

# Sorption of Perfluorinated Surfactants on Sediments<sup>†</sup>

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The sorption of anionic perfluorochemical (PFC) surfactants of varying chain lengths to sediments was investigated using natural sediments of varying iron oxide and organic carbon content. Three classes of PFC surfactants were evaluated for sorptive potential: perfluorocarboxylates, perfluorosulfonates, and perfluorooctyl sulfonamide acetic acids. PFC surfactant sorption was influenced by both sediment-specific and solution-specific parameters. Sediment organic carbon, rather than sediment iron oxide content, was the dominant sediment-parameter affecting sorption, indicating the importance of hydrophobic interactions. However, sorption also increased with increasing solution  $[Ca^{2+}]$  and decreasing pH, suggesting that electrostatic interactions play a role. Perfluorocarbon chain length was the dominant structural feature influencing sorption, with each  $CF_2$  moiety contributing 0.50–0.60 log units to the measured distribution coefficients. The sulfonate moiety contributed an additional 0.23 log units to the measured distribution coefficient, when compared to carboxylate analogs. In addition, the perfluorooctyl sulfonamide acetic acids demonstrated substantially stronger sorption than perfluorooctane sulfonate (PFOS). These data should prove useful for modeling the environmental fate of this class of contaminants.

## Introduction

The distribution of perfluorochemicals (PFCs) in the global environment has been well documented in recent years. Many PFCs are extremely environmentally persistent and can exert toxic effects when administered at high doses (1, 2). Despite their detection in sediments (3, 4), and in water bodies such as rivers (5, 6) and oceans (7), data on the partitioning of fluorochemicals between these media are scarce. Such data are inherently necessary both to model the fate of existing fluorochemicals released to aqueous environments and to evaluate the potential environmental fate of new fluorochemicals as they are developed.

In a recent study, Liu and Lee found sorption of 8:2 fluorotelomer alcohol to soils to be strongly correlated with the fraction of organic carbon ( $f_{oc}$ ) in the soil (8). While such behavior may be expected for neutral hydrophobic organic contaminants (HOCs), it is unclear whether the simple hydrophobic partitioning paradigm used to explain HOC sorption is applicable to all PFCs, particularly anionic PFC surfactants such as perfluorooctanesulfonate (PFOS). Previous work on the sorption of linear alkylbenzene sulfonate (LAS) surfactants demonstrated that solution parameters such as pH and

aqueous  $[Ca^{2+}]$  also affect sediment–water distribution coefficients (9). The existence of electrostatic interactions between the sulfonate moiety and mineral surfaces is supported by correlations between the amount of free iron oxide in the soils and LAS sorption (10) and sorption competition between LAS and other inorganic anions (11). Conversely, electrostatic interactions with sediment organic matter would likely be repulsive in nature due to the presence of negative charges on both the sorbate and the organic matter. Given the hydrophobicity and oleophobicity of the perfluorinated chain and the hydrophilicity of the sulfonate or carboxylate head groups, it is likely that both hydrophobic and electrostatic effects influence anionic PFC sorption.

The goal of this study was to examine various sorbent-specific, solution-specific, and chemical structure-specific parameters potentially affecting sorption of anionic PFC surfactants to sediments. We evaluated sorption of anionic PFCs to sediments of varying geochemical composition by selecting sediments with substantially different iron oxide and organic carbon content. In addition, we investigated the effects of pH and increasing electrolyte concentrations on PFC sorption. Last, by conducting sorption experiments with anionic PFC surfactants of differing chain length and head groups, we were able to quantitatively evaluate the contributions of these structural components to sorption potential.

## Materials and Methods

**Materials.** A purity-corrected equimolar stock standard solution containing perfluorooctanoate (PFOA), perfluorononanoate (PFNA), perfluorodecanoate (PFDA), perfluoroundecanoate (PFUnA), PFOS, perfluorodecanesulfonate (PFDS), 2-(*N*-methylperfluorooctanesulfonamido) acetic acid (*N*-MeFOSAA), and 2-(*N*-ethylperfluorooctanesulfonamido) acetic acid (*N*-EtFOSAA) was prepared in a 70/30 (v/v) methanol/aqueous ammonium hydroxide (0.01%) solution. Calcium chloride, sodium chloride, sodium hydroxide, 1 N hydrochloric acid, methanol, acetic acid, ammonium hydroxide, and ammonium acetate were purchased from Fisher Scientific. The internal standards [<sup>13</sup>C<sub>2</sub>] PFOA and [<sup>13</sup>C<sub>2</sub>] PFDA were purchased from Perkin-Elmer Life Sciences (Boston, MA), and Wellington Laboratories (Guelph, ON), respectively. Information on standard purity and sources is available in the Supporting Information.

The freshwater sediments used for this study were selected to reflect a variety of geochemical parameters potentially influencing anionic PFC sorption (Table 1) and were collected from various riverine and lacustrine sites throughout the U.S. Sediments were sieved (2.36 mm) prior to air drying and homogenized using a mortar and pestle. Air-dried sediments were  $\gamma$ -irradiated with 1–4 MRads to reduce biological activity.

All sorption experiments were conducted in 50 mL polystyrene (PS) centrifuge tubes. Previous work has suggested polypropylene (PP) to be the most suitable material for anionic PFC sorption experiments (12). However, in initial experiments, recoveries of controls from PS tubes were consistently higher than those achieved with PP or glass vials (unpublished data).

**Sorption Uptake Kinetics.** To determine an appropriate equilibration time, a sorption kinetic uptake experiment was conducted with Sediment 1. Triplicate sets of vials containing 5.0 g of Sediment 1 and 50 mL 500  $\mu$ M  $CaCl_2$  were spiked with equimolar stock PFC solutions to reach initial aqueous concentrations of 10 nM. The vials were then placed on an orbital shaker (Barnstead International, Dubuque, IA). Vials

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**TABLE 1. Sediment Characteristics<sup>a</sup>**

Sediment	org C %	sand %	silt %	clay %	CEC ( $\mu\text{mol/g}$ )	AEC ( $\mu\text{mol/g}$ )	measured pH	BET surface area ( $\text{m}^2/\text{g}$ )	DCB extractable ( $\mu\text{mol/g}$ )	
									Fe	Al
1	2.48	11	36	53	386	0.3	7.0	18	334	41
2	1.02	49	25	26	300	2.5	7.5	27	116	7
3	4.34	31	38	31	321	0.0	7.6	27	121	14
4	0.56	65	22	13	321	15.7 <sup>b</sup>	6.4	89	1025	171
5	9.66	80	15	5	222	0.9 <sup>c</sup>	5.7	8	268	90

<sup>a</sup> Org C% denotes percent organic carbon (dry weight), CEC denotes cation exchange capacity, AEC denotes anion exchange capacity (measured at pH 8), BET surface area denotes Brunauer Emmett and Teller surface area (measured with  $\text{N}_2$ ), and DCB denotes dithionite-citrate-bicarbonate extractable Fe or Al. <sup>b</sup> Measured at pH 7. <sup>c</sup> Measured at pH 6.

were periodically removed over 10 days and the aqueous PFC concentrations determined. For a subset of these samples, the sediment was dried, extracted, and analyzed for PFC content. A second set of triplicate vials containing only the aqueous phase was prepared and analyzed at each time point as controls.

**Sample Analysis.** Aqueous samples were analyzed directly via liquid chromatography tandem mass spectrometry (LC/MS/MS). Each 50 mL PS vial containing a sediment–aqueous mixture was centrifuged and an aqueous aliquot removed. This aliquot was diluted with methanol and centrifuged an additional 30 min before a subsample was transferred to an autosampler vial for analysis. Sediments were extracted using procedures similar to that previously described (3). Aqueous samples and extracts were analyzed via LC/MS/MS using instrumentation and under conditions previously described (3), with a few minor modifications (discussed in the Supporting Information).

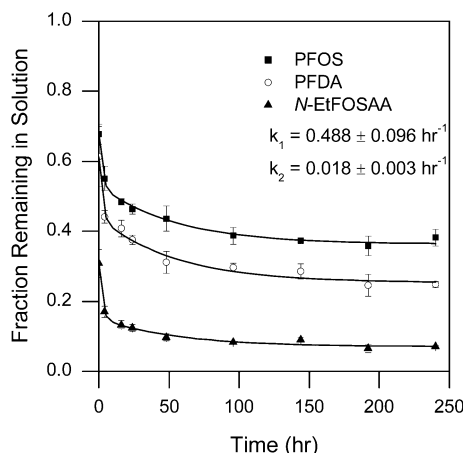
**Aqueous Solution Composition.** Unless otherwise specified, the initial aqueous solution used in sorption experiments consisted of 0.5 mM  $\text{CaCl}_2$ . This is within the range of previously reported sorption experiments for LAS with  $\text{CaCl}_2$  varying from 0.1 to 3.0 mM (9). As additional electrolytes were expected to be released from the sediment during equilibration, final aqueous concentrations of major metal ions were determined by inductively coupled plasma atomic emission spectroscopy. Initial aqueous PFC concentrations of 1–200 nM (approximately 0.5–100  $\mu\text{g/L}$ ) were achieved by adding 100  $\mu\text{L}$  of an equimolar stock solution to each vial containing 50 mL of the aqueous phase (controls) or 50 mL aqueous phase and air-dried sediment. The final methanol content of each vial was less than 0.2%. Sample pH was determined after centrifugation and removal of the subsample. To evaluate the effects of  $[\text{Ca}^{2+}]$  and  $[\text{Na}^+]$  on partitioning, subsequent experiments were conducted with Sediment 3 in which the  $\text{CaCl}_2$  and  $\text{NaCl}$  concentrations were varied from 0.1 to 50 mM and from 0.1 to 100 mM, respectively. Additional experiments were conducted with Sediment 3 in which the pH of the solution was varied by adding various volumes of 1 N HCl or 1 N NaOH to the 0.5 mM  $\text{CaCl}_2$  solutions prior to equilibration with the sediment, with the pH of the sediment slurry measured at the end of the experiment.

**Determination of Distribution Coefficients.** Distribution coefficients were determined via the aqueous loss method: aqueous concentrations were determined for all samples, and the corresponding sediment concentrations calculated. These calculations, as described in the Supporting Information, accounted for aqueous solution composition–dependent losses observed in the controls using a three-compartment equilibrium-based approach. The losses observed in the controls were rapid, suggesting the losses were likely surface-driven and not due to diffusion into the polystyrene vial walls. With the exceptions of *N*-MeFOSAA and *N*-EtFOSAA, these estimated losses to the vial/interface

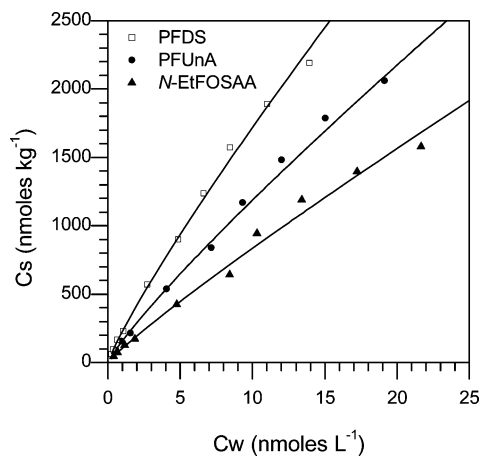
were typically less than 5%. For *N*-MeFOSAA and *N*-EtFOSAA, losses to the vial/interface of up to 44% were estimated, though most losses were much lower (12–20%). After equilibrating for 10 d on an orbital shaker, vials were removed and the aqueous PFC concentrations determined. Sediment from approximately one-third of all samples was also extracted and analyzed to verify the accuracy of this approach: when including the estimated losses, recoveries ranged from 63 ( $\pm 3$ ) to 120 ( $\pm 7$ ) % for triplicate vials, with an overall average mass balance for all samples and all analytes of 96 ( $\pm 10$ )% ( $n = 1250$ ). The only major outliers were *N*-MeFOSAA and *N*-EtFOSAA in Sediment 4, for which mass balances were consistently less than 75%, including estimated vial losses of approximately 20%. For these analytes in this sediment, distribution coefficients were calculated based on the actual sediment concentrations determined by extraction. Sorption coefficients were not calculated if the measured aqueous concentration accounted for >90% of the mass in the system (i.e., if less than 10% of the mass was taken up by the sediment).

**Results and Discussion**

**Sorption Kinetics.** As evident in Figure 1, several days of mixing were required to reach equilibrium in this study. Significant sorption occurred at the initial timepoint (i.e., after spiking the vial and vortexing for 30 s), with additional transfer to the sediment phase over the next several days. Not including the initial rapid uptake, the kinetic data were described quite well by a biexponential expression indicating both fast ( $k_1$ ) and slow ( $k_2$ ) uptake rates, with identical fitted rate constants for all analytes in tests for which significant sorption (i.e., >20% sorbed at 10 days) was observed (all but



**FIGURE 1. Sorption of *N*-EtFOSAA ( $\blacktriangle$ ), PFDA ( $\circ$ ), and PFOS ( $\blacksquare$ ), onto sediment 1 (at 0.1 kg/L). Error bars denote the standard deviation for each timepoint ( $n = 3$ ). Rate constants from the fit of the equation  $F_w = F_0 + F_1 \times \text{EXP}(-k_1 t) + F_2 \times \text{EXP}(-k_2 t)$ , where  $F_0$ ,  $F_1$ , and  $F_2$  are kinetically different fractions sorbing for each analyte.**



**FIGURE 2.** Sorption of *N*-EtFOSAA ( $\blacktriangle$ ), PFUnA ( $\bullet$ ), and PFDS ( $\square$ ), onto Sediment 3 (at 0.038 kg/L). Each data point represents an average of triplicate vials. Lines are the fitted Freundlich isotherms.

PFOA). This kinetic profile suggests a rapid initial transfer into the near surface boundary layer of the sediment aggregate, followed by a two-step diffusional transport into the aggregate's internal water and/or organic matter. In a previous LAS study, sediments were equilibrated for 4 h (9), while others examining PFOS sorption and PFOA sorption equilibrated for 48 and 24 h, respectively (12, 13). However, substantially longer times were required in the present study to achieve equilibrium. Though desorption experiments were not conducted, no statistical differences in aqueous concentrations were discernible between 192 and 240 h for any of the PFCs measured in this study. To ensure equilibrium had been reached, 240 h (10 days) was chosen for the subsequent sorption experiments.

**Linearity of Isotherms.** Many of the isotherms measured in this study were nonlinear (Figure 2, Supporting Information Table 1e). This nonlinearity is often described with respect to the Freundlich equation:

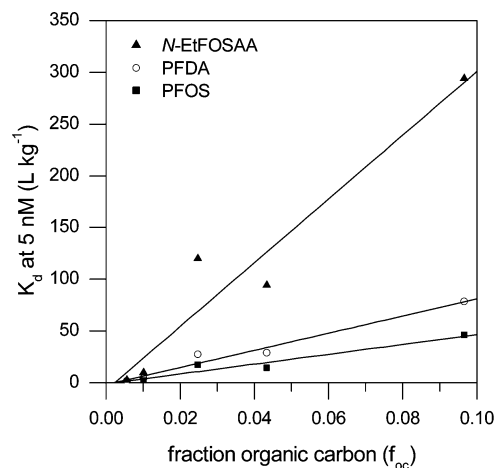
$$C_{\text{sed}} = K_f(C_w)^n \quad (1)$$

or

$$\log C_{\text{sed}} = n \log C_w + \log K_f \quad (2)$$

where  $n$  provides an indication of the nonlinearity ( $n = 1$  for a linear isotherm) and  $K_f$  the specific Freundlich sorption distribution coefficient expressed as [(pmoles/kg)(pmoles/L) $^{-n}$ ]. With  $C_{\text{sed}}$  (sediment concentration) expressed in pmoles/kg and  $C_w$  (aqueous concentration) expressed in pmoles/L, values of  $n$  measured in this study were typically between 0.75 and 1.00, with an average of approximately 0.90. The notable exceptions were for sorption of *N*-MeFOSAA and *N*-EtFOSAA on Sediment 4, for which  $n$  values were 0.70 and 0.68, respectively. Linear isotherms are typically expected when the sorption process can be described as equilibrium partitioning between two phases (14). In contrast, nonlinear isotherms can be attributed to adsorption site heterogeneity, sorbate-sorbate interactions (including repulsive electrostatic interactions), and other factors, as discussed elsewhere (9, 15).

One potential source of nonlinear isotherms is the possible competitive effects of the presence of other PFC surfactants in the mixed stock standard solution. However, initial tests comparing PFOS sorption to Sediment 1 alone and in the presence of the other PFC surfactants included in this study revealed nearly identical isotherms (Supporting Information Table 1a). Thus, all data presented reflect the distribution



**FIGURE 3.** Dependence of interpolated distribution coefficients ( $K_d$  values) on sediment organic carbon ( $f_{oc}$ ).

coefficients obtained from the multisolute batch sorption experiments.

A complication of nonlinear isotherms is that using extrapolated  $K_f$  values (eq 2) to compare sorption onto different sediments or under different solution conditions can lead to biased results. Thus, to allow comparison of distribution coefficients between different sediments and solutions, concentration-specific distribution coefficients (i.e.,  $K_d$  values) were interpolated for each system and analyte for an aqueous concentration of 5 nM (e.g., Supporting Information Table 1).

**Sorption of PFCs on Different Sediments.** As one of the goals of this study was to determine the most important sediment-specific parameters influencing sorption, sediments were selected to represent a wide range of geochemical parameters potentially influencing sorption (Table 1). Most importantly, sediment organic carbon varied from 0.56 to 9.66%, while iron oxide content varied from 116 to 1025  $\mu\text{mol/g}$ . As evidenced by low the AEC and high CEC (see Table 1), four of the sediments (1–3, 5) likely had net negative surface charges, while Sediment 4 likely exhibited a net positive surface due to its high iron oxide content (and consequently high AEC).

Despite previous observations of anionic surfactant sorption to iron oxide-rich materials (16), the dominant sediment parameter influencing sorption of anionic PFC surfactants in this study was sediment organic carbon (e.g.,  $f_{oc}$ ; Figure 3; Table 2). While one must be careful in drawing definitive conclusions from this small set of sediments ( $n = 5$ ), these data strongly suggest that sorption to organic matter is more important for anionic PFC surfactants than adsorption to mineral surfaces, at least for the range of concentrations examined in this study. This finding is also supported by sorption data previously collected for PFOA (13). Though anomalously high sorption was observed for Sediment 1 ( $f_{oc} = 0.0248$ ) for many analytes, the coefficient of determination of the interpolated  $K_d$  values vs  $f_{oc}$  was strong (Table 2). Sediment organic carbon-normalized distribution coefficients ( $K_{oc}$ ) obtained from these regressions are provided in Table 2. These values are slightly higher than the average log  $K_{oc}$  values, also reported in Table 2. As the goal of this specific set of experiments was to determine the sediment-specific parameters most responsible for sorption, extensive efforts to control the solution chemistry were not made. Thus, the pH of these systems varied from 5.7 to 7.5 (Table 1) and the  $[\text{Ca}^{2+}]$  varied from 0.1 to 11 mM (Supporting Information Table 1). It is likely that at least some of the variability observed in Figure 3 and Table 2 can be accounted for not only by the variable solution chemistry but also the heterogeneity of the

**TABLE 2. Sediment Organic Carbon-normalized Distribution Coefficients**

analyte	CF <sub>3</sub> -(CF <sub>2</sub> ) <sub>y</sub> -X		regression Log K <sub>oc</sub> ± SE (L/kg <sub>oc</sub> )	R <sup>2</sup>	n <sup>a</sup>	Log normal average Log K <sub>oc</sub> ± SE (L/kg <sub>oc</sub> )
	y	X				
PFOA	6	CO <sub>2</sub> <sup>-</sup>	2.11	N/A	(2)	2.06
PFNA	7	CO <sub>2</sub> <sup>-</sup>	2.50 ± 0.12	0.929	(3)	2.39 ± 0.09
PFDA	8	CO <sub>2</sub> <sup>-</sup>	2.92 ± 0.04	0.972	(5)	2.76 ± 0.11
PFUnA	9	CO <sub>2</sub> <sup>-</sup>	3.47 ± 0.04	0.977	(5)	3.30 ± 0.11
PFOS	7	SO <sub>3</sub> <sup>-</sup>	2.68 ± 0.09	0.928	(4)	2.57 ± 0.13
PFDS	9	SO <sub>3</sub> <sup>-</sup>	3.66 ± 0.05	0.957	(5)	3.53 ± 0.12
N-MeFOSAA	7	SO <sub>2</sub> N(CH <sub>3</sub> )CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>	3.35 ± 0.07	0.933	(5)	3.11 ± 0.16
N-EtFOSAA	7	SO <sub>2</sub> N(CH <sub>2</sub> CH <sub>3</sub> )CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>	3.49 ± 0.07	0.930	(5)	3.23 ± 0.18

<sup>a</sup> Number of sediments included in the regression.

organic carbon present in each sediment. Despite this variability, the measured log K<sub>oc</sub> value for PFOS is within the range previously observed by 3M Co. (log K<sub>oc</sub> = 2.57–3.1 L/kg<sub>oc</sub> (12)). In addition, if the average of the two PFOA log K<sub>oc</sub> values available from this study are used (log K<sub>oc</sub> of 2.06 L/kg<sub>oc</sub>, n = 2), these data are also consistent with that reported for PFOA by DuPont (log K<sub>oc</sub> 1.90–2.17 (13)).

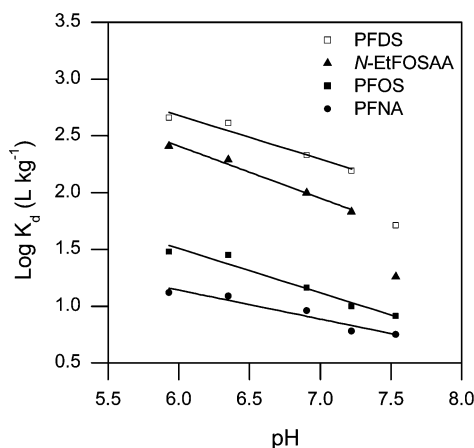
**Impact of Solution Parameters.** The impact of solution chemistry on the sorption of charged organic molecules has long been recognized (17). Although sediment organic carbon content was found to be the dominant sediment-specific parameter influencing sorption, this does not exclude the possibility that solution-specific parameters may also significantly affect anionic PFC sorption. Most sediment organic matter typically exists in a charged state due to the ionization of carboxyl and phenolic groups (14), and organic matter can often contribute substantially to the CEC of a soil or sediment because of these charged sites. Thus, any solution parameters that potentially influence the degree of ionization within the organic matter or the extent to which the charge penetrates into the solution (e.g., the thickness of the diffuse double layer) also warrant investigation. To this end, PFC sorption experiments were conducted with one sediment (Sediment 3), while the solution pH, [Na<sup>+</sup>], and [Ca<sup>2+</sup>] were varied.

**Solution pH.** Many investigators have demonstrated the importance of pH on organic anion sorption (17), though the dominant effects observed are typically due to the protonation/deprotonation of the organic acid near its pK<sub>a</sub>. As noted by Jafvert, however, this does not completely explain the pH dependence commonly observed (17). Many other system parameters are affected by pH changes, including factors such as the organic matter surface charge. As the pK<sub>a</sub> values of the C1–C11 PFCAs are expected to be less than 3.5 (18) and the pK<sub>a</sub> values of sulfonic acids are generally much lower than analogous carboxylic acids, it is likely that any pH effects observed are due to pH-dependent changes in the sorbent (such as organic matter charge) rather than protonation/deprotonation of the sorbate.

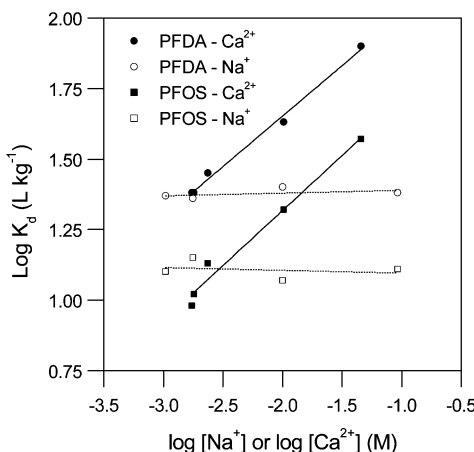
As might be expected from electrostatic theory, sorption of anionic PFCs to Sediment 3 increased with decreasing pH, with a rate of change of approximately 0.37 log units per unit pH (Figure 4; Supporting Information Table 2b). The pH range over which these experiments were conducted is comparable to the range of pH values observed with the different sediment materials (pH 5.7–7.5; Table 1). As shown in Figure 4, the change in log K<sub>d</sub> per unit pH varied slightly depending on the analyte, though it is unclear whether this variation is due to chemical-specific interactions or is simply an analytical artifact. Perhaps more interestingly, there was a significant drop in the observed K<sub>d</sub> for the most hydrophobic compounds at the highest pH measured (7.5). These unusually low K<sub>d</sub> values (which were omitted from the regressions) may be due to significant increases in the dissolved organic

carbon (DOC) at pH 7.5. Because DOC-associated PFCs would be included as aqueous-phase PFCs using the analytical protocol described in this study, a significant increase in the DOC present would bias the analytical results, yielding a lower-than-expected K<sub>d</sub>. However, the measured DOC for these systems was essentially constant (Supporting Information Table 4), suggesting a change in DOC was not responsible for these observations. A more detailed discussion of this potential effect is provided in the Supporting Information.

**Calcium and Sodium Effects.** As apparent in Figure 5, the concentrations of other cations in solution also impact the sediment–water distribution coefficients for anionic PFCs. For calcium, the average increase in log K<sub>d</sub> per log unit [Ca<sup>2+</sup>] was 0.36 ± 0.04. This change was more consistent for



**FIGURE 4. Effects of increasing pH on anionic PFC distribution coefficients.**



**FIGURE 5. Effects of increasing concentrations of metal cations on anionic PFC distribution coefficients.**

all analytes than the changes with pH, and is nearly twice the change per log unit  $[Ca^{2+}]$  observed for LAS (0.219) (9). Sodium did not significantly increase sorption of the anionic PFCs measured in this study. Such observations strongly suggest that the observed changes are not simply ionic strength effects, as these two experiments encompassed similar ranges in ionic strength (9–150 mM for Ca, 8–110 mM for Na). Others have also observed enhanced sorption of anionic organic chemicals to clays in the presence of divalent cations as opposed to monovalent cations at the same ionic strength (19), leading those authors to conclude that simple compression of the electrostatic double layer could not explain the observed effects. We interpret the effects of  $[Ca^{2+}]$  on sorption as a reduction in the charge present on the organic matter (i.e., a reduction in the potential,  $\psi$ ). This is also consistent with the changes in sorption with pH and  $[Na^+]$ : while specific functional groups present in the organic matter may change protonation states with changes in pH, specific interactions between these functional groups and  $[Na^+]$  are not expected.

With sediment, it is often difficult to experimentally vary parameters such as  $[Ca^{2+}]$  without also changing parameters such as pH, and vice versa. The fact that the measured  $[Ca^{2+}]$  increased from 1.1 mM at pH 7.5 to 22 mM at pH 5.9 suggests that the larger effects on sorption observed in this study as compared to the LAS study ( $\Delta \log K_d / \Delta pH \approx 0.37$  for PFCs vs 0.173 for LAS;  $\Delta \log K_d / \Delta \log [Ca^{2+}] \approx 0.36$  for PFCs vs 0.219 for LAS) (9) may have been due to simultaneous variations of multiple parameters. Differentiating between these effects so as to develop a model for a priori estimation of  $K_d$  values for simple anionic surfactants is the subject of ongoing research.

**Structural Features Affecting Sorption.** As is apparent in Figures 1–5 and Table 2, both the length of the perfluorocarbon tail and the functionality of the head group impact the sorption of the anionic PFC surfactant to sediment materials. Each  $CF_2$  moiety increased the distribution coefficient by approximately 0.5–0.6 log units for both the perfluorosulfonates and the perfluorocarboxylates. Though variable, this trend was consistent across all experiments, and is somewhat higher than the difference of 0.4–0.44 log units per  $CH_2$  moiety that has been reported previously (9). In energetic terms, this  $\sim 0.55$  log unit difference is equivalent to a difference in free energy of  $-750$  cal/mol, which is very close to the free energy of transfer (per  $CF_2$  moiety) from an aqueous to a micellar environment previously reported ( $-762 \pm 25$  cal/mol) (20). While it is unlikely that micelles or even hemimicelles are forming within the sediment organic matter, the similar values suggest that the change in free energy due to sorption of an anionic PFC surfactant monomer to the sediment is very similar to the free-energy change due to its movement from the bulk aqueous phase into a micelle. The fact that this energy difference is relatively consistent across the different sediments also suggests that interactions of the  $CF_2$  moiety with the different sorbents are very similar. Furthermore, this  $\sim 0.55$  log unit difference per  $CF_2$  moiety is very close to that predicted by others for absorption of fluorotelomer olefins and alcohols into humic acid from water ( $\sim 0.6$  log units per  $CF_2$  moiety) (21). Though describing sediment organic matter as a homogeneous phase is an oversimplification at best, these observations do support the suggestion that absorption, or, at the very least, limited penetration of the anionic PFC surfactants into the sediment organic matter is the dominant mechanism of sorption.

While the differences in  $K_d$  values per  $CF_2$  moiety are expected, also observed were consistent differences in  $K_d$  values between the perfluorosulfonates and perfluorocarboxylates of equal chain length (e.g., Figure 2). On average, the sorption of a perfluorosulfonate was 1.7 times stronger (0.23 log units) than the perfluorocarboxylate analog. As noted

previously, if only nonselective electrostatic interactions are possible, the differences in sorption between these two head groups should be minimal (14). Whether this observed difference is due to the slightly larger size of the sulfonate moiety as compared to the carboxylate moiety (leading to slightly more hydrophobicity) or specific electrostatic interactions for these moieties remains unclear.

**Implications.** With measured sediment–water distribution coefficients in hand, we felt it illustrative to revisit the assumption of Boulanger et al. that losses of PFCs from Lake Ontario due to sedimentation were likely negligible in comparison to outflow losses (22). Ignoring the impacts of solution-specific parameters on the measured  $K_d$  values observed in this study (i.e., using  $K_{oc}$  values only) and concerns over the validity of the measurements made in the Lake Ontario studies (23), we can evaluate the potential importance of sedimentation losses using the following equation:

$$F_{sed} = K_{sed,oc} C_{sed,oc} \quad (5)$$

where  $F_{sed}$  is the flux of anionic PFCs to sediments (kg/d),  $k_{sed,oc}$  is the flux of organic carbon to Lake Ontario bottom sediments (kg<sub>oc</sub>/d) estimated previously by Mackay ( $2.0 \times 10^9$  kg<sub>oc</sub>/yr or  $5.5 \times 10^6$  kg<sub>oc</sub>/d; (24)), and  $C_{sed,oc}$  (kg/kg<sub>oc</sub>) is the organic-carbon normalized particle concentration calculated from the reported aqueous concentrations (22) and measured  $K_{oc}$  values (this study). Using this equation and these values, losses of 0.03, 0.11, and 0.05 kg/d were estimated for PFOA, PFOS, and *N*-EtFOSAA respectively. Relative to the outflow losses estimated by Boulanger et al., it appears that sedimentation losses are indeed fairly negligible (0.1, 0.3, and 1.6% when compared to outflow losses for PFOA, PFOS, and *N*-EtFOSAA, respectively).

While sedimentation does not appear to be a major loss mechanism for anionic PFCs present in Lake Ontario, this does not necessarily mean that sediments are unimportant in determining the ultimate fate and distribution of anionic PFCs in the environment. Indeed, in a recent attempt to construct a global mass balance for PFOA, sedimentation, and burial was cited as one of only two major removal mechanisms for PFOA on the global scale, the other being transport to the deep ocean (25). Furthermore, several investigators have noted either increased concentrations of PFCs in benthic organisms (26) or in benthos-linked food webs (27). Further investigations into the bioavailability of sediment-bound anionic PFCs (and their precursors) to benthic organisms should help evaluate whether sediments will serve as long-term, stationary sources of PFCs to the biosphere.

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## Supporting Information Available

Additional details are available relating to analytical methodologies employed, sediment sources, procedures used to calculate  $K_d$  values, measured sorption isotherms, correlation analyses, and additional discussions of potential explanations of isotherm nonlinearity and structural features affecting

sorption. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## Literature Cited

- (1) Key, B. D.; Howell, R. D.; Criddle, C. S. Defluorination of organofluorine sulfur compounds by *Pseudomonas* sp. strain D2. *Environ. Sci. Technol.* **1998**, *32*, 2283–2287.
- (2) Giesy, J. P.; Kannan, K. Perfluorochemical surfactants in the environment. *Environ. Sci. Technol.* **2002**, *36*, 146a–152a.
- (3) Higgins, C. P.; Field, J. A.; Criddle, C. S.; Luthy, R. G. Quantitative determination of perfluorochemicals in sediments and domestic sludge. *Environ. Sci. Technol.* **2005**, *39*, 3946–3956.
- (4) Alzaga, R.; Salgado-Petinal, C.; Jover, E.; Bayona, J. M. Development of a procedure for the determination of perfluorocarboxylic acids in sediments by pressurised fluid extraction, headspace solid-phase microextraction followed by gas chromatographic–mass spectrometric determination. *J. Chromatogr., A* **2005**, *1083*, 1–6.
- (5) Hansen, K. J.; Johnson, H. O.; Eldridge, J. S.; Butenhoff, J. L.; Dick, L. A. Quantitative characterization of trace levels of PFOS and PFOA in the Tennessee River. *Environ. Sci. Technol.* **2002**, *36*, 1681–1685.
- (6) Moody, C. A.; Martin, J. W.; Kwan, W. C.; Muir, D. C. G.; Mabury, S. C. Monitoring perfluorinated surfactants in biota and surface water samples following an accidental release of fire-fighting foam into Etchicoke Creek. *Environ. Sci. Technol.* **2002**, *36*, 545–551.
- (7) So, M. K.; Taniyasu, S.; Yamashita, N.; Giesy, J. P.; Zheng, J.; Fang, Z.; Im, S. H.; Lam, P. K. S. Perfluorinated compounds in coastal waters of Hong Kong, South China, and Korea. *Environ. Sci. Technol.* **2004**, *38*, 4056–4063.
- (8) Liu, J. X.; Lee, L. S. Solubility and sorption by soils of 8:2 fluorotelomer alcohol in water and cosolvent systems. *Environ. Sci. Technol.* **2005**, *39*, 7535–7540.
- (9) Westall, J. C.; Chen, H.; Zhang, W.; Brownawell, B. J. Sorption of linear alkybenzenesulfonates on sediment materials. *Environ. Sci. Technol.* **1999**, *33*, 3110–3118.
- (10) Fink, D. H.; Thomas, G. W.; Meyer, W. J. Adsorption of anionic detergents by soils. *Water Pollut. Control Fed. J.* **1970**, *42*, 265–&.
- (11) Inoue, K.; Kaneko, K.; Yoshida, M. Adsorption of dodecylbenzenesulfonates by soil colloids and influence of soil colloids on their degradation. *Soil Sci. Plant Nutr.* **1978**, *24*, 91–102.
- (12) 3M. *Soil Adsorption/Desorption Study of Potassium Perfluorooctane Sulfonate (PFOS)*; 3M: St. Paul, MN, 2000, U.S. Environmental Protection Agency Docket AR 226-1030a 030.
- (13) duPont. *Adsorption/Desorption of Ammonium Perfluorooctanoate to Soil (OECD 106)*; E.I. du Pont de Nemours and Company: Wilmington, DE, 2003, U.S. Environmental Protection Agency Docket OPPT-2003-0012-040.
- (14) Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*, 2nd ed.; Wiley: Hoboken, NJ, 2003.
- (15) Brownawell, B. J.; Chen, H.; Collier, J. M.; Westall, J. C. Adsorption of organic cations to natural materials. *Environ. Sci. Technol.* **1990**, *24*, 1234–1241.
- (16) Volk, V. V.; Jackson, M. L. Alkyl benzene sulfonate and linear alkylate sulfonate adsorption by hydroxy iron and aluminum systems. *Water Pollut. Control Fed. J.* **1968**, *40*, 205–213.
- (17) Jafvert, C. T. Sorption of organic-acid compounds to sediments—initial model development. *Environ. Toxicol. Chem.* **1990**, *9*, 1259–1268.
- (18) Moroi, Y.; Yano, H.; Shibata, O.; Yonemitsu, T. Determination of acidity constants of perfluoroalkanoic acids. *B. Chem. Soc. Jpn.* **2001**, *74*, 667–672.
- (19) Dontsova, K. M.; Bigham, J. M. Anionic polysaccharide sorption by clay minerals. *Soil Sci. Soc. Am. J.* **2005**, *69*, 1026–1035.
- (20) La Mesa, C.; Sesta, B. Micelles in perfluorinated surfactant solutions. *J. Phys. Chem.* **1987**, *91*, 1450–1454.
- (21) Goss, K. U.; Bronner, G.; Harner, T.; Monika, H.; Schmidt, T. C. The partition behavior of fluorotelomer alcohols and olefins. *Environ. Sci. Technol.* **2006**, *40*, 3572–3577.
- (22) Boulanger, B.; Peck, A. M.; Schnoor, J. L.; Hornbuckle, K. C. Mass budget of perfluorooctane surfactants in Lake Ontario. *Environ. Sci. Technol.* **2005**, *39*, 74–79.
- (23) Field, J. A.; Simonich, S.; Barofsky, D. Comment on “Detection of perfluorooctane surfactants in Great Lakes water” and “Mass budget of perfluorooctane surfactants in Lake Ontario”. *Environ. Sci. Technol.* **2005**, *39*, 3883–3884.
- (24) Mackay, D. Modeling the long-term behavior of an organic contaminant in a large lake: Application to PCBs in Lake Ontario. *J. Great Lakes Res.* **1989**, *15*, 283–297.
- (25) Prevedouros, K.; Cousins, I. T.; Buck, R. C.; Korzeniowski, S. H. Sources, fate and transport of perfluorocarboxylates. *Environ. Sci. Technol.* **2006**, *40*, 32–44.
- (26) Martin, J. W.; Whittle, D. M.; Muir, D. C. G.; Mabury, S. A. Perfluoroalkyl contaminants in a food web from Lake Ontario. *Environ. Sci. Technol.* **2004**, *38*, 5379–5385.
- (27) Van de Vijver, K.; Hoff, P. T.; Das, K.; Van Dongen, W.; Esmans, E. L.; Jauniaux, T.; Bouquegneau, J.-M.; Blust, R.; de Coen, W. Perfluorinated chemicals infiltrate ocean waters: Link between exposure levels and stable isotope ratios in marine mammals. *Environ. Sci. Technol.* **2003**, *37*, 5545–5550.

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