been reported to be significantly higher than that of anionic surfactants.[52] Also, sorption of zwitterion 6:2 FTSA-PrB was found to be positively (but poorly, $R^2 = 0.52$) correlated with sand (negatively correlated with silt-plus-clay), while it showed no relationship with other candidate soil properties (Figure 4b). Furthermore, Barzen-Hanson et al.[11] reported that the K_d value of 6:2 FTSA-PrB positively correlated with effective cation exchange capacity (ECEC) that considers the effect of H^+, Al^{3+}, and Mn^{2+} for highly acidic soils. However, in this study, the effect of ECEC was not investigated.

Effect of Solution pH. Altering solution pH (approximately 3−8) substantially affected sorption of all PFASs examined here (Figure 5). For all PFASs, the K_d values decreased with the increase in solution pH. This was consistent with other previous soil/sediment sorption studies of anionic PFASs[12,31] and of organic acids.[53] Table S11 details the estimated pK_a values and the percentage dissociation at the four different pH scenarios.[54] The studied PFASs were grouped by their pK_a values: those with low pK_a values (≤ 2; PFAAs, FTSs, and other PFASs) and those with high pK_a values (> 2; nonionic FASAs and zwitterions). When pH increased from ~3 to 8, the log K_d values of the high-pK_a group (except C4 FASA) reduced by 1−2 log units, while the log K_d values of the low-pK_a group reduced by approximately 1 log unit. Particularly, with the increase of one pH unit, the K_d values for C3-C5 PFASs (including GenX and C4 FASA) decreased by an average of 0.05 ± 0.01 log units. A decrease of 0.1 ± 0.02 log unit in K_d values was observed for ≥C6 PFASs (including PFEtCHxS and ADONA). For C6, C8 FASA, and the zwitterions (high pK_a group), K_d values decreased by an average of 0.21 ± 0.06 log unit. These results are in good agreement with Barzen-Hanson et al.[11] for soil, but reductions in K_d were lower than that found by Higgins and Luthy[12] for sediment (relatively higher in organic carbon content), where there was a 0.37 log unit reduction observed per pH unit increment.

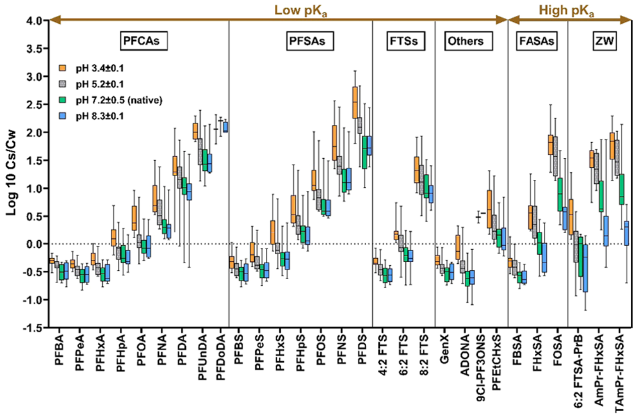


Figure 5. Box plot of logarithm (base 10) transformed K_d values of 29 PFASs at four solution pH (mean, minimum to maximum). ZW: zwitterions. PFDoDA $n = 1$ at pH 3.4 ± 0.1, $n = 2$ at pH 5.2 ± 0.1, $n = 3$ at pH 7.2 ± 0.5, and $n = 4$ at pH 8.3 ± 0.1. For 9Cl-PF3ONS, $n = 0$ at pH 3.4 ± 0.1 and 5.2 ± 0.1, $n = 2$ at pH 7.2 ± 0.5, and $n = 1$ at pH 8.3 ± 0.1, $n = 9$ for all zwitterions, $n = 10$ for other PFASs unless otherwise stated; n is the number of soils. pK_a is the negative log of the acid dissociation constant. pK_a ≤ 2 and > 2 were referred to "Low pK_a" and "High pK_a", respectively.

The effects of solution pH on K_d values varied among analytes, with compounds having a high pK_a showing greater changes with pH compared to compounds with a low pK_a. In fact, pK_a values of PFAAs, FTSs, GenX, ADONA, 9Cl-PF3ONS, and PFEtCHxS were negative, except for C4 and C5 PFCAs (1.07 and 0.34, respectively) (Table S11).[54] The estimated pK_a values were substantially lower than the values reported in the literature (available for some PFAAs only).[55,56] However, the reported pK_a values for those available in the literature are also substantially lower than 2. Between the studied pH range of 3.4−8.3, these PFASs remained deprotonated (except PFBA, PFPeA, and PFHxA with 0.46, 0.09, and 0.01% present as an uncharged ion at pH 3.4, respectively) (Table S11). In other words, the changes in pH within the studied range had little to no effect on the speciation of the low-pK_a PFASs. As the PFASs remained anionic, the pH-induced change in K_d values was attributed to changes in the surface charge and/or hydrophobicity of the soil surfaces. As pH increases, soil OC and clay minerals become progressively more negatively charged, causing electrostatic repulsion of anionic PFASs and reducing sorption.[51] At low pH, soil OC is more protonated, and hence this could enhance sorption significantly by contributing to both hydrophobic and electrostatic attraction. This was in good agreement with Gu et al.[51] and Higgins and Luthy,[12] suggesting that when pH changed, the changes of soil surface saturating cations affected the distribution coefficient of organic acids, including PFASs. Furthermore, short-chain PFASs preferentially partitioned to the aqueous phase (low K_d); thus, sorption was less affected by the changes of soil surface chemistry. This explained why shorter-chain PFASs in the low-pK_a group were less pH-sensitive than longer-chain PFASs for all PFAS groups (Figure 5).

On the other hand, the high-pK_a group showed greater pH-dependent changes in K_d compared to the low-pK_a group. Hence, within the studied range of solution pH, not only were there changes in soil surface chemistry but also changes in the speciation of the PFAS molecules that affected sorption. Conversely, the changes in sorption of zwitterion 6:2 FTSA-PrB were similar to the changes of other anionic PFASs of the low-pK_a group. This is in good agreement with the finding of Barzen-Hanson et al.,[11] who suggested that only the changes in soil surface chemistry contributed to the change of K_d values of X:2 FTSA-PrB. Interestingly, in the high-pK_a group, zwitterion AmPr-FHxSA (pK_{a1} 3.57, pK_{a2} 9.21) and TAmPr-FHxSA (pK_a 3.28) showed a high sensitivity to changes in pH from ~7 to 8 despite negligible changes in predicted speciation (Table S11). This implied that the modeled pK_a values for the two compounds could be too low. Similarly, the most drastic changes in K_d values of FASAs was apparent when solution pH increased from approximately 5 to 7. Hence, we further suggest the pK_a values of the zwitterions and FASAs to be higher than 4.[55]

■ ENVIRONMENTAL IMPLICATIONS

Understanding soil−water partitioning of PFASs is important for predicting the mobility and biological availability of PFASs in the environment and to develop more effective remediation/management strategies. PFAS structure and charge characteristics had a significant effect on K_d values. Longer-chain PFASs (≥C6) were preferentially adsorbed to the soil phase, while shorter-chain PFASs were more associated with the water phase. 9Cl-PF3ONS showed similar sorption behavior to PFOS. However, GenX and ADONA had lower K_d values than their predecessor, PFOA. Although PFOA, PFOS, and PFHxS have attracted the most concern at contaminated sites, shorter-chain PFASs have lower K_d values and are therefore much more mobile in the environment. This poses a greater challenge for management. High K_d values of the zwitterions, AmPr-FHxSA and TAmPr-FHxSA, indicated a high affinity for soil surfaces. Thus, these zwitterions may resist leaching and therefore persist in source-zone soils for longer.[18]

Sorption of PFASs onto soil is also affected by soil solid-phase properties. Apart from frequently studied soil properties (such as organic carbon, cation exchange capacity, soil pH, and soil texture), this study suggested soil micropore volume as an important soil factor for studying sorption of PFASs onto soil, especially long-chain PFASs. This study is also one of a limited number of studies that assessed the effect of soil micropore volume on sorption of PFASs. Multiple soil properties described sorption better than any single property. Sorption of anionic PFASs was affected by OC content, soil micropore volume, and silt-plus-clay content. For zwitterions, soil CEC, soil ESP, and soil pH were the main factors predicting sorption. Sorption of nonionic FASAs did not show clear relationships with any of the studied soil properties. Solution pH also affected sorption markedly, with K_d values increasing as solution pH was decreased. The magnitude of this effect is likely the result of the interplay between compound speciation (as affected by pK_a) and pH-induced changes in soil surface charge/hydrophobicity. It is also important to note that a number of the polyfluorinated substances studied can potentially undergo biotransformation, resulting in persistent PFAAs and other PFASs over time.[57−60] Hence, it is expected that the migration behavior of PFASs in soil at impacted sites may vary temporally and is highly site-specific.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.0c05705.

> Soil characterization, batch sorption experiment, quality assurance and quality control, data analysis, effects of specific soil properties on sorption of PFASs, and supplementary figures and tables (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The Queensland Alliance for Environmental Health Sciences (QAEHS), The University of Queensland, gratefully acknowledges the financial support of Queensland Health. This project was supported by an Australian Research Council Special Research Initiatives Project (SR180100005). The authors thank industrial project partners including Wellington Laboratories and Eurofins, and also thank Dr. Zhi Qu (School of Pharmacy, The University of Queensland) for assistance with BET analysis.

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https://dx.doi.org/10.1021/acs.est.0c05705
Environ. Sci. Technol. 2020, 54, 15883−15892