Congener-specific organic carbon-normalized soil and sediment-water partitioning coefficients for the C₁ through C₈ perfluoroalkyl carboxylic and sulfonic acids

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Organic carbon-normalized soil and sediment-water partitioning coefficients (Koc) were estimated for all C₁ through C₈ perfluoroalkyl carboxylic (PFCA) and sulfonic (PFSA) acid congeners. The limited experimental Koc data set for the straight chain C₇ through C₁₀ PFCAs and C₈ and C₁₀ PFSAs was correlated to SPARC and ALOGPS computationally estimated octanol-water partitioning/distribution constants and used to predict Koc values for both branched and linear C₁ through C₈ isomers. Branched and linear congeners in this homologue range are generally expected to have Koc values >1, leading to their accumulation in organic matter on sediments and soils, retardation during ground and pore water flow, and the preferential association with dissolved organic matter in aquatic systems. Both increasing perfluoroalkyl chain length and linearity increase Koc values with substantial intra- and inter-homologue variation and interhomologue mixing. Variability in Koc values among the PFCA and PFSA congeners will likely lead to an enrichment of more linear and longer-chain isomers in organic matter fractions, resulting in aqueous phases fractionated towards shorter-chain branched congeners. The expected magnitude of fractionation will require inclusion in source apportionment models and risk assessments. A comparison of representative established quantitative structure property relationships for estimating Koc values from octanol-water partitioning constants suggests that these equilibrium partitioning frameworks may be applicable towards modeling PFCA and PFSA environmental fate processes.

Keywords: Perfluorinated acids, perfluoroalkyl carboxylic acids, perfluoroalkyl sulfonic acids, soil and sediment partitioning, organic carbon.

Introduction

Perfluoroalkyl acids (PFAs) such as the perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSA) (Fig. 1) are contaminants widely distributed in the environment, and which display the capacity for long-range transport, bioconcentration and bioaccumulation, persistence, and a range of toxicological effects.[1−3] Most PFCAs (≥C₂; Cx designation herein refers to the length of the perfluoroalkyl chain) and all PFSA are currently thought to arise solely from the use of commercial perfluorinated surfactants, whereas the C₁ PFCA (trifluoroacetic acid [TFA]) is both used itself in industry and can also be formed via the oxidative degradation of various precursors such as hydrofluorocarbons, anesthetics, trifluoromethylbenzene-based pesticides, and waste incineration.[4] It has been suggested that continuous low level TFA releases from biological and/or geological sources must be present to account for the mass of this compound (thought to be in the hundreds of millions of tons) in global oceans, whereas terrestrial, freshwater, and atmospheric reservoirs are primarily anthropogenically derived.[5,6]

In general, total PFCA and PFSA concentrations in surface and ground waters and marine systems range widely from the low ng L⁻¹ to low mg L⁻¹ levels depending on age and the proximity to point and non-point sources of contamination.[7] Wastewaters from semiconductor fabrication plants using photolithographic techniques have the highest reported PFCA and PFSA levels to date, with concentrations reaching well into the mg L⁻¹ range,[8] and even up to low g L⁻¹ levels.[9] A number of regions in Asia, Europe, and North America are reporting samples analyzed from surface water and groundwater sources that exceed the state of New Jersey (USA) 40 ng L⁻¹ straight-chain...
PFCA and PFSA partitioning coefficients

C\textsubscript{7} PFCA 39 (n-perfluorooctanoic acid [n-PFOA]) guideline for drinking water and the 500 ng L\textsuperscript{-1} and 300 ng L\textsuperscript{-1} acceptable threshold values, respectively, for n-PFOA and the straight chain C\textsubscript{8} PFSA 89 (n-perfluorooctane sulfonic acid [n-PFOS]) in the state of Minnesota (USA).

Few studies have reported PFCA and PFSA levels in sediments, with concentrations ranging from below detection limits up to the low mg kg\textsuperscript{-1} dry weight (dw).[10-15] Even less work has been done on developing a database of PFA concentrations in soils.[16] A limited survey of soils from sites in Canada, Malawi, the United Kingdom, and Chile showed TFA was present at low ng g\textsuperscript{-1} dw levels at values similar to, or exceeding, that of other haloacetic acids.[17] At a German site involving the incorporation of contaminated materials into agricultural soils, n-PFOS and n-PFOA concentrations of up to 8,600 and 650 µg kg\textsuperscript{-1} dw, respectively, were found in the soil improvement material, resulting in soil concentrations of up to 5,500 and 910 µg kg\textsuperscript{-1} dw, respectively.[18] Surficial soils (<0.3 m depth) near a fluoropolymer manufacturing facility in West Virginia, USA, contained up to 170 µg kg\textsuperscript{-1} dw n-PFOA, with an exponential decrease in concentrations to only 13 µg kg\textsuperscript{-1} dw at 1 to 2 m depth, about 3 µg kg\textsuperscript{-1} dw at 5 to 6 m depth, and below detection limits at greater depths. Based on its ability to contaminate drinking water sources near this site, the West Virginia Department of Environmental Protection convened an expert panel (the C\textsubscript{8} Assessment of Toxicity Team) that recommended a soil screening level of 240 mg kg\textsuperscript{-1} dw for n-PFOA.[19]

To better understand the environmental fate of PFCAAs and PFSAAs, and to assist in the design and optimization of treatment processes, additional information is needed regarding their partitioning between various matrices. Laboratory scale sorption of the straight chain C\textsubscript{4} and C\textsubscript{8} PSAs and C\textsubscript{7} PFCA onto activated carbon (granular [GAC] and particulate [PAC]), zeolite, ion exchange resins, and wastewater sludge has been reported.[19-21] Increasing perfluoroalkyl chain length and a sulfonic acid head group (versus a carboxylic acid moiety) increased the sorption onto GAC.[20] For n-PFOS, the relative order of sorption effectiveness was GAC > zeolite > sludge, and increasing silica content was noted as improving sorption to zeolites.

n-PFOS was preferentially sorbed onto GAC and PAC in one study, whereas an amberlite anion exchange resin was found to be superior to GAC and PAC for removing n-PFOS from solution.[21] Work by Lampert et al. found that there were significant differences in removal efficiencies for n-PFOA and n-PFOS depending on the anion exchange resin type, but that a quaternary amine acrylic polymer resin could effectively remove both analytes,[19] which is perhaps expected for PFAs given how this cationic amine resin may be able to effectively mimic a proteinophilic sorption surface. In some cases, water treatment using activated carbon has been shown to be effective for removing longer chain PFAs such as n-PFOS from contaminated source waters,[15,22-24] PFAs, like their hydrocarbon fatty acid analogs, also sorb to inorganic surfaces such as sands, clays, iron oxides, calcium fluoride, and surface modified silicas[19,25,26] but organic matter sorption is thought to be dominant in most environmental systems and offer the most promise for treatment methods.

In contrast to the predominantly lipophilic character of nonpolar contaminants, the proteinophilic nature of the polar/ionic PFCAAs and PFSAAs is well established from both synthetic chemistry and toxicology perspectives. Perhaps because of the focus on their proteinophilic nature and the hydrophilic head group/oleophobic tail combination, a limited number of studies have investigated the partitioning of these compounds between more traditional organic materials and aqueous phases.[27-29] However, these studies have generally focussed on the longer straight chain (≥C\textsubscript{7}) isomers, with little information on the shorter chain congeners. This knowledge gap is of importance, since an inverse correlation was found between PFA chain length and the steady state biota sediment accumulation factors (BSAFs) using the aquatic oligochaete Lumbriculus variegatus,[12] highlighting the need to extend existing organic matter-water partitioning data sets for the longer chain PFCAAs and PFSAAs to the shorter chain congeners which may have higher BSAFs. It should also be noted that the difficulty of both measuring and estimating the partitioning constants and physicochemical properties of perfluorinated compounds in general has led to a significant amount of discussion in the literature,[7] potentially dissuading rigorous investments in extended experimental investigations.

With low reported rates of abiotic and biotic degradation for PFCAAs and PFSAAs, a focus is developing to better understand and model the partitioning behavior of these contaminants in natural and engineered systems. Due to the increasing awareness regarding the large number of potential congeners,[30] and the experimental costs in measuring a range of partitioning constants for each compound, there is also a need to apply computational tools against available experimental data sets to predict the physicochemical properties of these compounds for a greater number of individual congeners. In the present study, we synthesize the current state of the art regarding partitioning of PFCAAs and PFSAAs between organic carbon and aqueous matrices, and we present congener specific models that estimate the organic carbon normalized soil and sediment-water partitioning coefficients (K\textsubscript{OC}) for the C\textsubscript{1} through C\textsubscript{8} PFCA and PFSA congeners.
Methods and materials

Experimental organic carbon normalized soil and sediment-water partitioning coefficients (K_{oc}) for PFCA and PFSA congeners are from Higgins and Luthy. The numbering system for PFCA and PFSA congeners follows the approach outlined previously. SMILES molecular formats were used as computational inputs. For each congener, both the octanol-water partitioning constant (log P) value for the molecular form and the octanol-water distribution constant (log D) value for ionizable compounds were estimated using SPARC. The log P-values were also estimated using the ALOGPS program, which has been previously validated for a wide range of organic compounds. The P and D values are calculated and related according to the following equations where [HA] and [A^-] are the concentrations of neutral and anionic species in octanol (subscript o) and water (subscript w), respectively: P = [HA]_o/[HA]_w; P_i = [A^-]_o/[A^-]_w; and D = (P + P_i) × 10^{(pH−pK_a)}/(1+10^{pH−pK_a}). The reliance of SPARC estimated log D values on an underlying SPARC pK_a estimate warrants caution in the use and interpretation of these values. As we have previously shown, computational methods generally underestimate the pK_a values of longer-chain PFCA congeners and overestimate the pK_a values of PFSA congeners. In addition, substantial perfluoroalkyl chain branching effects on the estimated pK_a values (and hence, the electrostatic character of the PFA head groups) is predicted by the semiempirical PM6 method, but much reduced branching effects are predicted by SPARC.

Results and discussion

Linear relationships having the following equations were found between the SPARC calculated log P and log D values and the ALOGPS log P values with the corresponding sediment organic carbon normalized distribution coefficients (K_{oc}) for the straight chain C_7 through C_{10} PFCAs (Fig. 2(a)):

\[
\log K_{oc}(L \text{kg}^{-1}) = 0.438 \pm 0.018 \times \log P_{SPARC} − 0.651 \pm 0.140 (r = 0.998, P < 0.002) \text{[student's t-test]}
\]

\[
\log K_{oc}(L \text{kg}^{-1}) = 0.432 \pm 0.018 \times \log D_{SPARC} + 0.215 \pm 0.109 (r = 0.998, P < 0.002)
\]

\[
\log K_{oc}(L \text{kg}^{-1}) = 1.413 \pm 0.019 \times \log P_{ALOGPS} − 3.938 \pm 0.091 (r = 0.9998, P < 0.0002)
\]

Although only two data points were available for the PFSA (the straight chain C_8 and C_{10} congeners), similar slopes were observed for the P_{SPARC} and D_{SPARC} values across both PFA classes (about 0.43 to 0.45) but the P_{ALOGPS} slope was substantially higher for the PFSA (about 1.4) compared to the PFCAs (about 1.4).

Fig. 2. Correlations between SPARC calculated log P (circles) and log D (squares) and ALOGPS calculated log P (triangles) values and experimental sediment organic carbon normalized K_{oc} values for the (a) C_{7} through C_{10} PFCAs and (b) C_{8} and C_{10} PFSA congeners. Error bars are from the literature K_{oc} source.

The SPARC log P/D and ALOGPS log P methods overpredict the recently published experimental log D values of the straight chain C_7 through C_9 PFCAs and n-PFOS by up to several units. However, there are strong linear relationships between the experimental PFCA log D data set and the corresponding SPARC log P (m = 0.66, b = −2.31, r = 0.995), SPARC log D (m = 0.63, b = −0.96, r = 0.995), and ALOGPS log P (m = 1.48, b = −4.32, r = 0.996) values. In the absence of available experimental log P/D data for any PFSA congeners other than n-PFOS, and a complete lack of partitioning data for any branched PFCA or PFSA congeners, these relationships appear to support the use of adjusted computationally estimated log P/D surrogates for a broader suite of PFCA and PFSA congeners as applied in the current modeling approach. Calculated log K_{oc}/log D ratios using the respective data sets of Higgins and Luthy and Jing et al. for congeners with corresponding experiment data are as follows: n-PFOA, 1.1; n-perfluorononanoic acid (n-PFNA), 0.93; n-perfluorodecanoic acid (n-PFDeA), 0.95; and n-PFOS, 1.0. These values meet the criteria of Seth et al. which indicated caution in using experimental data for hydrophobic compounds with log K_{oc}/log D ratios outside the range of 0.1 to 1.0.

Using these regression equations for the PFCAs, P_{SPARC}, D_{SPARC}, and P_{ALOGPS} values were calculated for all C_{1} through C_8 congeners, and the corresponding K_{oc} values estimated via negative linear extrapolations of the relationship observed for the straight chain C_7 through C_10 isomers (Fig. 3). Given the linearity of the PFCA regressions and the agreement in slope values for the PFCAs and PFSA congeners using the P_{SPARC} and D_{SPARC} values, we also conducted
PFCA and PFSA partitioning coefficients

Fig. 3. Estimated congener specific $K_{oc}$ values for the C$_1$ through C$_8$ PFCAs using the (a) SPARC calculated log P, (b) SPARC calculated log D, and (c) ALOGPS calculated log P-values. Inset shows estimated $K_{oc}$ values for the C$_8$ PFCAs using the ALOGPS method.

analogous negative linear extrapolations to estimate $K_{oc}$ values for all C$_1$ through C$_8$ PFSA congeners (Fig. 4). For both classes, all three approaches predict significant intra- and inter-homologue differences in $K_{oc}$ values. However, only the $P_{SPARC}$ and $D_{SPARC}$ approaches predict inter-homologue mixing, whereby some estimated $K_{oc}$ values from a higher homologue group are lower than some estimated $K_{oc}$ values from lower homologue groups. For example, the linear C$_4$ PFCA and PFSA congeners are predicted to have higher $K_{oc}$ values than a number of the more branched C$_5$ through C$_8$ congeners, which implies a high degree of inter- and intra-homologue fractionation during the partitioning of PFA to soils and sediments and their movement through ground and pore waters.

The differential $K_{oc}$ values within and between homologue groups also calls attention to the need for greater use of homologue specific isotopically labeled standards during the extraction of PFA from environmental matrices (and congener specific standards once the synthetic methods become available). As expected from the available experimental data sets, all approaches suggest $K_{oc}$ values will decline with decreasing perfluoroalkyl chain length. The $P_{ALOGPS}$ approach suggests the greatest rate of $K_{oc}$ decline occurs as the chain length shortens, resulting in $K_{oc}$ values < 1 (log $K_{oc}$ < 0) for the ≤ C$_3$ PFCAs (e.g., perfluorobutanoic acids) and the ≤ C$_6$ PFSA (e.g., perfluorohexane sulfonic acids). In contrast, both the $P_{SPARC}$ and $D_{SPARC}$ approaches predict that almost all C$_1$ through C$_8$ PFCAs

Fig. 4. Estimated congener specific $K_{oc}$ values for the C$_1$ through C$_8$ PFSA using the (a) SPARC calculated log P, (b) SPARC calculated log D, and (c) ALOGPS calculated log P-values. Inset shows estimated $K_{oc}$ values for the C$_8$ PFSA using the ALOGPS method.
and PFSAs will have log $K_{oc}$ values $> 0$ (with the limited exceptions of C4 PFSA [log $K_{oc} = -0.24$] and C6 PFSA [log $K_{oc} = -0.05$] using the D_{SPARC} approach), and should accumulate in sediments and soils.

For PFA chain lengths $> C_8$, the number of possible branched congeners within each homologue is too great for a complete analysis. However, the $K_{oc}$ value branching patterns observed here for the C$_4$ through C$_9$ homologues are expected to apply to the higher homologues. In terms of estimating log $K_{oc}$ values for $> C_8$ straight chain PFCA s and PFSAs, Higgins and Luthy reported that “[e]ach CF$_2$ moiety increased the distribution coefficient [$K_d$] by approximately 0.5–0.6 log units for both the perfluorosulfonylates and the perfluorocarboxylates.” As a result, these authors indicate that log $K_{oc}$ values of straight-chain congeners outside their experimental range can be estimated by the addition or subtraction of $(n \times 0.55)$ log $K_{oc}$ units to one of their experimental log $K_{oc}$ values, where $n$ is the difference in perfluoralkyl chain length between the straight chain compound of interest and one of their experimental log $K_{oc}$ values.

Upon closer analysis, one observes that of the 5 sediment samples used for the experimental $K_{oc}$ determinations in ref.[27] only 2 samples (sediments 1 and 5) had complete data sets for all 4 PFCA analytes. For sediments 2 and 4, no n-PFOA or n-PFNA $K_{oc}$ data was available, and for sediment 3, no n-PFOA $K_{oc}$ data was obtained. Average $K_{oc}$ values were calculated across the 5 sediment samples, even where less than 5 data points were available for some analytes (n-PFOA and n-PFNA). This averaging approach would not be of concern if no systematic bias in any sediment samples was observed. However, sediments 1 and 5 have a higher average log $K_{oc}$ value than the corresponding average for sediments 2, 3, and 4 for n-PFDeA (2.98 $\pm$ 0.07 [SE] vs. 2.62 $\pm$ 0.11; $P < 0.1$) and n-PFUnA (3.51 $\pm$ 0.06 vs. 3.16 $\pm$ 0.11; $P < 0.1$).

Thus, the lack of data for sediments 2, 3, and 4 for n-PFOA, and sediments 2 and 4 for n-PFNA, suggests that the inherently lower $K_{oc}$ sediments for these analytes were not included in the data averaging process. As a result, had n-PFOA and n-PFNA data been available for these other sediments, it appears likely—given the trends observed for PFDeA and PFUnA—that average log $K_{oc}$ values with a full sediment data set (i.e., $n = 5$, rather than $n = 2$ and 3, respectively) for these 2 PFCA congeners would have been lower by about 0.2 log units. This result would similarly impact our regression equations and reduce our resulting log $K_{oc}$ estimates that are both based on this experimental data. Consequently, we note this issue with interest, as it highlights the need for additional experimental work to confirm whether the log $K_{oc}$ values of n-PFOA and n-PFNA may be lower than currently believed.

This systematic bias among the sediments with an incomplete analyte data set is also reflected in the differing calculated log $K_{oc}$ fragmental contributions from a -CF$_2$- group for the PFCA s ($f(CF_2)_{PFCA}$). When the average log $K_{oc}$ values from Table 2 in ref.[27] are regressed against perfluoroalkyl chain length, a $f(CF_2)_{PFCA}$ of 0.41 is obtained. Conversely, when each individual sediment sample log $K_{oc}$ data set (Table A1 in the Supporting Information from ref. [27]) is regressed against perfluoroalkyl chain length, and the resulting sediment-specific $f(CF_2)_{PFCA}$ values are averaged, a $f(CF_2)_{PFCA}$ of 0.53 results. With a complete data set for all analytes and sediments, and without any systematic $K_{oc}$ bias between sediments, these two analytic approaches should yield the same $f(CF_2)_{PFCA}$ value. The difference between these two $f(CF_2)_{PFCA}$ values raises the question as to whether the absence of complete analyte data sets for n-PFOA and n-PFNA biases the regression of average log $K_{oc}$ values against perfluoroalkyl chain length to yield an artificially low $f(CF_2)_{PFCA}$ value (0.41) below that of the assumed true value (0.53).

Conversely, $f(CF_2)_{PFCA}$ values could change as a function of chain length, and the $f(CF_2)_{PFCA}$ value of 0.55 obtained by averaging individual $K_{oc}$ regressions reflects the potentially higher $f(CF_2)_{PFCA}$ values of the n-PFDeA $\rightarrow$ n-PFUnA transition (since there is an absence of data for the $f(CF_2)_{PFCA}$ transitions from n-PFOA $\rightarrow$ n-PFNA and n-PFNA $\rightarrow$ n-PFDeA). The possible change in $f(CF_2)_{PFCA}$ values with perfluoroalkyl chain length is supported by the data set from sediments 1 and 5 (the only 2 sediments with complete log $K_{oc}$ values for all analytes). For these sediments, $f(CF_2)_{PFCA}$ values increase from 0.43 $\pm$ 0.04 [SE] for the n-PFOA $\rightarrow$ n-PFNA transition to 0.50 $\pm$ 0.06 for the n-PFNA $\rightarrow$ n-PFDeA transition to 0.53 $\pm$ 0.01 for the n-PFDeA $\rightarrow$ n-PFUnA transition. According to the conceptual model of $K_{oc}$ partitioning for PFCA s and PFSA set forward by Higgins and Luthy in their follow-up study,[28] the sorption of these analytes to sediment and soil organic carbon should likely be viewed as a dominantly interfacial process, whereby the hydrophilic head groups remain partially or fully solvated at the water-organic carbon interface and the hydrophobic perfluoroalkyl chains are solubilized in the organic carbon matrix.

In this regard, the possible variation in $f(CF_2)_{PFCA}$ as a function of perfluoroalkyl chain length that may be apparent in the $K_{oc}$ data of Higgins and Luthy[27] potentially agrees with the recent report by Psillakis et al.,[45] who suggest that the $f(CF_2)_{PFCA}$ values for enrichment of PFCA s at the air-water interface are not constant with perfluoroalkyl chain length. In contrast, for the log D data of Jing et al.,[29] which reflects only the relative bulk water and n-octanol phase effects, the strong linearity of their log D versus perfluoroalkyl chain length data ($r^2 \sim 1$) indicates no variation in $f(CF_2)_{PFCA}$ values for this bulk partitioning process. Such differential interface versus bulk phase partitioning behavior in $f(CF_2)_{PFCA}$ values could reflect the known variation in physicochemical properties of the solvents/sorbents near interfaces, particularly any declining concentration gradients of each solvent/sorbent in the other. In other words, a perfluoroalkyl acid oriented with
Table 1. Application of established literature approaches for estimating log $K_{oc}$ values from log P/D values towards representative PFCA and PFSA congeners using the SPARC and ALOGPS estimated log P-values, SPARC estimated log D-values, and the experimental log D data ($D_{exp}$) of Jing et al. [29] (only available for n-PFOA and n-PFOS).

| Laboratory and field experimental log $K_{oc}$ range | TFA | n-PFOA | n-PFOS |
|---------------------------------------------------|-----|--------|--------|
| Higgins and Luthy (2006) experimental log $K_{oc}$ range$^a$ | 0.25 to 1.77 | 1.1 to 3.2 | 1.6 to 4.8 |
| Experimental log D range$^b$ | n/a | 2.06 to 2.11 | 2.44 to 2.77 |
| | 1.92 | 2.37 to 2.53 |

| | $P_{SPARC}$ | $D_{SPARC}$ | $D_{exp}$ | $P_{SPARC}$ | $D_{SPARC}$ | $D_{exp}$ | $P_{SPARC}$ | $D_{SPARC}$ | $D_{exp}$ |
| Current study QSAR | 0.13 | 0.24 | −2.03 | n/a | 2.09 | 2.09 | 2.12 | n/a | 2.68 | 2.68 | 2.68 | n/a |
| Karickhoff et al. (1979) – general organic compounds$^c$ | 1.12 | 0.04 | 0.85 | n/a | 3.94 | 2.73 | 2.70 | 1.21 | 2.94 | 2.15 | 2.67 | 1.54 |
| Karickhoff et al. (1981) – general organic compounds$^d$ | 0.73 | 0.02 | 0.55 | n/a | 2.57 | 1.78 | 1.76 | 0.79 | 1.91 | 1.40 | 1.74 | 1.00 |
| Sabljic et al. (1995) – organic acids$^e$ | 1.39 | 0.36 | 1.13 | n/a | 4.08 | 2.92 | 2.89 | 1.47 | 3.12 | 2.37 | 2.86 | 1.79 |
| Sabljic et al. (1995) – organic acids and alcohols$^f$ | 1.34 | 0.53 | 1.13 | n/a | 3.44 | 2.54 | 2.52 | 1.40 | 2.69 | 2.10 | 2.49 | 1.65 |
| Seth et al. (1999) – general organic compounds$^{g}$ | 1.22 | −0.55 | 0.78 | n/a | 5.84 | 3.85 | 3.81 | 1.37 | 4.20 | 2.90 | 3.76 | 1.91 |
| Franco and Trapp (2008) – strong acids (pK$_a$ < 4)$^h$ | 1.74 | 1.55 | 1.69 | n/a | 2.22 | 2.02 | 2.01 | 1.75 | 2.05 | 1.92 | 2.01 | 1.81 |
| Franco and Trapp (2009) – ionizable organic compounds$^i$ | 1.74 | 1.55 | 1.69 | n/a | 2.22 | 2.02 | 2.01 | 1.75 | 2.05 | 1.92 | 2.01 | 1.81 |

$^a$ Range given spans the upper and lower limits of the regression and log normal average log $K_{oc}$ values as defined by the respective standard errors in ref. [27]. $^b$ Range given spans the upper and lower limits as defined by the respective standard errors in ref. [29]. $^c$ Calculated at a soil pH of 7 and pK$_a$ values of 0.5 for TFA,$^{[40]}$ 3.8 for n-PFOA,$^{[89]}$ and −5 for n-PFOS.$^{[43]}$
its head group at the interface could have a sequence of consecutive -CF2- groups that are not all in the same physicochemical environment—and which is reflected by a variation in \( f/(\text{CF}_2)_{n}\text{PFCA} \) values for -CF2- moieties that are progressively further from the interface as the perfluoroalkyl chain lengthens. This possible difference in the variability of \( f/(\text{CF}_2)_{n}\text{PFCA} \) values with perfluoroalkyl chain length for interfacial partitioning processes, versus a potential absence of the effect for bulk phase partitioning processes, has important implications for understanding the environmental and biological effects of PFCAs and PFSAs, and warrants further investigation.

As efforts accelerate towards improved congener specific analytical methods and environmental partitioning measurements of branched PFA congeners, increasing focus is being placed on modeling the fate of the branched isomers and incorporating their potentially different environmental and toxicological behavior into multimedia and isomers and incorporating their potentially different environmental and toxicological behavior into multimedia and biological effects of PFCAs and PFSAs, and warrants further investigation.

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The surfactant nature of PFAs has led a number of researchers and regulatory agencies to question the applicability of well established partitioning coefficients such as log P/D and octanol-air (K_{oa}) constants, as well as the more general fugacity approach, in describing (either directly or with proxies) the behavior of PFCA and PFSAs in abiotic and biotic systems. For example, it has been stated that soil and sediment adsorption coefficients (K_{so}) of PFAs “cannot be estimated with conventional quantitative structure relationship models (QSARs).” The rational given for this is that PFAs partition into proteinophilic environments, which are assumed to not be reasonably represented by the lipophilic surrogate of octanol solvents, and that predicted K_{ow} values “may underestimate the accumulation of [PFAs] into organisms and other environmental media.”

Yet, with such definitive statements and assumptions being made over a decadal time scale in the literature, we find it surprising that no prior systematic evaluation of existing computational methods for estimating log P/D values (or similar partitioning constants) has been made for PFAs and subsequently compared to experimental partitioning constants using the wide number of available structure-activity models in the literature that were trained using a broad diversity of other contaminant types. Potential modifications (if required) to existing partitioning constant assessment frameworks for PFAs is an efficient means of improving our knowledge base on these compounds, particularly if the models can be targeted by judicious selection and calibration with appropriate congeners for experimental test work validation. Relying on a purely empirical experimental database of PFA partitioning behavior, as has been proposed, is both unsatisfactory and perhaps unnecessary.

Furthermore, prior hypotheses regarding the organic partitioning behavior of PFAs were often made using the water and octanol solubilities and vapor pressures of PFA salts (e.g., potassium, lithium, and/or ammonium salts), and subsequent calculations of log P values and Henry’s law constants using the properties of these salts. These comparisons are of concern for a number of reasons. PFA salts are significantly more soluble in water (i.e., order of magnitude scales), and similarly much less soluble in less polar solvents such as octanol, than their molecular acid equivalents. While the PFA salts may be the primary industrial compound in use, following their release to environmental and biological systems, the initial ion pair (e.g., a PFA anion and potassium, lithium, or ammonium cation [other cations are also in use industrially]) will reach a water column enriched in branched isomers.
Since PFA concentrations in all environmental and biological compartments (i.e., mg L\(^{-1}\) concentrations at the highest, but more typically in the ng L\(^{-1}\) to low µg L\(^{-1}\) range) make them minor constituents of any solvent-solute system, the resulting ion that is paired with a PFA anion will be dominated by the major ions already existing in solution, and not necessarily the source cation. Neither potassium, lithium, nor ammonium are major ions in any aquatic system (except for some brine lakes in terms of potassium and highly eutrophic reducing environments with respect to ammonium). Likewise, while potassium dominates the cation signature of intracellular fluids, it is only a minor ion in plasma and of extracellular fluids.[51] Ammonium ions are also unstable in aerobic environments, being quite readily and sequentially oxidized to nitrite and nitrate ions.

As well, the likely favored ion pair for PFAs in aquatic systems or in vivo is difficult to estimate given the very large number of possible counterions. These range from common simple major cations such as protons, sodium, potassium, calcium, magnesium, etc., to large macromolecules such as proteins and humic substances that can have positively charged regions containing both hydrophilic and hydrophobic cavities, and with which PFAs may prefer to associate with and/or sorb to compared with small and entirely hydrophilic cations. In addition, the relative association/formation constants (K\(_f\)) of the possible ion pairs are not known and would involve too great an expense of time and resources to determine for all possible PFA congeners. Consequently, equilibrium speciation models cannot presently be applied to PFA ion pairing in solution. Less computationally expensive methods for estimating the partitioning behavior of organic compounds are also often not able to handle a number of the possible cations that could be paired with PFA anions.

Consequently, the best models for initial screening and preliminary model development regarding partitioning of PFAs into organic matrices are the acids (i.e., proton counterions), particularly since many partitioning processes (e.g., dissolution in relatively nonpolar solvents, volatilization) likely only take place to any significant degree as the molecular acid form. We do note, however, that previous work has established the effects of chain branching and the head group counterion (e.g., H\(^+\), Na\(^+\), Li\(^+\), K\(^+\), NH\(_4^+\), Mg\(^{2+}\)) on the physicochemical properties of PFAs.[52] Although only one branched PFA was available for testing in this historical study (the terminal monomethyl branched C\(_8\) PFCA 88), both branching and the counterion identity had significant effects on properties such as the critical micelle concentrations and Krafft points. Consequently, future work will need to better define the counterion effects on PFA behavior, but with our current level of uncertainty on this front, a default to assessments with the acid form seems the most productive first step.

Perfluoroalkyl branching influences on the electrostatic role of the acid head groups during partitioning between organic matter and water is also of interest. Following the generation of their initial PFA K\(_{oc}\) data set, subsequent modeling efforts by Higgins and Luthy to better understand both the perfluoroalkyl chain hydrophobic and acid head group electrostatic effects they observed for PFA sorption (and that of other surfactants such as linear alkylbenzene sulfonates) came to the conclusion that the K\(_{oc}\) values were empirically derived and did not explicitly account for pH and dissolved cation effects.[28] However, the electrostatic contributions from this approach account primarily for differences in the nature of the head group among the various surfactants, rather than the effects of chain branching with a constant head group identity. Of the 161 possible C\(_1\) through C\(_8\) congeners within each PFA class, only 8 have linear perfluoroalkyl chains.[30] As we have demonstrated in prior work, various computational approaches yield differing predictions regarding charge magnitudes and distributions on the PFA head groups within a particular class,[40–43,53] resulting in a current degree of ambiguity as to the role of branching on PFA head group charge distributions. Further progress in this area will require a continuing evaluation as authentic branched PFA standards become available for experimental evaluation and calibration of existing computational studies, and well as the possible extension and refinement of current computational methods to these compound classes.

Only recently have reliable experimentally determined log D values[29] become available for any PFCAs or PFSAs upon which to calibrate the computational inputs. During historical testing of the straight chain C\(_8\) PFSA 89 (n-PFOS), it was reported that a third layer formed between the octanol and water phases.[48,50] This result is readily explained by the conceptual partitioning model developed by Higgins and Luthy,[27,28] whereby their results were best understood by viewing PFAs as being sorbed onto the surface of the organic matter at the interface with the aqueous phase. Thus, the hydrophobic perfluoroalkyl tail is solubilized in the organic phase, whereas the hydrophilic head group remains mostly in the aqueous phase. Consequently, in addition to the freely dissolved partitioning/distribution behavior examined by Jing et al.[29] organic partitioning of PFAs should be viewed as a joint volume-surface-volume normalized process (perhaps not unexpected for a class of surfactants) rather than the strictly volume-volume normalized process assumptions for traditional lipophilic contaminants.

In other words, sufficient quantities of PFAs may exist at aqueous-organic interfaces that these domains need explicit consideration when quantifying PFA partitioning, in addition to the quantities of PFAs also existing in the two traditional domains (i.e., freely dissolved in the aqueous and organic domains). This view potentially still
allows us to use the established experimental methods for determining partitioning, but with a realization that the data may also need to be normalized to the interfacial surface area between the two phases of interest. One key hypothesis of interest during laboratory testing of PFA partitioning in the presence of aqueous and organic phases is whether the freely dissolved aqueous phase concentrations of PFAs are reduced in the presence of organic matter, and whether this effect (if present) can be quantified. The work of Higgins and Luthy \cite{27} and the work herein clearly demonstrate the ability to quantitatively and predictively describe the partitioning of PFAs in the presence of an organic carbon phase. Regardless of whether the PFAs are dominantly freely dissolved in the organic matter or are dominantly present at the aqueous-organic interface, the compounds are removed from the freely dissolved aqueous phase. Therefore, traditional partitioning test work—with some minor conceptual, calculational, and potential experimental modifications—should allow us to probe how these contaminants are likely to behave under relevant environmental conditions.

For example, future log P/D testing on PFAs should determine total concentrations dissolved in the bulk aqueous and octanol phases and—also accounting for any sorption to the container—include a system mass balance (through knowledge of the cross-sectional octanol-water contact area) to determine the surface area normalized concentration of the compound. This type of experimental work yields the following three partitioning constants for the PFA: (1) conventional P/D value obtained via dividing the total PFA concentration in the aqueous layer by that in the octanol layer (which ideally will agree with the values reported by Jing et al. \cite{29} using their novel experimental approach); (2) modified P/D value obtained by dividing the total concentration of the PFA in the aqueous layer by the surface area normalized total concentration of PFA at the interface; and (3) a composite P/D constant that divides the total volumetric concentration in the aqueous phase by both the total surface area normalized interface concentration and the total volumetric concentration in the octanol.

This recognition of the potentially important interfacial presence of PFAs in environmental and biological systems could readily utilize the pre-existing theoretical framework as expounded by Valsaraj \cite{54,55} and Hoff et al. \cite{56} Such experimental work on a series of straight chain PFCAs and PFSAs for which authentic standards are readily available, and for which we already have field and laboratory traditional log D/K_{oc} data available, would greatly assist in our understanding of the sorption mechanisms. As well, the work would help in developing conceptual and computational models of the resulting processes that allow model extension to the remaining PFA congeners and application of the results to more quantitative environmental and pharmacokinetic modeling.

Other than the work of Higgins and Luthy \cite{27} there appear to be no other laboratory studies that directly and methodically estimate K_{oc} values across a range of PFA homologues. Previous laboratory and field work is generally limited to reporting on single PFA congeners (TFA, n-PFOA, and n-PFOS), resulting in possible concerns about the intercomparability of the K_{d} and K_{oc} values among the different soil and sediment types and analytical methods used by various investigators. As noted by Higgins and Luthy, \cite{27} their data agrees with studies by Dupont and 3M that report log K_{oc} values of 1.9 to 2.2 for n-PFOA and 2.6 to 3.1 for n-PFOS, respectively. In three soil types (sand, f_{oc} = 0.043; sandy loam, f_{oc} = 0.013; loam, f_{oc} = 0.026), van Dijk reported K_{d} values < 0.2 L kg^{-1} for TFA. \cite{57} Using the relationship K_{d} = f_{oc} × K_{oc}, \cite{58} this translates into an estimated log K_{oc} upper limit of < 1.2 which agrees with our log K_{oc} estimates of 0.13 (SPARC log P), 0.24 (SPARC log D), and −2.03 (ALOGPS). In a broader study of TFA sorption to 54 soils from North America and Europe, \cite{59} log K_{oc} values (calculated from the reported K_{d} and f_{om} values using the formula K_{d} = 0.58 × f_{om} × K_{oc}) \cite{58} ranged from 0.25 to 1.77 (mean = median = 1.12), in reasonable agreement with our SPARC P and D based estimates, in the earlier work of van Dijk \cite{57} and field manipulation experiments in an experimental forest. \cite{60} The ALOGPS approach appears to underestimate the K_{oc} value for TFA.

One notable finding of Richey et al. was that anions such as sulfate were found to competitively inhibit TFA sorption. \cite{59} Assuming the soil retention behavior of all PFCAs and the PFSAs also can be competitively inhibited by major anions, this implies that significant PFA sorption may not be observed in some ground waters with high ionic strengths. However, Higgins and Luthy \cite{27} reported that the longer chain PFAs exhibited greater sediment sorption in the presence of calcium. Thus, the ground water major ion signature will be important in determining to what extent PFA sorption occurs. For example, Higgins and Luthy \cite{27} found that sodium did not enhance PFA sorption, so when coupled with the results of Richey et al., \cite{59} this implies that negligible PFA sorption may occur in a ground water with a major ion sodium sulfate signature, but that PFAs may be potentially immobilized in a calcium chloride brine signature, and that some intermediate mobility may be displayed in a calcium sulfate dominated system. Differential partitioning of PFAs also appears likely between marine, fresh, and ground waters with their different hydrogeochemical signatures, such that experimental data and computational estimates derived from near distilled water conditions will need site specific correction factors before they are applied to an aquatic system. The use of a multidimensional response surface methodology approach may be a promising means for incorporating the effects of multiple ion concentrations in an overall predictive equation towards the aqueous-organic partitioning of PFAs.

Field estimates of log K_{oc}/K_{d} values for n-PFOA and n-PFOS can also be made based on measured concentrations in sediments and the overlying water column. We note the absence of similar field data for TFA. Based on the data.
of Becker et al. in the Roter Main River near Bayreuth, Germany, \( K_d \) values ranged from 1.5 to 3.0 L kg\(^{-1} \) for n-PFOA and 17 to 42 L kg\(^{-1} \) for n-PFOS.\(^{11} \) Only a range of sediment organic carbon levels across all samples of 0.06 to 0.8\% was reported, precluding a detailed calculation of \( K_{oc} \) values, although this information suggests that the log \( K_{oc} \) values for these sediments could range between 2.3 to 3.2 for n-PFOA and 3.3 to 4.8 for n-PFOS. Senthilkumar et al. provided concentrations of straight chain \( C_4 \), \( C_6 \), and \( C_8 \) PFSAs and \( C_7 \) and \( C_{11} \) PFCAs in sediments and river waters from Japan.\(^{10} \) Analysis of their data for n-PFOA and n-PFOS (the only two analytes with levels above detection limits in sediments) yields log \( K_d \) values ranging from 1.1 to 2.5 for n-PFOA and 1.6 to 3.4 for PFOS. Odaka and Masunaga measured levels of n-PFOA and n-PFOS in Tokyo Bay.\(^{61} \) Our analysis of their data shows field log \( K_d \) values ranging from 1.6 to 2.4 for n-PFOA and 2.3 to 3.9 for n-PFOS. Yu et al. also reported sewage sludge derived log \( K_d \) values ranging from 3.0 to 3.5 for n-PFOS and 2.4 to 2.8 for n-PFOA.\(^{62} \) The data of Houde et al.\(^{46} \) yield a log \( K_d \) of 3.3 for n-PFOS between sediments and the overlying water column in Lake Ontario. Unfortunately, the lack of organic carbon concentrations in sediments from these four studies prevents a comparison to measured and estimated log \( K_{oc} \) values. In general, however, there appears to be good agreement between the laboratory and field measurements of \( K_{oc} / K_d \) values for PFAs.

To determine whether existing QSARs for predicting \( K_{oc} \) values based on estimated and experimental log \( P/D \) inputs could also be applied to the PFAs, we choose a representative suite of established literature \( K_{oc} = \log P/D \) regressions and applied them to TFA, n-PFOA, and n-PFOS using the SPARC and ALOGPS estimated log \( P/D \) values (Table 1). In general, reasonable agreement was found between the range of estimated and experimental \( K_{oc} \) values using the various approaches, which further calls into question the prior literature dismissals of applying such equilibrium partitioning approaches towards these compounds. There appears to be no reason why traditional fugacity-based approaches and lipophilic partitioning models cannot be applied for screening level assessments of PFA behavior in environmental systems, particularly if the results are supported by a limited experimental data set. As more experimental data becomes available, existing partitioning QSARs can also be retrained to include this new contaminant class.

Similarly, caution must be further exercised in making general assumptions regarding the congener specific partitioning and migration factors of PFAs in various types of soils and sediments. We have already discussed the potential influence of the hydrogeochemical signature on PFA partitioning, but the congener identity and organic content of the soil or sediment will also play a major role on resulting mobility designations (Fig. 5). Using commonly accepted \( K_d \) based contaminant mobility ranges,\(^{63} \) we see that no \( C_1 \) through \( C_8 \) PFA congener can be designated as either an immobile or conservative movement end member independent of estimated \( K_{oc} \) value. Rather, all PFA congeners examined here will have varying mobility designations of at least three mobility classes depending on the organic carbon content of the sorbing matrix (and in many cases, the mobility will span from either end member).

In addition, the inter- and intra-homologue variation in mobility is evident in Figure 5, whereby the linear \( C_7 \) PFSA\(^ 4 \) (n-PFBS) is expected to have an essentially equivalent ground and pore water mobility rating as the branched \( C_8 \) PFSA\(^ 28 \) congener, despite the four perfluorocarbon difference between the respective chains. Consequently, the mobility of PFAs in soils and sediment pore waters will need to be assessed on a case specific basis that takes into account the intrinsic properties of both the congener and the solid matrix. Support for this predicted differential mobility of PFA congeners in groundwater comes from a study of PFA contaminated groundwater at military bases,\(^{64} \) whereby changes in the concentration ratio of the straight-chain \( C_8;C_6 \) PFSA moving farther from the point surface infiltration source at one of the sites supports our predicted lower \( K_{oc} \) values (and hence, \( K_d \) values) for the \( C_6 \) PFSAs relative to the longer chained counterpart.

PFAs have also been studied in municipal wastewater treatment plants (WWTPs),\(^{7} \) where sorption of contaminants to organic matter and settling with particulates in grit chambers, trickling filters, rotating biological contactors, and primary/secondary clarifiers, as well as sorption to activation carbon if this polishing step is present, is a major removal process from the final effluent stream. Although it has been previously noted that a means of estimating \( K_{oc} \) values for the \( C_1 \) through \( C_8 \) PFAs would be valuable in better understanding PFA profiles within WWTPs,\(^{65} \) the potential range of PFA precursors that
are subject to biological and physicochemical degradation into PFAs (e.g., perfluoroalkyl sulfonamides, fluorotelomers, etc.) in the wastewater influent (as well as in soils) is vast.\[66–72\] This issue makes source apportionment and mass balances nearly impossible given our current limited knowledge regarding congener specific kinetic and thermodynamic parameters for degradation and partitioning. A similar caveat must be applied to ground and pore water modeling of PFAs. Biogeochemical processes that degrade PFA precursors in soils and sediments could greatly complicate the application, calibration, and interpretation of any PFA partitioning efforts. However, as more kinetic and degradation product data becomes available for PFA precursors, this additional information can be included in congener specific multimedia models for a more reliable understanding of how these contaminants are behaving in both natural and engineered systems.

The potential for partitioning of PFAs into sediments and on soils, and the \( K_{oc} \) based controls on these processes, has large implications for our understanding of how these contaminants behave in aquatic systems. Sediments with PFA reservoirs that act as future source inputs to the overlying water column following a highly contaminated pulse input, as well as a general source of these contaminants to benthic organisms and lacustrine food webs, have also been discussed elsewhere.\[12,14,73,74\] Yet, in some cases, any impedence of PFA transport from upstream watershed sources towards marine deposition has been entirely dismissed (i.e., assumed that PFA inputs move with instream and ground water retardation factors \( [R_f] \) at unity) without detailed consideration.\[75\] The field mobility of the longer chain PFAs such as n-PFOS and n-PFOA has not been determined, and inferences regarding the appearance of dissolved phase PFAs in streams whereby nearby surface application of waste solids to soils has occurred \[76\] must presently be restricted to a range of possible transport mechanisms that include hindered and/or unhindered surface and/or ground water transport or erosion and surface transport of PFA containing particulates followed by PFA desorption in receiving waters. Caution must also be exercised in neglecting sorption losses to sediments in riverine PFA mass balance studies, particularly where only PFAs are monitored in upstream and downstream waters and wastewater inputs and a mass balance is achieved, as has been previously done.\[77\] In these studies, PFA precursors could be degrading in situ within a particular stream reach as an additional (and unaccounted for) PFA input with fluxes that offset PFA losses to sediments.

Similarly, Wujcik et al. stated that no TFA was removed by soil retention in watersheds as part of their mass balances for the terminal Mono Lake in California and Pyramid Lake in Nevada,\[78\] despite earlier definitive studies showing significant TFA retention in some watersheds.\[59,60,79\] Work that neglected soil retention of TFA in watersheds in Germany reported average TFA concentrations in river waters that were 1.3-fold higher than found in precipitation, but since the authors stated that regional evaporation (and assumed negligible volatilization losses of TFA from terrestrial and aquatic ecosystems) should lead to aquatic TFA levels about twice that of precipitation, an unknown reservoir or removal process was invoked to explain the discrepancy. Yet, if one assumes about 30 to 40% TFA retention in these German forests, at the lower mid-point of the range (20 to 60%) of what was reported in organic forest soils for the northeastern U.S.\[59,60,79\] this difference is readily explained with an already known removal mechanism.

Another study of concentrations and mass fluxes of TFA in aquatic systems from Switzerland also ignored sediment partitioning and soil retention.\[80\] PFA losses to sediments were also ignored in a mass balance of these compounds in Lake Ontario,\[81\] but a subsequent analysis of potential sorption sensitivity towards this assumption suggested it was valid under the site specific conditions.\[27\] However, sedimentation rates in mostly oligotrophic lakes such as Lake Ontario (http://www.epa.gov/glnpo/glindicators/water/trophic.html) are expected to be much lower than in more eutrophic systems and/or lakes with large sediment inputs (such as behind hydroelectric dams). In these alternate cases, sedimentation rates may play a dominant removal mechanism for PFAs from upstream aquatic inputs, and the neglect of sediment losses for these contaminants would overestimate PFA impacts on downstream systems, and underestimate risks for the direct receiving water body from PFA trapping, recycling, and subsequent release. Furthermore, any dam removal efforts may also need to explicitly consider the potentially large PFA reservoirs trapped in their impoundments.\[82\]

Conclusions

Congener specific organic carbon normalized soil and sediment-water partitioning \( (K_{oc}) \) coefficients were estimated for the \( C_1 \) through \( C_8 \) perfluoroalkyl carboxylic acids (PFCAs) and sulfonic acids (PFSAs) using SPARC and ALOGPS derived octanol-water partitioning/distribution constants calibrated to experimental values for the straight-chain \( C_7 \) through \( C_{10} \) PFCAs and \( C_8 \) and \( C_{10} \) PFSAs. The results suggest that almost all \( C_1 \) through \( C_8 \) PFCA and PFSA congeners should accumulate in organic matter on sediments and soils, and the movement of these compounds through ground waters and pore waters will be retarded via the organic carbon partitioning process. Estimated \( K_{oc} \) values within each compound class generally increase with increasing chain length and increase with increasing linearity of the perfluoroalkyl chain. Substantial intra- and inter-homologue variation in \( K_{oc} \) values is expected. Interhomologue mixing of \( K_{oc} \) values may complicate interpretations...
of these compounds behave in soil and sediment systems. The expected congener specific variation in $K_{oc}$ values will preferentially fractionate isomer profiles towards longer-chain linear congener dominance in the organic matter, leaving an aqueous system enriched in lower homologue branched congeners with less affinity for organic matter partitioning. This isomeric fractionation will require inclusion in source apportionment models and risk assessments. Existing quantitative structure property relationships were also found to reasonably model the experimental $K_{oc}$ values of representative congeners, suggesting that established equilibrium partitioning frameworks may be applicable towards modeling PFCA and PFSA environmental fate processes. None of the C$_1$ through C$_8$ PFCA or PFSA congeners is expected to have a single pore or ground water mobility index independent of the organic matter content in the surrounding matrix. As a result, generalities regarding the subsurface or sediment in situ mobility of these compounds do not appear valid, necessitating a congener and site specific analysis of migration and partitioning behavior.

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