Congener specific organic carbon normalized soil and sediment-water partitioning coefficients for the C_1 through C_8 perfluorinated alkylsulfonic and alkylcarboxylic acids

SIERRA RAYNE[1]* and KAYA FOREST[2]

[1]*Department of Chemistry, University of Winnipeg, Winnipeg, Manitoba, Canada*

[2]*Department of Chemistry, Okanagan College, Penticton, British Columbia, Canada*

ABSTRACT

Organic carbon normalized soil and sediment-water partitioning (K_{oc}) coefficients were estimated for all C_1 through C_8 perfluorinated alkylsulfonic acid (PFSA) and alkylcarboxylic acids (PFCA) congeners. The limited experimental K_{oc} dataset for the straight chain C_7 through C_{10} PFCAs and C_8 and C_{10} PFSAs was correlated to SPARC and ALOGPS computationally estimated octanol-water partitioning constants and used to predict K_{oc} values for both branched and linear C_1 through C_8 isomers. All branched and linear congeners in this homologue range are expected to have K_{oc} 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

_____

*Address correspondence to Sierra Rayne, Department of Chemistry, University of Winnipeg, Winnipeg, Manitoba, Canada; Phone: +1 204 786 9265, Fax: +1 204 775 2114; E-mail: rayne.sierra@gmail.com

1

increasing perfluoroalkyl chain length and linearity increase K_{oc} values with substantial intra- and inter-homologue variation and interhomologue mixing. Variability in K_{oc} 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 estimated K_{oc} values from octanol-water partitioning constants suggests that equilibrium partitioning frameworks may be applicable towards modeling PFCA and PFSA environmental fate processes and warrants further study using other partitioning coefficients for which suitable experimental data is available.

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

2

INTRODUCTION

Perfluoroalkyl acids (PFAs) such as the perfluoroalkyl sulfonic acids (PFSAs) and perfluoroalkyl carboxylic acids (PFCAs) (Fig. 1) are now well established as contaminants widely distributed in the environment that display the capacity for long range transport, bioaccumulation, persistence, and a range of toxicological effects.[1-7] Longer chain ($\geq C_2$) PFCAs and all PFSAs are currently thought to arise solely from the use of commercial perfluorinated surfactants, whereas the C_1 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.[8-10] 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 (ca. 250 to 300 million tons) in global oceans, whereas terrestrial, freshwater, and atmospheric reservoirs are primarily anthropogenically derived.[8,11,12] In general, total PFSA and PFCA 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 nonpoint sources of contamination.
[3,7,11-74] Wastewaters from semiconductor fabrication plants using photolithographic techniques have the highest reported PFA levels to date, with concentrations reaching well into the mg L^{-1} range,[75] and even up to g L^{-1} levels.[76] A number of regions in Asia, Europe, and North America are now reporting samples analyzed from surface water sources that exceed the state of New Jersey (USA) 40 ng L^{-1} straight chain C_7 PFCA **39** (n-PFOA) guideline for drinking water and the 500 ng L^{-1} and 300 ng L^{-1} acceptable threshold values for n-PFOA and the straight chain C_8 PFSA **89** (n-PFOS) in the state of Minnesota (USA). Few studies have reported PFA levels in sediments, with concentrations ranging from below detection limits up to the low mg kg^{-1} dry weight.[32,77-80] Even less work has been done on developing a database of PFA concentrations in soils.[62] A limited survey of soils from sites in Canada,

3

Malawi, the United Kingdom, and Chile showed TFA was present at low ng g^{-1} levels at values similar to, or exceeding, that of other haloacetic acids.[81]

To better understand the environmental fate of PFAs and to assist in the design and optimization of treatment processes, additional information is needed regarding PFA partitioning between various matrices. Laboratory scale sorption of the straight chain C$_4$ and C$_8$ PFSAs and C$_7$ PFCA onto activated carbon (granular (GAC) and particulate (PAC)), zeolite, ion exchange resins, and wastewater sludge has been reported.[7,82-84] Increasing perfluoroalkyl chain length and a sulfonic acid head group (versus a carboxylate moiety) increased the sorption onto GAC.[83] 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-PFOA from solution.[84] Recent 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,[82] which is perhaps expected for PFAs given how this cationic amine resin may be able to effectively mimic a proteinophilic sorption surface. Interestingly, Lampert et al. have also indirectly provided clear support for a n-PFOA pK_a of between 3 and 4 during their evaporation treatment studies on this compound. No evaporative losses of the analyte were found at neutral pH values, whereas substantial losses were observed at pH 2.6, supporting our claims,[85] and that of others,[86-88] for an operational pK_a value of about 3 to 4, rather than previous estimates near zero.[89-91] In some cases, water treatment using activated carbon has been shown to be effective for removing longer chain PFAs such as n-PFOA from contaminated source waters.[20,54-56,70] PFAs, like their hydrocarbon fatty acid analogs,[92,93] also sorb to inorganic surfaces such as sands, clays, iron oxides, calcium fluoride, and surface modified silicas.[82,94,95] but organic matter

4

sorption is thought to be dominant in most environmental systems and offer the most promising for treatment methods.

In contrast to the predominantly lipophilic character of nonpolar contaminants, the proteinophilic nature of the polar/ionic PFAs is well established from both synthetic chemistry and toxicological perspectives. For example, in synthetic chemistry, PFAs such as TFA are effective protein solvents and are used for making derivatives of amino acids and carbohydrates.[26] In biological systems, PFAs tend to associate with and potentially covalently bind to proteins such as albumin and in protein rich regions of the body such the blood, kidneys, and the liver.[96-98] This proteinophilic behavior in vivo results in large bioconcentration factors (BCFs) and bioaccumulation factors (BAFs) in protein rich tissues such as the liver, blood, and kidneys for longer chain PFAs.[1,2,4,6,14,22,25,41,61,78,99-104] The affinity for protein surfaces has also been recently exploited by the use of molecularly imprinted chitosan polymer adsorbents to remove PFAs from waste streams.[105] 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 PFAs between more traditional organic materials and aqueous phases. [106,107] However, these studies have been limited to the longer chain ($>C_7$) PFAs, with little available 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,[78] highlighting the need to extend existing organic matter-water partitioning datasets for the longer chain PFAs to the shorter chain congeners who 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 (PFCs) in general has led to a significant amount of discussion in the literature,[85-91,108-113] potentially dissuading rigorous investments in extended experimental investigations.

5

With low reported rates of abiotic and biotic degradation for PFAs, a focus is developing to better understand and model the partitioning behavior of PFAs in natural and engineered systems. Due to the increasing awareness of the large number of potential PFA congeners,[114] and the experimental costs in measuring a range of partitioning constants for each isomer, our recent efforts [85,99,109-111,115] have been concentrated on using computational tools and available experimental datasets to predict the physicochemical properties of these compounds. In the present study, we synthesize the current state of the art regarding partitioning of PFAs between organic carbon and aqueous environments and present a congener specific model that estimates the organic carbon normalized soil and sediment-water partitioning (K_{oc}) coefficients for the C_1 through C_8 PFCA and PFSA isomers.

METHODS AND MATERIALS

Experimental organic carbon normalized soil and sediment-water partitioning (K_{oc}) coefficients for PFCA and PFSA congeners are from Higgins and Luthy.[106] The numbering system for PFSA and PFCA congeners follows the approach outlined previously.[114] SMILES molecular formats [116,117] of the unionized acid form of each PFA congener were used as computational inputs. For each PFA congener, both the $\log_{10} K_{ow}$ value ($\log_{10} P$ for the molecular form) and the $\log_{10} D_{octanol}$ lipophilicity value for ionizable compounds were estimated using SPARC [118-122] The $\log_{10} P$ values were also estimated using the ALOGPS approach [123-125] which has been previously validated for a wide range of organic compounds.[126] The $\log_{10} P_i$ value for the ionized form is not calculable by ALOGPS. The P, P_i, and D values are calculated and related according to the following equations where [HA] and [A$^-$] are the concentrations of neutral and anionic PFA species in octanol (subscript o) and water (subscript w), respectively: $P=[HA]_o/[HA]_w$; $P_i=[A^-]_o/[A^-]_w$; and $D=(P+P_i\times10^{(pH-pKa)})/(1+10^{(pH-pKa)})$.[127] For comparative

6

purposes with the straight chain C_1 PFCA congener and the C_8 PFCA and PFSA congeners, log P values were also calculated using the following methods within the ALOGPS 2.1 program: AC log P, AB/Log P, COSMOFrag, miLogP, ALOGP, MLOGP, KOWWIN, XLOGP2, and XLOGP3.[124] The reliance of SPARC estimated log_{10} 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 PFCAs [85] and overestimate the pK_a values of PFSAs.[110] 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.[85,110,115]

RESULTS AND DISCUSSION

Linear relationships having the following equations were found between the SPARC calculated log_{10} K_{ow} and log_{10} $D_{octanol}$ values and the ALOGPS log_{10} 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_{10} K_{oc} (L kg_{oc}^{-1}) = 0.438±0.018 × log_{10} $K_{ow,SPARC}$ − 0.651±0.140 (r=0.998, p<0.002 [student's t-test]); log_{10} K_{oc} (L kg_{oc}^{-1}) = 0.432±0.018 × log_{10} $D_{octanol,SPARC}$ + 0.215±0.109 (r=0.998, p<0.002); and log_{10} K_{oc} (L kg_{oc}^{-1}) = 1.413±0.019 × log_{10} P_{ALOGPS} − 3.938±0.091 (r=0.9998, p<0.0002). Although only two datapoints were available for the PFSAs (the straight chain C_8 and C_{10} congeners), similar slopes were observed for the $K_{ow,SPARC}$ and $D_{octanol,SPARC}$ values across both PFA classes (ca. 0.43 to 0.45) but the P_{ALOGPS} slope was substantially higher for the PFSAs (ca. 4.1) compared to the PFCAs (ca. 1.4) (Fig. 2(b)): log_{10} K_{oc} (L kg_{oc}^{-1}) = 0.453 × log_{10} $K_{ow,SPARC}$ − 0.561; log_{10} K_{oc} (L kg_{oc}^{-1}) = 0.439 × log_{10} $D_{octanol,SPARC}$ − 1.181; and log_{10} K_{oc} (L kg_{oc}^{-1}) = 4.082 × log_{10} P_{ALOGPS} − 14.627.

7

Using these regression equations for the PFCAs, $K_{ow,SPARC}$, $D_{octanol,SPARC}$, and P_{ALOGPS} values were calculated for all C_1 through C_8 congeners and the corresponding K_{oc} values estimated via negative linear extrapolation 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 PFSAs using the $K_{ow,SPARC}$ and $D_{octanol,SPARC}$ values, we also conducted an analogous negative linear extrapolation 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 $K_{ow,SPARC}$ and $D_{octanol,SPARC}$ approaches predict interhomologue 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 PFCA 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 PFAs to soils and sediments and their movement through ground waters 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 PFAs from environmental matrices (and congener specific standards once the synthetic methods become available). As expected from the available experimental datasets, 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 as the chain shortens, resulting in K_{oc} values <1 ($\log_{10} K_{oc}<0$) for the $\leq C_3$ PFCAs (e.g., perfluorobutanoic acids) and the $\leq C_6$ PFSAs (e.g. perfluorohexane sulfonic acids). In contrast, both the $K_{ow,SPARC}$ and $D_{octanol,SPARC}$ approaches predict that almost all C_1 through C_8 PFCAs and PFSAs will have $\log_{10} K_{oc}$ values >0 (with the limited exceptions of C_4 PFSA **1** ($\log_{10} K_{oc}=-0.24$) and C_5 PFSA **3** ($\log_{10} K_{oc}=-0.05$) using the $D_{octanol,SPARC}$ approach) and should accumulate in sediments and soils.

8

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 pharmacokinetic models. All approaches predict substantial branching effects on K_{oc} values, with intrahomologue variation of up to two $\log_{10} K_{oc}$ units for both the C_8 PFCAs and PFSAs using the $K_{ow,SPARC}$ and $D_{octanol,SPARC}$ proxies and about 0.3 (PFCAs) to 0.9 (PFSAs) units for the P_{ALOGPS} approach (insets given for the C_8 congeners in Fig. 3(c) and 4(c) to illustrate branching effect). Similar branching effects are evident for each of the three methods across both PFA classes, indicating that the PFA equilibrium sediment partitioning process is likely to preferentially enrich the linear congeners of each homologue over the corresponding branched isomers compared to the dissolved phase water column signature. As a result, direct comparisons of linear and branched PFA profiles in sediments are not likely valid, and some form of a reconstruction approach will be required to back-calculate dissolved water column signatures as part of an overall source apportionment strategy. We also note that these findings assume equilibration between the sediments and water column, but with the relatively slow kinetics found experimentally for PFA sediment-water partitioning, some aquatic sediments (particularly in rivers with temporally varying PFA inputs) may not be at such equilibrium. For this reason, equilibrium and kinetic studies are required on branched congeners once sufficiently pure authentic standards are available in order to examine whether rate constants for partitioning display perfluoroalkyl chain branching influences. Our predictions that linear PFA congeners should have higher K_{oc} values than branched isomers is supported by the limited available field evidence. Houde et al. examined the fractionation and bioaccumulation of a small subset of C_8 PFSA isomers in a Lake Ontario food web and found a similar isomer profile in organisms and sediments, both of which suggested that partitioning into organic matter is preferred by more linear congeners.[61] These findings also support our prior work on estimating bioconcentration factors for

9

PFAs which also showed that BCFs for linear isomers are expected to be higher than branched counterparts.[99]

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 K_{ow} and octanol-air (K_{oa}) constants, as well as the more general fugacity approach, in describing (either directly or as modified surrogate proxies) the behavior of PFAs in abiotic and biotic systems.[6,102,128] For example, it has been stated that soil and sediment adsorption coefficients (K_d) of PFAs "cannot be estimated with conventional quantitative structure relationship models (QSARs)."[6] 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."[6] 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 current computational methods for estimating K_{ow} (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,[102] is both unsatisfactory and perhaps unnecessary.

Furthermore, assessments regarding the organic partitioning behavior of PFAs are often made using the

10

water and octanol solubilities and vapor pressures of PFA salts (e.g., potassium, lithium, and/or ammonium salts), and subsequent calculations of K_{ow} values and Henry's law constants using the properties of these salts.[6,128] 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 new ion pairing equilibrium with the major and minor ion signature of the surrounding medium. Since PFA concentrations in all environmental and biological compartments (i.e., mg/L concentrations at the highest, but more typically in the ng/L to low μg/L 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.[129]

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 have positively charged regions containing both hydrophilic and hydrophobic cavities that 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

11

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 both 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.[130] 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 the initial PFA K_{oc} dataset, 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.[107] 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

12

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.[114] 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,[85,109,115] 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.

No definitive experimentally determined $\log_{10} K_{ow}$ values are available for any PFCAs or PFAs from which to calibrate the computational inputs. During K_{ow} 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.[6,128] This result is readily explained by the conceptual partitioning model developed by Higgins and Luthy,[106,107] 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, 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 volume-volume normalized process assumptions for traditional lipidic contaminants. In other words, sufficient quantities of PFAs exist at the aqueous-organic interface that this domain needs 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 layers). 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

13

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 [106] 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 freely dissolved in the organic matter or are 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 K_{ow} testing on PFAs could determine total concentrations dissolved in the bulk aqueous and octanol phases and – also accounting for any sorption to the container – perform a system mass balance (through knowledge of the cross-sectional octanol-water contact area) to determine the surface area normalized concentration of the PFA. This type of experimental work yields the following three partitioning constants for the PFA: (1) conventional $D_{octanol}$ value obtained via dividing the total PFA concentration in the aqueous layer by that in the octanol layer; (2) modified $D_{octanol}$ 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 partitioning 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. 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 K_{oc} data available, would greatly assist in our understanding of the sorption mechanisms. As well, the work would help in developing conceptual and

14

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. We also note that preliminary results using the acid form suggest a $\log_{10} K_{ow}$ value of 1.23 for n-PFOS,[82] more than 2.3 $\log_{10}$ units above the calculated value (-1.08; based on solubilities in octanol and water) for the potassium salt given by other studies [6,102] and 2 to 3 $\log_{10}$ units below the $K_{ow,SPARC}$ (4.7), $D_{octanol,SPARC}$ (3.4), and P_{ALOGPS} (4.2) estimates. The experimental details behind this preliminary K_{ow} report are lacking, so it is difficult to assess whether it could potentially be a significant underestimate due to the extraction and analysis difficulties known for PFSA determinations, as well as from failing to account for sorption losses and the possible presence of a significant interfacial layer. However, these findings, and our computational estimates, suggest the prior approach of estimating PFA K_{ow} values by using relative solubilities of one of the many possible PFA salts in the two phases significantly underestimates the organic partitioning behavior of these compounds. $Log_{10} K_{ow}$ values ranging from -2.1 to +0.5 are given for TFA in an environmental risk assessment review for this compound,[26] which compare to our estimates of 1.78 (SPARC K_{ow}), 0.06 (SPARC $D_{octanol}$), and 1.35 (ALOGPS). To the best of our knowledge, there are no reliable peer reviewed experimental estimates or calculations on a K_{ow} value for the C_7 PFCA **39** (n-PFOA).

Other than the work of Higgins and Luthy [106] used for our estimates, 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. 3M studies reported $\log_{10} K_{oc}$ values of 1.1 for n-PFOA and between 2.6 and 3.1 for n-PFOS.[102] The 3M n-PFOS $\log_{10} K_{oc}$ range agrees with the value of 2.68 reported by Higgins and

15

Luthy,[106] but the 3M $\log_{10} K_{oc}$ value for n-PFOA is significantly lower than the corresponding value

(2.11) reported by these independent researchers. 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.[26] Using the relationship

$K_d = f_{oc} \times K_{oc}$,[131] this translates into an estimated $\log_{10} K_{oc}$ upper limit of <1.2 which agrees with our

$\log_{10} K_{oc}$ estimates of 0.13 (SPARC K_{ow}), 0.24 (SPARC $D_{octanol}$), and -2.03 (ALOGPS). In a broader

study of TFA sorption to 54 soils from North America and Europe,[132] log K_{oc} values (calculated from

the reported K_d and f_{om} values using the formula $K_d = 0.58 \times f_{om} \times K_{oc}$ [131]) ranged from 0.25 to 1.77

(mean=median=1.12), in reasonable agreement with our SPARC K_{ow} and $D_{octanol}$ estimates, the earlier

work of van Dijk,[26] and field manipulation experiments in an experimental forest.[133] 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.[132] Assuming the soil retention

behavior of longer chain 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 [106] 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 [106]

found that sodium did not enhance PFA sorption, so when coupled with the results of Richey et al.,[132]

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. We encourage researchers to consider the use of a multidimensional response surface

16

methodology approach to incorporate the effects of multiple ion concentrations in an overall predictive equation of the aqueous-organic partitioning of PFAs.

Field estimates of $\log_{10} K_{oc}$ 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.[77] 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 $\log_{10} K_{oc}$ 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.[32] Analysis of their data for n-PFOA and n-PFOS (the only two analytes with levels above detection limits in sediments) yields $\log_{10} K_{oc}$ 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.[134] Our analysis of their data shows field $\log_{10} K_{oc}$ 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 $\log_{10} K_{oc}$ values ranging from 3.0 to 3.5 for n-PFOS and 2.4 to 2.8 for n-PFOA.[43] In general, there appears to be good agreement between the laboratory and field measurements of K_{oc} values for the PFAs.

To determine whether the existing QSARs for predicting K_{oc} values based on K_{ow} inputs could also be applied to the PFAs, we choose a representative suite of established literature K_{oc}-K_{ow} regressions and applied them to TFA, n-PFOA, and n-PFOS using the SPARC and ALOGPS estimated partitioning constants for the molecular PFA species (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

17

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 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 dataset. As more experimental data also 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,[135] 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_4 PFSA **4** (n-PFBuS) is expected to have an essentially equivalent ground and pore water mobility rating as the branched C_8 PFSA **28** congener, despite the four carbon difference in chain lengths. 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 ground water comes from a study of PFA contaminated ground water at military bases,[31] whereby changes in the concentration ratio of the straight chain C_8:C_6 PFSAs moving farther from the point surface infiltration

18

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) [7,33,37,42,43,48-50,64,69,80,136-141] 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,[137] 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. [136,140-146] 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

19

benthic organisms and lacustrine food webs, have also been discussed elsewhere.[25,78,80,147] Yet, in some cases, any impedence of PFA transport from upstream watershed sources towards marine deposition has been entirely dismissed (i.e., PFA inputs move with in stream and ground water retardation factors (R_f) at unity) without detailed consideration.[27] 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 [21] 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.[37] 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,[40] despite earlier definitive studies showing significant TFA retention in some watersheds.[132,133,148] 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

20

in organic forest soils for the northeastern U.S.,[132,133,148] 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.[74] PFA losses to sediments were also ignored in a mass balance of these compounds in Lake Ontario,[149] but a subsequent analysis of potential sorption sensitivity towards this assumption was shown to likely be valid under the site specific conditions.[106] However, sedimentation rates in mostly oligotrophic lakes such as Lake Ontario (http://www.epa.gov/glnpo/glindicators/water/trophica.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.[150]

CONCLUSIONS

Congener specific organic carbon normalized soil and sediment-water partitioning (K_{oc}) coefficients were estimated for the C_1 through C_8 perfluorinated alkylsulfonic acids (PFSAs) and alkylcarboxylic acids (PFCAs) using SPARC and ALOGPS derived octanol-water partitioning 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 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 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 how 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 water or ground water mobility index independent of the organic matter content in the surround matrix. As a result, generalities regarding the subsurface or sediment in situ mobility of these compounds do not

22

appear valid, necessitating a congener and site specific analysis of migration and partitioning behavior.

ACKNOWLEDGMENTS

23

REFERENCES

[1] Conder, J.M.; Hoke, R.A.; De Wolf, W.; Russell, M.H.; Buck, R.C. Are PFCAs bioaccumulative? A critical review and comparison with regulatory criteria and persistent lipophilic compounds. Environ. Sci. Technol. **2008**, *42*, 995-1003.

[2] Houde, M.; Martin, J.W.; Letcher, R.J.; Solomon, K.R.; Muir, D.C.G. Biological monitoring of polyfluoroalkyl substances: A review. Environ. Sci. Technol. **2006**, *40*, 3463-3473.

[3] Fromme, H.; Tittlemier, S.A.; Volkel, W.; Wilhelm, M.; Twardella, D. Perfluorinated compounds – Exposure assessment for the general population in western countries. Int. J. Hyg. Environ. Health. 2009, in press, 10.1016/j.ijheh.2008.04.007.

[4] Giesy, J.P.; Kannan, K. Perfluorochemical surfactants in the environment. Environ. Sci. Technol. 2002, 36, 146A-152A.

[5] Kennedy, G.L.; Butenhoff, J.L.; Olsen, G.W.; O'Connor, J.C.; Seacat, A.M.; Perkins, R.G.; Biegel, L.B.; Murphy, S.R.; Farrar, D.G. The toxicology of perfluorooctanoate. Crit. Rev. Toxicol. **2004**, *34*, 351-84.

[6] Beach, S.A.; Newsted, J.L.; Coady, K.; Giesy, J.P. Ecotoxicological evaluation of perfluorooctanesulfonate (PFOS). Rev. Environ. Contam. Toxicol. **2006**, *186*, 133-74.

[7] Schultz, M.; Barofsky, D.; Field, J. Fluorinated alkyl surfactants. Environ. Eng. Sci. **2004**, *20*, 487-501.

[8] Frank, H.; Christoph, E.H.; Holm-Hansen, O.; Bullister, J.L. Trifluoroacetate in ocean waters. Environ. Sci. Technol. 2002, 36, 12-15.

[9] Ellis, D.A.; Mabury, S.A.; Martin, J.W.; Muir, D.C.G. Thermolysis of fluoropolymers as a potential source of halogenated organic acids in the environment. Nature **2001**, *412*, 321-324.

[10] Ellis, D.; Moody, C.; Mabury, S. Trifluoroacetic acid and longer chain perfluoro acids: Sources

24

and analysis. In *The Handbook of Environmental Chemistry: Volume 3N/2002 – Organofluorines*; Springer Berlin / Heidelberg: Berlin, Germany, 2002; 103-120.

[11]   Jordan, A.; Frank, H. Trifluoroacetate in the environment: Evidence for sources other than HFC/ HCFCs. Environ. Sci. Technol. **1999**, *33*, 522-527.

[12]   Scott, B.F.; Macdonald, R.W.; Kannan, K.; Fisk, A.; Witter, A.; Yamashita, N.; Durham, L.; Spencer, C.; Muir D.C.G. Trifluoroacetate profiles in the Arctic, Atlantic, and Pacific Oceans, Environ. Sci. Technol. 2005, 39, 6555-6560.

[13]   Ericson, I.; Nadal, M.; van Bavel, B.; Lindström, G.; Domingo, J. Levels of perfluorochemicals in water samples from Catalonia, Spain: Is drinking water a significant contribution to human exposure? Env. Sci. Pollut. Res. **2008**, *15*, 614-619.

[14]   Boulanger, B.; Vargo, J.; Schnoor, J.L.; Hornbuckle, K.C. Detection of perfluorooctane surfactants in Great Lakes water. Environ. Sci. Technol. **2004**, *38*, 4064-4070.

[15]   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.

[16]   Loos, R.; Wollgast, J.; Huber, T.; Hanke, G. Polar herbicides, pharmaceutical products, perfluorooctanesulfonate (PFOS), perfluorooctanoate (PFOA), and nonylphenol and its carboxylates and ethoxylates in surface and tap waters around Lake Maggiore in Northern Italy. Anal. Bioanal. Chem. **2007**, *387*, 1469-1478.

[17]   Nakayama, S.; Strynar, M.J.; Helfant, L.; Egeghy, P.; Ye, X.; Lindstrom, A.B. Perfluorinated compounds in the Cape Fear drainage basin in North Carolina. Environ. Sci. Technol. **2007**, *41*, 5271-5276.

[18]   Saito, N.; Sasaki, K.; Nakatome, K.; Harada, K.; Yoshinaga, T.; Koizumi, A. Perfluorooctane sulfonate concentrations in surface water in Japan. Arch. Env. Contam. Toxicol. **2003**, *45*, 149-

25

158.

[19]   Saito, N.; Harada, K.; Inoue, K.; Sasaki, K.; Yoshinaga, T.; Koizumi, A. Perfluorooctanoate and

         perfluorooctane sulfonate concentrations in surface water in Japan. J. Occup. Health. **2004**, *46*,

         49-59.

[20]   Wilhelm, M.; Kraft, M.; Rauchfuss, K.; Hölzer, J. Assessment and management of the first

         German case of a contamination with perfluorinated compounds (PFC) in the Region Sauerland,

         North Rhine-Westphalia. J. Toxicol. Environ. Health A. **2008**, *71*, 725-733.

[21]   Skutlarek, D.; Exner, M.; Färber, H. Perfluorinated surfactants in surface and drinking waters.

         Environ. Sci. Pollut. Res. Int. **2006**, *13*, 299-307.

[22]   Sinclair, E.; Mayack, D.T.; Roblee, K.; Yamashita, N.; Kannan, K. Occurrence of perfluoroalkyl

         surfactants in water, fish, and birds from New York State. Arch. Environ. Contam. Toxicol. **2006**,

         50, 398-410.

[23]   So, M.K.; Miyake, Y.; Yeung, W.Y.; Ho, Y.M.; Taniyasu, S.; Rostkowski, P. Perfluorinated

         compounds in the Pearl River and Yangtze River of China. Chemosphere **2007**, *68*, 2085-2095.

[24]   Schultz, M.M.; Barofsky, D.F.; Field, J.A. Quantitative determination of fluorotelomer sulfonates

         in groundwater by LC MS/MS. Environ. Sci. Technol. **2004**, *38*, 1828-1835.

[25]   Moody, C.A.; Martin, J.W.; Kwan, W.C.; Muir, D.C.G.; Mabury, S.A. Monitoring perfluorinated

         surfactants in biota and surface water samples following an accidental release of fire-fighting

         foam into Etobicoke Creek. Environ. Sci. Technol. **2002**, *36*, 545-551.

[26]   Boutonnet, J.C.; Bingham, P.; Calamari, D.; de Rooij, C.; Franklin, J.; Kawano, T.

         Environmental risk assessment of trifluoroacetic acid. Human Ecol. Risk Assess. **1999**, *5*, 59-

         124.

[27]   McLachlan, M.S.; Holmstrom, K.E.; Reth, M.; Berger, U. Riverine discharge of perfluorinated

         carboxylates from the European continent. Environ. Sci. Technol. **2007**, *41*, 7260-7265.

26

[28]   Harada, K.; Saito, N.; Sasaki, K.; Inoue, K.; Koizumi, A. Perfluorooctane sulfonate

        contamination of drinking water in the Tama River, Japan: Estimated effects on resident serum

        levels. Bull. Environ. Contam. Toxicol. **2003**, *71*, 31-36.

[29]   Rostkowski, P.; Yamashita, N.; So, I.M.K.; Taniyasu, S.; Lam, P.K.S.; Falandysz, J.

        Perfluorinated compounds in streams of the Shihwa Industrial Zone and Lake Shihwa, South

        Korea. Environ. Toxicol. Chem. **2006**, *25*, 2374-2380.

[30]   Moody, C.A.; Hebert, G.N.; Strauss, S.H.; Field, J.A. Occurrence and persistence of

        perfluorooctanesulfonate and other perfluorinated surfactants in groundwater at a fire-training

        area at Wurtsmith Air Force Base, Michigan, USA. J. Environ. Monit. **2003**, *5*, 341-345.

[31]   Moody, C.A.; Field, J.A. Determination of perfluorocarboxylates in groundwater impacted by

        fire-fighting activity. Environ. Sci. Technol. **1999**, *33*, 2800-2806.

[32]   Senthilkumar, K.; Ohi, E.; Sajwan, K.; Takasuga, T.; Kannan, K. Perfluorinated compounds in

        river water, river sediment, market fish, and wildlife samples from Japan. Bull. Environ. Contam.

        Toxicol. **2007**, *79*, 427-431.

[33]   Plumlee, M.H.; Larabee, J.; Reinhard, M. Perfluorochemicals in water reuse. Chemosphere

        2008, *72*, 1541-1547.

[34]   Hoehn, E.; Plumlee, M.H.; Reinhard, M. Natural attenuation potential of downwelling streams

        for perfluorochemicals and other emerging contaminants. Water Sci. Technol. **2007**, *56*, 59-64.

[35]   Cheng, J.; Vecitis, C.D.; Park, H.; Mader, B.T.; Hoffmann, M.R. Sonochemical degradation of

        perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in landfill groundwater:

        Environmental matrix effects. Environ. Sci. Technol. **2008**, *42*, 8057-8063.

[36]   Murakami, M.; Imamura, E.; Shinohara, H.; Kiri, K.; Muramatsu, Y.; Harada, A. Occurrence and

        sources of perfluorinated surfactants in rivers in Japan. Environ. Sci. Technol. **2008**, *42*, 6566-

        6572.

27

[37] Huset, C.A.; Chiaia, A.C.; Barofsky, D.F.; Jonkers, N.; Kohler, H.E.; Ort, C. Occurrence and mass flows of fluorochemicals in the Glatt Valley watershed, Switzerland. Environ. Sci. Technol. **2008**, *42*, 6369-6377.

[38] So, M.K.; Taniyasu, S.; Yamashita, N.; Giesy, J.P.; Zheng, J.; Fang, Z. Perfluorinated compounds in coastal waters of Hong Kong, South China, and Korea. Environ. Sci. Technol. **2004**, *38*, 4056-4063.

[39] Cahill, T.M.; Seiber, J.N. Regional distribution of trifluoroacetate in surface waters downwind of urban areas in northern California, U.S.A. Environ. Sci. Technol. **2000**, *34*, 2909-2912.

[40] C.E. Wujcik; Cahill, T.M.; Seiber, J.N. Determination of trifluoroacetic acid in 1996-1997 precipitation and surface waters in California and Nevada. Environ. Sci. Technol. **1999**, *33*, 1747-1751.

[41] Morikawa, A.; Kamei, N.; Harada, K.; Inoue, K.; Yoshinaga, T.; Saito, N. The bioconcentration factor of perfluorooctane sulfonate is significantly larger than that of perfluorooctanoate in wild turtles (Trachemys scripta elegans and Chinemys reevesii): An Ai river ecological study in Japan. Ecotoxicol. Environ. Safety. **2006**, *65*, 14-21.

[42] Zushi, Y.; Takeda, T.; Masunaga, S. Existence of nonpoint source of perfluorinated compounds and their loads in the Tsurumi River basin, Japan. Chemosphere **2008**, *71*, 1566-1573.

[43] Yu, J.; Hu, J.; Tanaka, S.; Fujii, S. Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) in sewage treatment plants. Water Res. **2009**, in press, 10.1016/j.watres.2009.03.009.

[44] Nielsen, O.J.; Scott, B.F.; Spencer, C.; Wallington, T.J.; Ball, J.C. Trifluoroacetic acid in ancient freshwater. Atmos. Environ. **2001**, *35*, 2799-2801.

[45] Fujii, S.; Tanaka, S.; Hong Lien, N.; Qiu, Y.; Polprasert, C. New POPs in the water environment: Distribution, bioaccumulation and treatment of perfluorinated compounds - A review paper. J. Wat. Res. Supply Res. Technol. - AQUA **2007**, *56*, 313-326.

28

[46] Frank, H.; Klein, A.; Renschen, D. Environmental trifluoroacetate. Nature **1996**, *382*, 34.

[47] Taniyasu, S.; Kannan, K.; So, M.K.; Gulkowska, A.; Sinclair, E.; Okazawa, T. Analysis of fluorotelomer alcohols, fluorotelomer acids, and short- and long-chain perfluorinated acids in water and biota. J. Chromatogr. A **2005**, *1093*, 89-97.

[48] Alzaga, R.; Bayona, J.M. Determination of perfluorocarboxylic acids in aqueous matrices by ion-pair solid-phase microextraction-in-port derivatization-gas chromatography-negative ion chemical ionization mass spectrometry. J. Chromatogr. A **2004**, *1042*, 155-162.

[49] Tseng, C.; Liu, L.; Chen, C.; Ding, W. Analysis of perfluorooctanesulfonate and related fluorochemicals in water and biological tissue samples by liquid chromatography-ion trap mass spectrometry. J. Chromatogr. A **1996**, *1105*, 119-126.

[50] González-Barreiro, C.; Martínez-Carballo, E.; Sitka, A.; Scharf, S.; Gans, O. Method optimization for determination of selected perfluorinated alkylated substances in water samples. Anal. Bioanal. Chem. **2006**, *386*, 2123-2132.

[51] Moody, C.A.; Kwan, W.C.; Martin, J.W.; Muir, D.C.; Mabury, S.A. Determination of perfluorinated surfactants in surface water samples by two independent analytical techniques: Liquid chromatography/tandem mass spectrometry and ^{19}F NMR. Anal. Chem. **2001**, *73*, 2200-2206.

[52] Weremiuk, A.M.; Gerstmann, S.; Frank, H. Quantitative determination of perfluorinated surfactants in water by LC-ESI-MS/MS. J. Sep. Sci. **2006**, *29*, 2251-2255.

[53] Zhao, X.; Li, J.; Shi, Y.; Cai, Y.; Mou, S.; Jiang, G. Determination of perfluorinated compounds in wastewater and river water samples by mixed hemimicelle-based solid-phase extraction before liquid chromatography-electrospray tandem mass spectrometry detection. J. Chromatogr. A **2007**, *1154*, 52-59.

[54] Emmett, E.A.; Shofer, F.S.; Zhang, H.; Freeman, D.; Desai, C.; Shaw, L.M. Community

exposure to perfluorooctanoate: Relationships between serum concentrations and exposure sources. J. Occup. Environ. Med. **2006**, *48*, 759-770.

[55]   Emmett, E.A.; Zhang, H.; Shofer, F.S.; Freeman, D.; Rodway, N.V.; Desai, C. Community exposure to perfluorooctanoate: Relationships between serum levels and certain health parameters. J. Occup. Environ. Med. **2006**, *48*, 771-779.

[56]   Wilhelm, M.; Hölzer, J.; Dobler, L.; Rauchfuss, K.; Midasch, O.; Kraft, M. Preliminary observations on perfluorinated compounds in plasma samples (1977-2004) of young German adults from an area with perfluorooctanoate-contaminated drinking water. Int. J. Hyg. Environ. Health. **2009**, *212*, 142-145.

[57]   Hölzer, J.; Midasch, O.; Rauchfuss, K.; Kraft, M.; Reupert, R.; Angerer, J. Biomonitoring of perfluorinated compounds in children and adults exposed to perfluorooctanoate-contaminated drinking water. Environ. Health Perspect. **2008**, *116*, 651-657.

[58]   Yamashita, N.; Taniyasu, S.; Petrick, G.; Wei, S.; Gamo, T.; Lam, P.K.S. Perfluorinated acids as novel chemical tracers of global circulation of ocean waters. Chemosphere **2008**, *70*, 1247-1255.

[59]   Takazawa, Y.; Nishino, T.; Sasaki, Y.; Yamashita, H.; Suzuki, N.; Tanabe, K.; Shibata, Y. Occurrence and distribution of perfluorooctane sulfonate and perfluorooctanoic acid in the rivers of Tokyo. Wat. Air Soil Poll. **2009**, in press, 10.1007/s11270-008-9958-7.

[60]   Davis, K.L.; Aucoin, M.D.; Larsen, B.S.; Kaiser, M.A.; Hartten, A.S. Transport of ammonium perfluorooctanoate in environmental media near a fluoropolymer manufacturing facility. Chemosphere **2007**, *67*, 2011-2019.

[61]   Houde, M.; Czub, G.; Small, J.M.; Backus, S.; Wang, X.; Alaee, M. Fractionation and bioaccumulation of perfluorooctane sulfonate (PFOS) isomers in a Lake Ontario food web. Environ Sci Technol. **2008**, *42*, 9397-9403.

[62]   Prevedouros, K.; Cousins, I.T.; Buck, R.C.; Korzeniowski, S.H. Sources, fate and transport of

30

perfluorocarboxylates. Environ. Sci. Technol. **2006**, *40*, 32-44.

[63] Simcik, M.F.; Dorweiler, K.J. Ratio of perfluorochemical concentrations as a tracer of atmospheric deposition to surface waters. Environ. Sci. Technol. **2005**, *39*, 8678-8683.

[64] Murakami, M.; Shinohara, H.; Takada, H. Evaluation of wastewater and street runoff as sources of perfluorinated surfactants (PFSs). Chemosphere **2009**, *74*, 487-493.

[65] Ju, X.; Jin, Y.; Sasaki, K.; Saito, N. Perfluorinated surfactants in surface, subsurface water and microlayer from Dalian Coastal waters in China. Environ. Sci. Technol. **2008**, *42*, 3538-3542.

[66] Wei, S.; Chen, L.Q.; Taniyasu, S.; So, M.K.; Murphy, M.B.; Yamashita, N. Distribution of perfluorinated compounds in surface seawaters between Asia and Antarctica. Mar. Pollut. Bull. **2007**, *54*, 1813-1818.

[67] Miyake, Y.; Yamashita, N.; Rostkowski, P.; So, M.K.; Taniyasu, S.; Lam, P.K.S. Determination of trace levels of total fluorine in water using combustion ion chromatography for fluorine: A mass balance approach to determine individual perfluorinated chemicals in water, J. Chromatogr. A **2007**, *1143*, 98-104.

[68] Kim, S.; Kannan, K. Perfluorinated acids in air, rain, snow, surface runoff, and lakes: relative importance of pathways to contamination of urban lakes. Environ. Sci. Technol. **2007**, *41*, 8328-8334.

[69] Becker, A.M.; Gerstmann, S.; Frank, H. Perfluorooctane surfactants in waste waters, the major source of river pollution. Chemosphere **2008**, *72*, 115-121.

[70] Takagi, S.; Adachi, F.; Miyano, K.; Koizumi, Y.; Tanaka, H.; Mimura, M. Perfluorooctanesulfonate and perfluorooctanoate in raw and treated tap water from Osaka, Japan. Chemosphere **2008**, *72*, 1409-1412.

[71] Yamashita, N.; Kannan, K.; Taniyasu, S.; Horii, Y.; Okazawa, T.; Petrick, G. Analysis of perfluorinated acids at parts-per-quadrillion levels in seawater using liquid chromatography-

tandem mass spectrometry. Environ. Sci. Technol. **2004**, *38*, 5522-5528.

[72]   Yamashita, N.; Kannan, K.; Taniyasu, S.; Horii, Y.; Petrick, G.; Gamo, T. A global survey of
       perfluorinated acids in oceans. Mar. Pollut. Bull. **2005**, *51*, 658-668.

[73]   Cahill, T.M.; Thomas, C.M.; Schwarzbach, S.E.; Seiber, J.N. Accumulation of trifluoroacetate in
       seasonal wetlands in California. Environ. Sci. Technol. **2001**, *35*, 820-825.

[74]   Berg, M.; Muller, S.R.; Muhlemann, J.; Wiedmer, A.; Schwarzenbach, R.P. Concentrations and
       mass fluxes of chloroacetic acids and trifluoroacetic acid in rain and natural waters in
       Switzerland. Environ. Sci. Technol. **2000**, *34*, 2675-2683.

[75]   Lin, A.Y.; Ch, S.; Panchangam, A.; Lo, C. The impact of semiconductor, electronics and
       optoelectronic industries on downstream perfluorinated chemical contamination in Taiwanese
       rivers. Environ. Poll. **2009**, *157*, 1365-1372.

[76]   Tang, C.Y.; Fu, Q.S.; Robertson, A.P.; Criddle, C.S.; Leckie, J.O. Use of reverse osmosis
       membranes to remove perfluorooctane sulfonate (PFOS) from semiconductor wastewater.
       Environ. Sci. Technol. **2006**, *40*, 7343-7349.

[77]   Becker, A.M.; Gerstmann, S.; Frank, H. Perfluorooctanoic acid and perfluorooctane sulfonate in
       the sediment of the Roter Main river, Bayreuth, Germany. Environ. Poll. **2008**, *156*, 818-820.

[78]   Higgins, C.P.; McLeod, P.B.; MacManus-Spencer, L.A.; Luthy, R.G. Bioaccumulation of
       perfluorochemicals in sediments by the aquatic oligochaete Lumbriculus variegatus. Environ.
       Sci. Technol. **2007**, *41*, 4600-4606.

[79]   Nakata, H.; Kannan, K.; Nasu, T.; Cho, H.; Sinclair, E.; Takemurai, A. Perfluorinated
       contaminants in sediments and aquatic organisms collected from shallow water and tidal flat
       areas of the Ariake Sea, Japan: Environmental fate of perfluorooctane sulfonate in aquatic
       ecosystems. Environ. Sci. Technol. **2006**, *40*, 4916-4921.

[80]   Higgins, C.P.; Field, J.A.; Criddle, C.S.; Luthy, R.G. Quantitative determination of

32

perfluorochemicals in sediments and domestic sludge. Environ. Sci. Technol. **2005**, *39*, 3946-3956.

[81]   Scott, B.F.; Spencer, C.; Martin, J.W.; Barra, R.; Bootsma, H.A.; Jones, K.C. Comparison of haloacetic acids in the environment of the Northern and Southern Hemispheres. Environ. Sci. Technol. **2005**, *39*, 8664-8670.

[82]   Lampert, D.J.; Frisch, M.A.; Speitel, J. Removal of perfluorooctanoic acid and perfluorooctane sulfonate from wastewater by ion exchange. Pract. Period. Haz. Tox. Radioact. Waste Mgmt. **2007**, *11*, 60-68.

[83]   Ochoa-Herrera, V.; Sierra-Alvarez, R. Removal of perfluorinated surfactants by sorption onto granular activated carbon, zeolite and sludge. Chemosphere **2008**, *72*, 1588-1593.

[84]   Yu, Q.; Zhang, R.; Deng, S.; Huang, J.; Yu, G. Sorption of perfluorooctane sulfonate and perfluorooctanoate on activated carbons and resin: Kinetic and isotherm study. Water Res. **2009**, *43*, 1150-1158.

[85]   Rayne, S.; Forest, K.; Friesen, K.J. Computational approaches may underestimate pK_a values of longer-chain perfluorinated carboxylic acids: Implications for assessing environmental and biological effects. J. Environ. Sci. Health A **2009**, *44*, 317-326.

[86]   Burns, D.C.; Ellis, D.A.; Li, H.; McMurdo, C.J.; Webster, E. Experimental pK_a determination for perfluorooctanoic acid (PFOA) and the potential impact of pK_a concentration dependence on laboratory-measured partitioning phenomena and environmental modeling. Environ. Sci. Technol. **2008**, *42*, 9283-9288.

[87]   Ellis, D.A.; Webster, E. Response to Comment on "Aerosol enrichment of the surfactant PFO and mediation of the water-air transport of gaseous PFOA". Environ. Sci. Technol. **2009**, *43*, 1234-1235.

[88]   McMurdo, C.J.; Ellis, D.A.; Webster, E.; Butler, J.; Christensen, R.D.; Reid, L.K. Aerosol

33

enrichment of the surfactant PFO and mediation of the water-air transport of gaseous PFOA. Environ. Sci. Technol. **2008**, *42*, 3969-3974.

[89]   Goss, K. The pK$_a$ values of PFOA and other highly fluorinated carboxylic acids. Environ. Sci. Technol. **2008**, *42*, 456-458.

[90]   Goss, K. The pK$_a$ values of PFOA and other highly fluorinated carboxylic acids – Correction. Environ. Sci. Technol. **2008**, *42*, 5032.

[91]   Mader, B.T. Comment on "Aerosol enrichment of the surfactant PFO and mediation of the water-air transport of gaseous PFOA". Environ. Sci. Technol. **2009**, *43*, 1232-1233.

[92]   Barcelona, M.; Atwood, D. Gypsum-organic interactions in the marine environment: Sorption of fatty acids and hydrocarbons. Geochim. Cosmochim. Acta. **1979**, *43*, 47-53.

[93]   Meyers, P.A.; Quinn, J.G. Factors affecting the association of fatty acids with mineral particles in sea water. Geochim. Cosmochim. Acta **1973**, *37*, 1745-1759.

[94]   McNamee, C.E.; Matsumoto, M.; Hartley, P.G.; Mulvaney, P.; Tsujii, Y.; Nakahara, M. Interaction forces and zeta potentials of cationic polyelectrolyte coated silica surfaces in water and in ethanol: Effects of chain length and concentration of perfluorinated anionic surfactants on their binding to the surface. Langmuir **2001**, *17*, 6220-6227.

[95]   Johnson, R.L.; Anschutz, A.J.; Smolen, J.M.; Simcik, M.F.; Penn, R.L. The adsorption of perfluorooctane sulfonate onto sand, clay, and iron oxide surfaces. J. Chem. Engr. Data. **2007**, *52*, 1165-1170.

[96]   Luebker, D.J.; Hansen, K.J.; Bass, N.M.; Butenhoff, J.L.; Seacat, A.M. Interactions of fluorochemicals with rat liver fatty acid-binding protein. Toxicology **2002**, *176*, 175-185.

[97]   Jones, P.D.; Hu, W.; De Coen, W.; Newsted, J.L.; Giesy, J.P. Binding of perfluorinated fatty acids to serum proteins. Environ. Toxicol. Chem. **2003**, *22*, 2639-2649.

[98]   Vanden Heuvel, J.P.; Kuslikis, B.I.; Peterson, R.E. Covalent binding of perfluorinated fatty acids

to proteins in the plasma, liver and testes of rats. Chem. Biol. Interact. **1992**, *82*, 317-328.

[99] Rayne, S.; Forest, K.; Friesen, K.J. Estimated bioconcentration factors (BCFs) for the C_4 through C_8 perfluorinated alkylsulfonic acid (PFSA) and alkylcarboxylic acid (PFCA) congeners. J. Environ. Sci. Health A. **2009**, *44*, in press.

[100] Martin, J.W.; Mabury, S.A.; Solomon, K.R.; Muir, D.C.G. Bioconcentration and tissue distribution of perfluorinated acids in rainbow trout (Oncorhynchus mykiss). Environ. Toxicol. Chem. **2003**, *22*, 196-204.

[101] Martin, J.W.; Mabury, S.A.; Solomon, K.R.; Muir, D.C.G. Dietary accumulation of perfluorinated acids in juvenile rainbow trout (Oncorhynchus mykiss). Environ. Toxicol. Chem. **2003**, *22*, 189-95.

[102] Giesy, J.; Mabury, S.; Martin, J.; Kannan, K.; Jones, P.; Newsted, J. Perfluorinated compounds in the Great Lakes. In *Persistent Organic Pollutants in the Great Lakes*; Springer: New York, NY, USA, 2006; 391-438.

[103] Taniyasu, S.; Kannan, K.; Horii, Y.; Hanari, N.; Yamashita, N. A survey of perfluorooctane sulfonate and related perfluorinated organic compounds in water, fish, birds, and humans from Japan. Environ. Sci. Technol. **2003**, *37*, 2634-2639.

[104] Kannan, K.; Tao, L.; Sinclair, E.; Pastva, S.D.; Jude, D.J.; Giesy, J.P. Perfluorinated compounds in aquatic organisms at various trophic levels in a Great Lakes food chain. Arch. Environ. Contam. Toxicol. **2005**, *48*, 559-566.

[105] Yu, Q.; Deng, S.; Yu, G. Selective removal of perfluorooctane sulfonate from aqueous solution using chitosan-based molecularly imprinted polymer adsorbents. Water Res. **2008**, *42*, 3089-3097.

[106] Higgins, C.P.; Luthy, R.G. Sorption of perfluorinated surfactants on sediments. Environ. Sci. Technol. **2006**, *40*, 7251-7256.

35

[107] Higgins, C.P.; Luthy, R.G. Modeling sorption of anionic surfactants onto sediment materials: An a priori approach for perfluoroalkyl surfactants and linear alkylbenzene sulfonates. Environ. Sci. Technol. **2007**, *41*, 3254-3261.

[108] Goss, K.; Bronner, G. What is so special about the sorption behavior of highly fluorinated compounds? J. Phys. Chem. A **2006**, *110*, 9518-22.

[109] Rayne, S.; Forest, K.; Friesen, K.J. Relative gas-phase free energies for the C_3 through C_8 linear and branched perfluorinated sulfonic acids: Implications for kinetic versus thermodynamic control during synthesis of technical mixtures and predicting congener profile inputs to environmental systems. J. Mol. Struct. THEOCHEM. **2008**, *869*, 81-82.

[110] Rayne, S.; Forest, K.; Friesen, K.J. Extending the semi-empirical PM6 method for carbon oxyacid pK_a prediction to sulfonic acids: Application towards congener-specific estimates for the environmentally and toxicologically relevant C_1 through C_8 perfluoroalkyl derivatives. Nat. Prec. **2009**, http://hdl.handle.net/10101/npre.2009.2922.1.

[111] Rayne, S.; Forest, K.; Friesen, K.J. Linear free energy relationship based estimates for the congener specific relative reductive defluorination rates of perfluorinated alkyl compounds. J. Environ. Sci. Health A **2009**, *9*, in press.

[112] Goss, K.; Bronner, G.; Harner, T.; Hertel, M.; Schmidt, T.C. The partition behavior of fluorotelomer alcohols and olefins. Environ. Sci. Technol. **2006**, *40*, 3572-3577.

[113] Arp, H.P.H.; Niederer, C.; Goss, K. Predicting the partitioning behavior of various highly fluorinated compounds. Environ. Sci. Technol. **2006**, *40*, 7298-7304.

[114] Rayne, S.; Forest, K.; Friesen, K.J. Congener-specific numbering systems for the environmentally relevant C_4 through C_8 perfluorinated homologue groups of alkyl sulfonates, carboxylates, telomer alcohols, olefins, and acids, and their derivatives. J. Environ. Sci. Health A **2008**, *43*, 1391-1401.

36

[115] Rayne, S.; Forest, K. ADME/Tox WEB in silico predictions of longer chain perfluoroalkyl carboxylic acid pK_a values are more accurate than other computational methods. Nat. Prec. **2009**, http://hdl.handle.net/10101/npre.2009.2936.1.

[116] Weininger, D. SMILES, a chemical language and information system. 1. Introduction to methodology and encoding rules. J. Chem. Inf. Comp. Sci. **1988**, *28*, 31-36.

[117] Weininger, D.; Weininger, A.; Weininger, J.L. SMILES. 2. Algorithm for generation of unique SMILES notation. J. Chem. Inf. Comp. Sci. **1989**, *29*, 97-101.

[118] Sparc On-Line Calculator, University of Georgia and the United States Environmental Protection Agency, http://ibmlc2.chem.uga.edu/sparc/.

[119] Carreira, L.; Hilal, S.; Karickhoff, S. Estimation of chemical reactivity parameters and physical properties of organic molecules using SPARC. In *Theoretical and Computational Chemistry: Quantitative Treatment of Solute/Solvent Interactions*; Elsevier Publishers: St. Louis, MO, USA, 1994.

[120] Hilal, S.H.; Karickhoff, S.W.; Carreira, L.A. A rigorous test for SPARC's chemical reactivity models: Estimation of more than 4300 ionization pK_as. Quant. Struct.-Act. Relation. **1995**, *14*, 348-355.

[121] Hilal, S.; Karickhoff, S.; Carreira, L.A. Prediction of the solubility, activity coefficient and liquid/liquid partition coefficient of organic compounds. QSAR Comb. Sci. **2004**, *23*, 709-720.

[122] Hilal, S.; Karickhoff, S.; Carreira, L. Prediction of the vapor pressure boiling point, heat of vaporization and diffusion coefficient of organic compounds. QSAR Comb. Sci. **2003**, *22*, 565-574.

[123] Tetko, I.V. Computing chemistry on the web. Drug Discov. Today. **2005**, *10*, 1497-1500.

[124] On-line Lipophilicity (logP), Water Solubility (LogS) & pK_a Prediction, Virtual Computational Chemistry Laboratory, http://www.vcclab.org/lab/alogps/start.html.

37

[125] Tetko, I.V.; Gasteiger, J.; Todeschini, R.; Mauri, A.; Livingstone, D.; Ertl, P. Virtual computational chemistry laboratory - design and description. J. Comput. Aided Mol. Des. **2005**, *19*, 453-463.

[126] Mannhold, R.; Poda, G.I.; Ostermann, C.; Tetko, I.V. Calculation of molecular lipophilicity: State-of-the-art and comparison of log P methods on more than 96,000 compounds. J. Pharm. Sci. **2009**, *98*, 861-893.

[127] Kah, M.; Brown, C.D. Log D: Lipophilicity for ionisable compounds. Chemosphere **2008**, *72*, 1401-1408.

[128] OECD. *Hazard Assessment of Perfluorooctane Sulfonate (PFOS) and Its Salts.* Organization for Economic Co-operation and Development: Paris, France, 2002.

[129] Costanzo, L.S. *Physiology*; Saunders Elsevier: Philadelphia, USA, 2006.

[130] Shinoda, K.; Hato, M.; Hayashi, T. Physicochemical properties of aqueous solutions of fluorinated surfactants. J. Phys. Chem. **1972**, *76*, 909-914.

[131] Montgomery, J.H. *Groundwater Chemicals Desk Reference*; Lewis: Boca Raton, FL, USA, 2000.

[132] Richey, D.G.; Driscoll, C.T.; Likens, G.E. Soil retention of trifluoroacetate. Environ. Sci. Technol. **1997**, *31*, 1723-1727.

[133] Berger, T.W.; Tartowski, S.L.; Likens, G.E. Trifluoroacetate retention in a northern hardwood forest soil. Environ. Sci. Technol. **1997**, *31*, 1916-1921.

[134] Ryosuke, O.; Shigeki, M. Environmental behavior of perfluorinated surfactants in Tokyo Bay. J. Japan Soc. Wat. Environ. **2006**, *29*, 221-228.

[135] Sposito, G. *The Chemistry of Soils*; Oxford University Press: New York, NY, USA, 1989.

[136] Schultz, M.M.; Higgins, C.P.; Huset, C.A.; Luthy, R.G.; Barofsky, D.F.; Field, J.A. Fluorochemical mass flows in a municipal wastewater treatment facility. Environ. Sci. Technol. **2006**, *40*, 7350-7.

38

[137] Schultz, M.M.; Barofsky, D.F.; Field, J.A. Quantitative determination of fluorinated alkyl substances by large-volume-injection liquid chromatography tandem mass spectrometry-characterization of municipal wastewaters. Environ. Sci. Technol. **2006**, *40*, 289-295.

[138] Guo, R.; Zhou, Q.; Cai, Y.; Jiang, G. Determination of perfluorooctanesulfonate and perfluorooctanoic acid in sewage sludge samples using liquid chromatography/quadrupole time-of-flight mass spectrometry. Talanta **2008**, *75*, 1394-1399.

[139] Loganathan, B.G.; Sajwan, K.S.; Sinclair, E.; Senthil Kumar, K.; Kannan, K. Perfluoroalkyl sulfonates and perfluorocarboxylates in two wastewater treatment facilities in Kentucky and Georgia. Water Res. **2007**, *41*, 4611-4620.

[140] Boulanger, B.; Vargo, J.D.; Schnoor, J.L.; Hornbuckle, K.C. Evaluation of perfluorooctane surfactants in a wastewater treatment system and in a commercial surface protection product. Environ. Sci. Technol. **2005**, *39*, 5524-5530.

[141] Sinclair, E.; Kannan, K. Mass loading and fate of perfluoroalkyl surfactants in wastewater treatment plants. Environ. Sci. Technol. 2006, 40, 1408-1414.

[142] Wang, N.; Szostek, B.; Buck, R.C.; Folsom, P.W.; Sulecki, L.M.; Capka, V. Fluorotelomer alcohol biodegradation - direct evidence that perfluorinated carbon chains breakdown. Environ. Sci. Technol. **2005**, *39*, 7516-7528.

[143] Liu, J.; Lee, L.S.; Nies, L.F.; Nakatsu, C.H.; Turcot, R.F. Biotransformation of 8:2 fluorotelomer alcohol in soil and by soil bacteria isolates. Environ. Sci. Technol. **2007**, *41*, 8024-8030.

[144] Sáez, M.; de Voogt, P.; Parsons, J.R. Persistence of perfluoroalkylated substances in closed bottle tests with municipal sewage sludge. Environ. Sci. Pollut. Res. Int. **2008**, *15*, 472-477.

[145] Parsons, J.R.; Sáez, M.; Dolfing, J.; de Voogt, P. Biodegradation of perfluorinated compounds. Rev. Environ. Contam. Toxicol. **2008**, *196*, 53-71.

[146] Wang, N.; Szostek, B.; Buck, R.C.; Folsom, P.W.; Sulecki, L.M.; Gannon, J.T. 8-2 Fluorotelomer

alcohol aerobic soil biodegradation: Pathways, metabolites, and metabolite yields. Chemosphere **2009**, in press, doi:10.1016/j.chemosphere.2009.01.033.

[147] 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.

[148] Likens, G.E.; Tartowski, S.L.; Berger, T.W.; Richey, D.G.; Driscoll, C.T.; Frank, H.G. Transport and fate of trifluoroacetate in upland forest and wetland ecosystems. Proc. Natl. Acad. Sci. USA. **1997**, *94*, 4499-4503.

[149] 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.

[150] Rayne, S.; Friesen, K.J. Contaminant trapping behind large dams: A mini-review. Nat. Prec. **2009**, http://hdl.handle.net/10101/npre.2009.2965.1.

[151] Karickhoff, S.W.; Brown, D.S.; Scott, T.A. Sorption of hydrophobic pollutants on natural sediments. Water Res. **1979**, *13*, 241-248.

[152] Karickhoff, S.W. Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils. Chemosphere **1981**, *10*, 833-846.

[153] Sabljic, A.; Güsten, H.; Verhaar, H.; Hermens, J. QSAR modelling of soil sorption: Improvements and systematics of log K_{OC} vs. log K_{OW} correlations. Chemosphere **1995**, *31*, 4489-4514.

[154] Seth, R.; Mackay, D.; Muncke, J. Estimating the organic carbon partition coefficient and its variability for hydrophobic chemicals. Environ. Sci. Technol. **1999**, *33*, 2390-2394.

[155] Franco, A.; Trapp, S. Estimation of the soil-water partition coefficient normalized to organic carbon for ionizable organic chemicals. Environ. Toxicol. Chem. **2008**, *27*, 1995-2004.

FIGURE CAPTIONS

Figure 1. General structures of perfluoroalkyl sulfonic acids (PFSAs) and carboxylic acids (PFCAs).

Figure 2. Correlations between SPARC calculated $\log_{10} K_{ow}$ (circles) and $D_{octanol}$ (squares) and ALOGPS calculated $\log_{10} P$ (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} PFSAs. Error bars are from the literature K_{oc} source.[106]

Figure 3. Estimated congener specific K_{oc} values for the C_1 through C_8 PFCAs using the (a) SPARC calculated K_{ow}, (b) SPARC calculated $D_{octanol}$, (b) , and (c) ALOGPS calculated $\log_{10} P$ values. Inset shows estimated K_{oc} values for the C_8 PFCAs using the ALOGPS method.

Figure 4. Estimated congener specific K_{oc} values for the C_1 through C_8 PFSAs using the (a) SPARC calculated K_{ow}, (b) SPARC calculated $D_{octanol}$, (b) , and (c) ALOGPS calculated $\log_{10} P$ values. Inset shows estimated K_{oc} values for the C_8 PFSAs using the ALOGPS method.

Figure 5. Ground water mobility domains based on K_d (L kg^{-1}) values [135] for selected PFCA and PFSA congeners across a range of K_{oc} and soil organic carbon content (f_{oc}) values.

41

Table 1. Application of established literature approaches for estimating organic carbon normalized soil and sediment-water

partioning coefficients (K_{oc}) from K_{ow} values towards representative PFA congeners.

	TFA		n-PFOA		n-PFOS	
Laboratory and field experimental range	0.25 to 1.77		1.1 to 3.2		1.6 to 4.8	
Higgins and Luthy (2006)[a] experimental	n/a		2.11		2.68	
	$K_{ow,SPARC}$	P_{ALOGPS}	$K_{ow,SPARC}$	P_{ALOGPS}	$K_{ow,SPARC}$	P_{ALOGPS}
Current study QSAR	0.13	-2.03	2.09	2.12	2.68	2.68
Karickhoff et al. (1979)[b]	1.12	0.85	3.94	2.70	2.94	2.67
Karickhoff et al. (1981)[c]	0.73	0.55	2.57	1.76	1.91	1.74
Sabljic et al. (1995) – organic acids[d]	1.39	1.13	4.08	2.89	3.12	2.86
Sabljic et al. (1995) – organic acids and alcohols[d]	1.34	1.13	3.44	2.52	2.69	2.49
Seth et al. (1999)[e]	0.62	0.47	2.19	1.50	1.63	1.48
Franco and Trapp (2008) – strong acids ($pK_a<4$)[f]	1.74	1.69	2.22	2.01	2.05	2.01

[a] ref. [106]. [b] ref. [151]. [c] ref. [152]. [d] ref. [153] [e] ref. [154]. [f] ref. [155].

42

F₂ₙ₊₁Cₙ structures:

$C_x; x = n$
PFSAs

$C_x; x = n+1$
PFCAs

Fig. 1

Fig. 2

Fig. 3

45

Fig. 4

46

Fig. 5