SUBURFACE FATE AND TRANSPORT OF POLY- AND PERFLUOROALKYL SUBSTANCES

by

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ABSTRACT

Poly and perfluoroalkyl substances (PFASs) are fluorinated chemicals that have been the focus of many recent studies because of their widespread use, persistence, bioaccumulative potential, toxicity, and distribution in the environment. Because of their unique properties, PFASs are used in a wide variety of products including food paper packaging products, stain repellants, nonstick coatings, and fire fighting foams. Releases of PFASs to the environment and impact to groundwater has occurred through land application of biosolids as well as through use of fire fighting foams known as aqueous film-forming foam (AFFF). Because of the potential risk associated with exposure to these compounds, it is important to understand their subsurface fate and transport.

The present study investigated the occurrence and fate of PFASs from land-applied municipal biosolids by evaluating the levels, mass balance, desorption, and transport of perfluoroalkyl acids (PFAAs) and PFAA precursors in soils receiving application of municipal biosolids at various loading rates. PFOS was the dominant PFAS in both biosolids and biosolids-amended soil. Concentrations of PFASs in soil increased linearly with increasing biosolids loading rate, enabling development of a model for predicting PFAS soil levels based on cumulative biosolids loading rates. Mass balance calculations showed a loss of PFAA precursors in soil relative to the mass applied in biosolids, suggesting precursor transformation. Laboratory desorption experiments indicated that the leaching potential of PFASs decreases with increasing chain length and that previously derived organic-carbon normalized partition coefficients may not be accurate predictors of the desorption of long-chain PFAAs from biosolids-amended soils. Trace levels of PFAAs were also detected in soil cores from biosolids-amended soils to depths of 120 cm, suggesting potential movement of these compounds within the soil profile over time and confirming the higher transport potential for short-chain PFAAs in soils amended with municipal biosolids.

This study also investigated PFAA sorption to multiple soils in the presence of nonaqueous phase liquid (NAPL) and nonfluorinated AFFF surfactants. Sorption of small-chain PFAAs did not follow the chain-length dependent trend observed for longer chain-length PFAAs. NAPL and nonfluorinated AFFF surfactants all had varying impacts on sorption on longer chain (>6 CF_2 groups) PFAAs. The primary impact of NAPL was observed in low f_{oc} soil where Freundlich n-values increased when NAPL was present. Impacts of nonfluorinated AFFF surfactants varied with surfactant and soil. In general, the anionic surfactant sodium decyl sulfate (SDS) had chain-length dependent impacts on sorption. Increases in sorption were noted for the smallest compounds and these increases diminished in magnitude with increasing chain length. An amphoteric surfactant, n,n-dimethyldodecylamine n-oxide(AO), significantly increased sorption for the longer chain PFAAs in a positively charged soil. Changes in sorption caused by SDS and AO may be due to mixed hemimicelle formation, competitive sorption, or changes to PFAA solubility. Short-chain PFAA sorption generally increased in the presence of NAPL, SDS, and AO. These results demonstrate detailed site-specific information will likely be needed to model PFAA transport at AFFF-impacted sites.

Finally, column studies in multiple solid phases were used to understand 1-D advective transport of PFAAs with respect to the equilibrium batch sorption data. Overall, behavior was chain-length dependent, though short chain PFAA behavior was again notable, confirming equilibrium studies. Comparison of equilibrium and column sorption results showed the potential for nonequilibrium behavior, particularly in soils with appreciable organic carbon content and for longer chain PFAAs. Nonequilibrium was confirmed to be the result of rate-limited sorption. Mass transfer coefficients were fitted from the data and found to vary with organic carbon content. This may be due to intraparticle diffusion into the organic matter matrix .

This study initiates an understanding of the subsurface fate and transport of PFASs at the equilibrium and 1-dimensional scales. Additional research is needed to understand how

these results translate to larger scales towards the end goal of reliable site characterization and remediation of PFASs.

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Surface area of vial	A_v
Concentration of NAPL	C_{NAPL}
Solid phase concentration	C_s
Solid phase concentration of type 1 (equilibrium) sites	C_s^e
Solid phase concentration of type 2 (kinetic) sites	C_s^k
Aqueous phase concentration	C_w
Relative concentration	C/C_0
Fraction of type 1 (equilibrium)sorption sites	f
Fraction of NAPL in soil	f_{NAPL}
Fraction of organic carbon	f_{oc}
First order mass transfer coefficient	k
Solid water distribution coefficient	K_d
Solid water distribution coefficient, column	K_{dcol}
Solid water distribution coefficient, batch equilibrium	K_{deq}
Freundlich sorption coefficient	K_f
NAPL-water partitioning coefficient	K_{NAPL}
Organic carbon normalized distribution coefficient	K_{oc}
Mass of soil in the reactor	M_s
Mass of analyte in solid phase before desorption	m_s^0
Total mass	M_T

Mass of analyte lost to the desorption reactor vial	m_v
Mass of analyte in the aqueous phase	M_w
Mass of analyte in the aqueous phase at equilibrium	m_w
Freundlich isotherm linearity	n
Retardation factor	R
Ratio of vial surface area to aqueous phase	R_{av}
Volume of the aqueous phase	V_w
Porosity	θ
Soil bulk density	ρ_b
Surface area normalized concentration of analyte on the vial	σ_{av}

LIST OF ABBREVIATIONS

1H,1H,2H,2H-perfluorooctane sulfonate	6:2 FtSA
1H,1H,2H,2Hpefluorodecane sulfonate	8:2 FtSA
Aqueous film-forming foam	AFFF
Artificial groundwater	AGW
ammonium perfluorooctanoate	APFOA
n,n-dimethyldodecylamine n-oxide	AO
Breakthrough curve	BTC
Critical micelle concentration	CMC
Critical separate phase concentration	CSPC
Cetyltrimethylammonium bromide	CTAB
2-(N-ethylperfluorooctane sulfonamido) acetic acid	EtFOSAA
Fire protection training area	FPTA
Flourotelomer alcohol	FTOH
Liquid chromatography tandem mass spectrometry	LC-MS/MS
Lithium perfluorooctane sulfonate	LiPFOS
Limit of quantitation	LOQ
Metropolitan Water Reclamation District of Greater Chicago	MDRDGC
Multiple reaction monitoring	MRM
Non-aqueous phase liquid	NAPL
Polycyclic aromatic hydrocarbon	PAH

Polychlorinated biphenyl	PCB
Perfluoroalkyl acid	PFAA
Poly- and perfluoroalkyl substance	PFAS
Perfluorobutanoic acid	PFBA
Perfluorobutane sulfonate	PFBS
Perfluoroalkyl carboxylates	PFCA
Perfluorodecanoic acid	PFDA
Perfluorododecanoic acid	PFDoA
Perfluorodecane sulfonate	PFDS
Perfluoroheptanoc acid	PFHpA
Perfluoroheptane sulfonate	PFHpS
Perfluorohexanoic acid	PFHxA
Perfluorohexane sulfonate	PFHxS
Perfluorononanoic acid	PFNA
Perfluorooctanoic acid	PFOA
Perfluorooctane sulfonate	PFOS
Perfluoropentanoic acid	PFPeA
Acid dissociation constant	pK_a
Perfluoroalkane sulfonate	PFSA
Perfluoroundecanoic acid	PFUnA
Provisional health advisory	PHA
Partially miscible organic solvent	PMOS
2-(N-methylperfluorooctane sulfonamido) acetic acid	MeFOSAA

Sodium dodecylbenzene sulfonate	SDBS
Sodium decyl sulfate	SDS
Trichloroethylene	TCE

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CHAPTER 1

INTRODUCTION AND BACKGROUND

Poly- and perfluoroalkyl substances (PFASs) are fluorinated chemicals that have been the focus of many recent studies because of their widespread use, persistence, bioaccumulative potential, toxicity, and distribution in the environment [1, 2]. PFASs in this study consist primarily of an acidic functional group attached to a saturated fluorocarbon tail. The carbon-fluorine bond in the tail is the strongest known covalent bond and lends these compounds unique characteristics including chemical and thermal stability, hydrophobicity, and lipophobicity. They therefore have a wide variety of uses in food paper packaging products, stain repellants, nonstick coatings, and fire fighting foams [3]. Because of growing concerns about the potential exposure to PFASs in soil and groundwater, provisional health advisories and residential soil screening guidance values were developed [4, 5] by the U.S. Environmental Protection Agency (USEPA) for two PFASs. Drinking water provisional health advisories for perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS) are 0.4 $\mu g/L$ and 0.2$\mu g/L$, respectively. In addition, EPA's residential soil screening guidance values for PFOA and PFOS are 16,000 $\mu g/kg$ and 6,000 $\mu g/kg$, respectively.

Because of their widespread use, PFASs have been detected in the influent, effluent, and sludge (biosolids) at municipal wastewater treatment plants (WWTPs) [6–8]. In addition to the terminal "endproduct" perfluoroalkyl acids (PFAAs), biosolids also contain a variety of PFASs that could be transformed to PFAAs over time [7, 9]. As of 2004, 7.2 million dry tons of biosolids were generated in the U.S. each year, and approximately 49% were applied to agricultural lands as fertilizer [10]. Though the land application of biosolids in the U.S. is regulated, no regulations are currently in place with respect to PFASs in biosolids. In Decatur, Alabama, industrially-contaminated biosolids were applied to land used for grazing cattle and growing crops, resulting in PFAS detections in soil, beef, grass, and groundwater from the biosolids-amended fields [11, 12]. While PFASs are known to be present in municipal biosolids [7], it remains unclear whether the application of typical municipal biosolids to agricultural soil could pose any potential PFAS-related risks for human and ecological health.

PFASs have also been released to the environment through use of fire fighting foams known as aqueous film-forming foams (AFFF). Used in fighting fuel fires, AFFF is often utilized by fire-fighting facilities, the hydrocarbon industry, and the military [13]. Repeat use of AFFF to extinguish fires at fire protection training areas (FPTAs) has led to the presence of PFAAs in groundwater at $\mu g/L$ to mg/L levels [14–16]. AFFF formulations often include solvents and both fluorinated and hydrocarbon surfactants [14, 17]. Transport of PFAAs in groundwater at FPTAs may thus be impacted by other AFFF components and by co-contaminants released during training exercises, such as fuels or chlorinated solvents, which may exist as non-aqueous phase liquids (NAPLs). Previous work has investigated sorption of PFOS to NAPL-contaminated soil and in the presence of hydrocarbon surfactants [18, 19]. To the best of our knowledge, behavior of multiple PFAAs in the presence of NAPL or hydrocarbon surfactants specific to AFFF has not been documented.

1.1 Objectives

The objectives of this work was to determine the subsurface transport potential of PFASs by studying the occurence and desorption in biosolids-ammended soils, and sorption and column transport under conditions specific to AFFF-impacted facilities. Specifically, a preliminary study of PFAS transport potential was completed using biosolids, biosolids-ammended soils, and soil cores (Chapter 2). Batch equilibrium PFAS studies were completed to investigate sorption in mixed PFAA and co-contaminant systems relevant to AFFF-impacted facilities (Chapter 3). Finally, to further the understanding of transport behavior of PFASs in groundwater, advective 1-dimensional (1-D) column transport experiments were conducted and the results compared to previous equilibrium sorption studies (Chapter 4).

1.2 Background

The following section provides background and research hypotheses related to this work.

1.2.1 Target Compounds

Target PFASs included in this study consisted primarily of perfluoroalkyl carboxylates (PFCAs) and perfluoroalkane sulfonates (PFSAs) (Table 1.1). These compounds consist of a saturated fluorocarbon tail and either a carboxylic acid (PFCA) or sulfonate (PFSA) head group. The acid-dissociation constants (pK_a) of PFASs is the subject of some debate [20, 21]; however, they are generally accepted to be low (pKa<3.8). Because all experiments in this work were conducted at circumneutral pH, the neutral form of the PFASs was assumed to be negligible. As mentioned, PFASs have unique characteristics such as a fluorocarbon tail that is both hydro- and lipophobic. These characteristics are due in part to the characteristics of fluorine and the resulting strength of the C-F bond. Fluorine shields the carbon, and the bond is not very polarizable; however, fluorine is a very small atom and therefore shields the carbon without much steric stress [22].

PFAS nomenclature used in this dissertation follows the guidance of a recently issued paper providing a classification and terminology scheme to make references to PFASs consistent [23]. PFAS is a general term referring to perfluoroalkyl and polyfluoroalkyl substances (PFASs). PFAA refers specifically to the perfluoroalkyl acids on which much of this study focused. Exceptions include the consideration of PFAA precursors 2-(N-methylperfluorooctane sulfonamido) acetic acid (MeFOSAA) and 2-(N-ethylperfluorooctane sulfonamido) acetic acid (EtFOSAA) in Chapter 2. Additionally, PFAA precursors, 1H,1H,2H,2H-perfluorooctane sulfonate (6:2 FtSA) and 1H,1H,2H,2Hpefluorodecane sulfonate (8:2 FtSA) were utilized in spiking solutions in Ch3, though poor analytical results preculded inclusion of the results for data anlaysis. Finally, Chapter 2 was published prior to publication of the guidance on PFAS terminology, so different acronyms were included in the original publication (e.g. perfluorochemical (PFC) in lieu of PFAS), though it has been updated to use the more recent guidance in this dissertation.

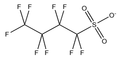
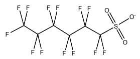
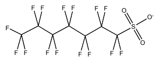
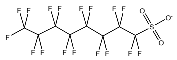
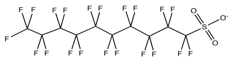
1.2.2 Occurrence in Biosoids and Biosolids Amended Soils

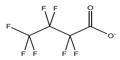
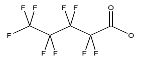
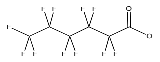
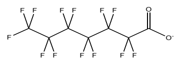
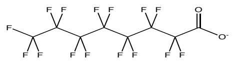
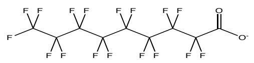
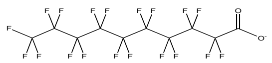
Previous work has detected PFASs in both industrial and municipal biosolids [7, 24, 25]. In municipal biosolids, total concentrations of PFASs ranged from 176 to 3390 ng/g. The dominant PFASs detected were N-EtFOSAA acetic acid (21.3-544 ng/g), which is thought to be a PFOS precursor, and PFOS (14.4-2610 ng/g) [7]. Samples of biosolids amended soils from a site receiving industrial biosolids found elevated concentrations of PFASs including PFDA ($\leq$990 ng/g), perfluorododecanoic acid ($\leq$530 ng/g), PFOA ($\leq$320 ng/g), and PFOS ($\leq$410 ng/g) [24]. PFAS measurements with depth at this facility reflected the potential for lower mobility of longer chain compounds as well as the transformation of fluorotelomer alcohols into PFCAs [24, 25]. These studies show the potential for biosolids as a source of PFASs to the environment and that there is the continued potential for formation of PFCAs and PFSAs once biosolids are land applied.

1.2.3 Occurrence in AFFF-impacted Groundwater

AFFF formulations are proprietary and may vary within and between manufacturers; however, they are typically composed of a solvent, fluorinated surfactants, and hydrocarbon surfactants [13]. AFFF are often used to extinguish hydrocarbon-fuel fires, so it is not surprising that AFFF components and/or transformation products have been detected in groundwater at fire training facilities [14–16]. Concentrations of various PFASs have been detected in groundwater at AFFF-contaminated sites in concentrations as high as 15 mg/L [14–16]. Concentrations of PFASs in groundwater were measured at Naval Air Station Fallon (Nevada), Tyndall Air Force Base (Florida) and Wurthsmith Air Force Base (Michigan). Overall, 1H,1H,2H,2H-perfluorooctane sulfonate (6:2 FtS), a fluorotelomer sulfonate (FtS) was detected at the highest concentration, followed by PFOA. At Naval Air Station Fallon, PFCAs comprised 75% of total PFASs detected at the site, whereas 82% of total PFASs detected at Tyndall Air Force Base were comprised of FtS.

Table 1.1: Target PFASs included in this study

Compound	**Abbreviation**	**Structure**	**Properties**
PERFLUOROALKYL SULFONATES (PFSAs)			
Perfluorobutane sulfonate	PFBS		Mol. Wt.: 299.09 S_w: N/A CMC: N/A K_{oc}: N/A
Perfluorohexane sulfonate	PFHxS		Mol. Wt.: 399.11 S_w: N/A CMC: N/A K_{oc}: N/A
Perfluoroheptane sulfonate	PFHpS		Mol. Wt.: 449.11 S_w: N/A CMC: 7859 mg/L[22] K_{oc}: N/A
Perfluorooctane sulfonate	PFOS		Mol. Wt.: 499.12 S_w: N/A CMC: 3781 mg/L[22] K_{oc}: 2.57[26]
Perfluorodecane sulfonate	PFDS		Mol. Wt.: 599.14 S_w: N/A CMC: N/A K_{oc}: 3.53[26]

PERFLUOROCARBOXYLIC ACIDS (PFCAs)			
Perfluorobutanoic acid	PFBA		Mol. Wt.: 213.03 S_w: Miscible CMC: 156222 mg/L[22] K_{oc}: N/A
Perfluoropentanoic acid	PFPeA		Mol. Wt.: 263.04 S_w: N/A CMC: 139411$mg/$[22] K_{oc}: N/A
Perfluorohexanoic acid	PFHxA		Mol. Wt.: 313.05 S_w: N/A CMC: 20818 mg/L[22] K_{oc}: N/A
Perfluoroheptanoic acid	PFHpA		Mol. Wt.: 363.05 S_w: N/A CMC: 18153 mg/L[22] K_{oc}: N/A
Perfluorooctanoic acid	PFOA		Mol. Wt.: 413.06 S_w: N/A CMC: 3800 mg/L[22] K_{oc}: 2.06[26]
Perfluorononanoic acid	PFNA		Mol. Wt.: 463.07 S_w: N/A CMC: 1945 mg/L[22] K_{oc}:2.39[26]
Perfluorodecanoic acid	PFDA		Mol. Wt.: 513.08 S_w: 5131 mg/L[27] CMC: 431 mg/L[22] K_{oc}:2.76[26]

These results indicate that PFASs are present at these sites as the result of AFFF application and that groundwater PFAS concentrations are present as high as the parts per million range.

1.2.4 PFAS Sorption and Retardation

Previous work has been completed looking at the sorption of PFASs to sediment (Table 1.1) [26]. These studies have found that sorption is influenced by both sorbent properties, sorbate properties, and solution chemistry [26]. Higgins and Luthy (2006) found that the primary sorbent factor influencing sorption is the f_{oc}, and this finding was confirmed by subsequent studies [28]. Sorbate factors such as the perfluoroalkyl tail length and head group also influence sorption with distribution coefficients (K_d) increasing 0.5-0.6 log units with each addition of a CF_2 moiety to the perfluoroalkyl tail and K_d values for PFSAs approximately 1.7 times higher than values for PFCAs of the same chain length [26]. Finally, Higgins and Luthy (2006) also found that sorption increased with increasing $[Ca^{2+}]$ and decreasing pH. The latter indicates that sorption is at least partially due to electrostatic interactions, while the chain-length dependence of the PFAS sorption, evident in the organic carbon-normalized distribution coefficients (K_{oc}) measured in previous work (Table 1.1), suggests that hydrophobic interactions play a role as well [26].

Studies of PFAS sorption to minerals also support a combination of hydrophobic and electrostatic interactions [28, 29]. Sorption of PFOS to goethite was studied with varying pH and ionic strength. Sorption to goethite was found to increase with decreasing pH, consistent with electrostatic interactions [29]. The point of zero charge (pH_{pzc}) for goethite in previous work was pH 9.4. At pH values of seven to nine, an increase in [NaCl] lead to an increase in sorption despite the fact that the increasing ionic strength would cause a double layer compression effect [29]. This supports non-electrostatic interactions of PFAS sorption to goethite, such as hydrophobic interactions [29]. PFOS sorption to silica surfaces was found to be only weakly dependent on pH and ionic strength [29]. This is likely an indicator of the importance of mechanisms outside of electrostatic forces, potentially hydrophobic interactions between the PFOS tail and the silica surface [29]. At a pH 3, sorption of PFOS to silica increased and also showed a positive correlation with ionic strength. This may indicate that at lower pH values, sorption of PFOS to silica began to include more electrostatic interactions [29]. In addition to indicating that both hydrophobic and electrostatic interactions play a role in PFAS sorption, these data also suggest that both the organic carbon and mineral content of the sorbent could be important to PFAS transport.

Equilibrium, laboratory sorption experiments indicate that sorption of PFASs is chain-length dependent, and this trend is supported by observations of PFAS leaching with depth in soils amended with industrial biosolids. Washington et al. (2010) studied PFAS concentrations from the surface to 150 cm depth in a field in Decatur, Alabama that had been amended with industrially contaminated biosolids. These biosolids were generated at a wastewater treatment facility that had received waste streams from industries generating and using fluorochemicals [24]. This study found preferential leaching of short-chain PFASs, suggesting that there is less retardation of short-chain PFASs in the subsurface. These results are also supported by groundwater PFAS concentrations at AFFF-contaminated sites. Moody and Field (1999) measured PFCA concentrations in groundwater in the vicinity of a fire training area at Naval Air Station Fallon. They found that from the source zone to the outer edge of the plume, short-chain PFCA concentrations decreased by as much as 85%, whereas long-chain PFCA concentrations decreased by as much as 93% [14].

1.2.5 Impacts of Co-Contaminants on PFAS Sorption

Because AFFF are used to extinguish hydrocarbon fuel fires, PFAS transport at FPTAs may also be impacted by co-contaminants such as nonfluorinated AFFF components, hydrocarbon fuel components, and chlorinated solvents [13], some of which may be present as NAPL. In the presence of co-contaminants, complex factors have the potential to impact PFAS transport, including changes in sorption due to dissolved phase co-contaminants and changes in sorption due to the presence of NAPLs.

The presence of dissolved phase co-contaminants may impact PFAS transport in various ways. Dissolved phase organic co-contaminants may lead to cosolvency effects thereby decreasing sorption and retardation of target compounds [30–32]. This effect, known as cosolvency, is thought to be limited to situations when cosolvents include completely miscible organic solvents (e.g. methanol and acetone) or polar partially miscible organic solvents (PMOS; e.g. o-cresol and nitrobenzene) [31, 32]. In addition to cosolvency, it is possible for cosolutes to impact target compound transport if they compete for the same sorption sites as the target compound [33].

Studies of PFAS sorption in the presence of dissolved phase co-contaminants are extremely limited. Sorption of PFOS in the presence of both a cationic and anionic surfactant has been studied [19]. In the presence of cetyltrimethylammonium bromide (CTAB), a cationic surfactant, sorption of PFOS increased. It is likely that the positive, ammonium end of CTAB has an electrostatic interaction with negatively charged soil, leaving the hydrophobic tail of CTAB to act as a sink for PFOS. The effect of sodium dodecylbenzene sulfonate (SDBS), an anionic surfactant, was variable. SDBS caused increased sorption of PFOS at low SDBS concentrations but caused decreased sorption at higher SDBS concentrations. In addition to impacting sorption, SDBS led to an increase in PFOS solubility, and it is likely that the latter effect was dominant at higher SDBS concentrations. How other surfactants impact PFAS sorption may be important as AFFF contain both fluorinated and hydrocarbon surfactants. Finally, researchers have looked at the impact of PFASs on the mobility of polycyclic aromatic hydrocarbons (PAHs) [40,41]. The mobility of compounds other than PFASs is outside the scope of this study; however it is worthy to note that both ammonium perfluorooctanoate (APFOA) and lithium perfluorooctane sulfonate (LiPFOS) increased the solubilities of naphthalene, phenanthrene, and pyrene by as much as 20 times the aqueous solubility [34, 35]. The studies summarized above clearly indicate that the presence of dissolved co-contaminants can both increase and decrease subsurface transport of PFASs.

It is possible that NAPL will be present and may impact PFAS transport at AFFF contaminated sites. NAPL has been documented to act as as sink for some organic contaminant [36]. How NAPL may impact PFAS transport is, however, unclear. PFASs are surfactants and may partition to the NAPL-water interface and increase PFAS sorption. Conversely, because PFAS tails are both hydro- and lipophobic sorption to NAPL may not be favorable, and NAPL may block PFASs from soil sorbent sites. Only one study has been completed that looks at the impact of NAPL on PFOS transport. In this study, researchers studied sorption of PFOS to soil, soil contaminated with crude oil, and black carbon under varying solution conditions [18]. They concluded that the presence of NAPL increased sorption of PFOS, that sorption of PFOS to crude oil was stronger than that to soil, and that sorption of PFOS to black carbon was not stronger than that observed with other forms of organic carbon. However, these experiments were conducted with only one PFAS, and sorption experiments were limited to water-NAPL-soil systems without any separate consideration of water-NAPL systems.

1.2.6 Hypotheses

1. **Hypothesis 1: A combination of laboratory and field studies of soils amended with municipal biosolids will demonstrate chain length-dependent transport potential of PFASs.**

   Concentrations of PFCAs and PFSAs measured in municipal biosolids range from 5 to 152 ng/g and 55 to 3370 ng/g, respectively [7]. A large percentage of biosolids generated in the U.S. are land-applied as fertilizer; furthermore, studies have established the transport potential of PFASs from industrial biosolids and shown subsequent impact to drinking and surface water [24]. It is therefore important to establish the risk associated with the potential fate and transport of PFASs in typical, municipal biosolids. Studies of the leaching of biosolids-borne PFASs can also help to establish the transport potential of these compounds from other sources, such as AFFF-impacted sites.

If PFASs, including both PFAAs and PFAA precursors, in typical municipal biosolids are transferred to biosolids-amended soils, their environmental fate will depend on several processes. PFAA precursors may be transformed to PFAAs over time, while the PFAAs themselves may either accumulate in the surface soil and/or leach into the subsurface. The potential accumulation and/or leaching of PFASs in soils amended with typical municipal biosolids has not been documented. Additionally, there is no prior work documenting transformation of PFAA precursors in soils amended with typical municipal biosolids, though transformation of fluorotelomer alcohols in soils receiving industrially-contaminated biosolids has been documented [25]. Furthermore, there are no studies investigating leaching of PFAAs or PFAA precursors in soils amended with typical municipal biosolids. Previous work with industrially-contaminated biosolids has suggested the potential for PFAA leaching, particularly for shorter chained PFAAs [24]. Finally, equilibrium partitioning can provide an idea of the leaching potential of organic contaminants. Relevant work has been done investigating equilibrium partitioning of PFASs in spiked sediment-water systems [7], and these data suggest a greater leaching potential for short-chain PFAAs under equilibrium conditions. However, previous work with other organic chemicals in biosolids [37] suggests soil-water partitioning coefficients derived from adsorption experiments do not accurately predict desorption behavior from biosolids, particularly under field conditions. For example, the desorptive release of biosolids-borne chemicals such as triclosan and triclocarban is often incomplete. To this end, desorption data from laboratory batch experiments using field samples of biosolids-amended soils were completed and coupled with evaluation of PFAS concentrations in biosolids-amended soil cores to evaluate the fate and transport of PFASs applied to soils via municipal biosolids.

2. **Hypothesis 2: The sorption of PFASs to soil and aquifer material will behave consistently with that previously observed in sediment at low concentrations (ng/L-$\mu g/L$) [26]; however sorption in the $\mu g/L$-mg/L range will be**

increasingly nonlinear. Overall, transport will be chain-length dependent with transport potential inversely related to PFAS chain length.

Previous work on PFAS sorption has been completed at various concentration ranges with sediment, soil, and minerals and has observed a variety of trends with sorbent properties, solution chemistry, and PFAS structure . It is apparent from previous work that the majority of studies have focused on more dilute PFAS concentrations in the ng/L to $\mu g/L$ range. Additionally, with the exception of one study [26], previous research has focused only on PFOS without including additional PFASs [18, 28, 29]. A variety of PFASs have been measured in groundwater at AFFF-contaminated sites at concentrations as high as 15 mg/L [14–16]. Therefore, to fully understand transport of PFASs at AFFF-contaminated sites it will be necessary to understand equilibrium sorption of a range of PFASs at concentrations higher than previously studied.

Due to their low pKa, PFAAs are negatively charged at ambient pH [20], suggesting that electrostatic interactions with positively charged surfaces would play a role in PFAA sorption. Nonetheless, studies at concentrations of ng/L to $\mu g/L$ have shown that hydrophobic interactions with sorbent surfaces may play a more dominant role. Higgins and Luthy (2006) showed that organic carbon content was the primary sorbent factor influencing sorption of PFASs, and PFAS sorption increased with increasing chain length. Tang et al. (2010) found that sorption of PFOS to negatively charged silica surfaces was greater than that to positively charged goethite. Collectively, these results suggest the dominance of hydrophobic interactions in PFAS sorption, consistent with other organic compounds that are anionic at circumneutral pH [38]. In most cases, sorption of PFASs to soil, mineral, and sediment phases was found to be nonlinear [18, 26, 28, 29]. For example, sorption isotherms of PFASs to sediment that were fit with the Freundlich isotherm had n values ranging from 0.75 – 1 [26]. Though the hydrophobic interactions are thought to dominate PFASs at this concentration range, electrostatic interactions are also thought to play a role. Solution chemistry, such as pH and ionic strength, has been found to impact sorption of PFASs to sediment, soil, and mineral surfaces, which is likely due to the changes these factors elicit on electrostatic interactions between PFASs and solid surfaces [18, 26, 28, 29]. The current study tested sorptive behavior of PFAAs in single-PFAA vs. mixed-PFAA systems to examine competitive effects and at concentrations relevant to AFFF-impacted sites.

3. **Hypothesis 3: Sorption of PFASs will increase in the presence of NAPL, and the tendency of dissolved phase co-contaminants to impact PFAS transport through competitive sorption will vary based on the cosolute and sorbent type. Cosolvency effects will not be observed for the co-contaminants proposed for this research.**

   Additional contaminants including jet fuel and trichloroethylene may also be present in conjunction with PFASs at AFFF-contaminated sites [13]. Therefore, to fully understand transport of PFASs at AFFF-contaminated sites it will be necessary to understand sorption of PFASs in the presence of both NAPL and dissolved phase co-contaminants. A previous study of PFOS sorption to oil-contaminated soil concluded that PFOS sorption to oil-contaminated soil was increased over that to uncontaminated soil, suggesting that NAPL may increase sorption and therefore retardation of PFASs [18]. However, these results need to be extended to other PFAAs and other forms of NAPL before definitive conclusions can be drawn.

   The limited previous studies that are available for PFASs in the presence of dissolved phase co-contaminants show that sorption can both increase and decrease as a result of additional solutes [19]. As previously mentioned, changes in PFAS transport in the presence of co-solutes may result from competitive sorption. Such effects will differ based on the co-solute present. Competitive sorption is also thought to depend on the sorbent type and sorption mechanism of the co-solute vs. PFASs. For example, researchers have found that two solutes may not exhibit competition in a sorbent to which sorption of each solute is linear, whereas the same two solutes will exhibit competition in a sorbent to which sorption of the solutes is nonlinear [39]. Even if sorption of two solutes to a sorbent is nonlinear, they still may not compete against each other if they are using different types of mechanisms or sorption to different sites [39, 40]. These results indicate that changes to PFAS transport in the presence of co-contaminants have the potential to be both sorbent- and co-solute- specific. Changes in PFAS transport may also arise if cosolutes lead to cosolvency effects. Cosolvency effects are primarily observed with completely water-iscible organic solvents [30], which are not being used in this study. So it is hypothesized cosolvency will not impact PFAS mobility. This study investigated PFAA sorption in soils amended with NAPL, and in systems containing representative non-fluorinated AFFF surfactants. Conceptual models were developed to provide potential explanations for the observed changes in PFAA sorption. Results of this study were used to make initial predictions of relative advective transport of PFAAs.

4. **Hypothesis 4. Due to potential nonequilibrium conditions, transport parameters determined in spiked laboratory batch experiments may not adequately describe PFAS transport in an advective scenario. However overall trends such as chain-length and f_{oc} dependent transport will still apply.**

   In ideal transport, sorption is presumed to be instantaneous under the assumption that it occurs at much faster rates than the residence time of groundwater [41]. If advective transport is ideal then PFAA transport could be predicted using results of batch equilibrium studies. However, sorption and desorption can be rate-limited [41]. Various mechanisms have been proposed to explain this behavior, including interactions with organic matter [42]. Rate-limited transport is sometimes characterized by early breakthrough and/or tailing of compounds in column breakthrough curves (BTCs). Accurate prediction of compounds exhibiting rate-limited behavior will require not only equilibrium sorption results but mass transfer coefficients. This study conducted low flow column experiments at environmentally relevant pore-water velocities to determine if previously measured batch-equilibrium data could be used to accurately describe PFAA transport. Flow interruption experiments were completed at higher pore water velocities to determine if rate-limited sorption impacted PFAA transport. Results of flow interruption and low flow experiments were used to examine potential implications of these processes to the remediation of groundwater contaminated with PFAAs.

1.3 Dissertation Organization

This dissertation is organized into five chapters. Chapter 1 provides a general introduction and background including research objectives and hypotheses tested and Chapter 5 provides a summary, conclusions, and recommendations for future work. The remaining three chapters are manuscripts that either have been or are being prepared for publichation. Details of these manuscripts are provided below. Where necessary, the supporting information for these chapters is provided in associated appendices.

- Chapter 2 is entitled "Occurrence and fate of Perfluorochemicals in soil following the land application of municipal biosolids" by Jennifer Guelfo Sepulvado, Andrea C. Blaine, Lakhwinder S. Hundal, and Christopher P. Higgins has been published in Environmental Science & Technology [43]. This paper addresses Hypothesis 1 and describes the occurrence of PFAS in biosolids and biosolids amended soils. PFAS occurrence in biosolids amended soils was evaluated with loading rate in plots receiving varying amounts of biosolids and with depth in biosolids amended soil cores. In addition, the leaching potential of biosolids was studied in laboratory batch desorption experiments. Results were used to make an initial prediction of the transport potential of PFASs.

- Chapter 3 is entitled "Subsurface transport potential of perfluoroalkyl substances acids at aqueous film-forming foam (AFFF)-impacted sites" by Jennifer L. Guelfo and Christopher P. Higgins has been published in Environmental Science & Technology [44]. This paper addresses Hypotheses 2 and 3 and investigates the equilbrium sorption of PFAAs under conditions relevant to AFFF-impacted sites. This includes investigation of sorption at concentrations relevant to impacted sites, sorption when multiple PFAAs are present, sorption in the presence of NAPL, and sorption in the presence of nonfluorinated hydrocarbon surfactants. Results were also used to make initial predictions of the advective transport potential of PFAAs.

- Chapter 4 is entitled "Transport Potential of Perfluoroalkyl Acids (PFAAs) at AFFF-impacted Sites: 1-Dimensional Column Studies" by Jennifer L. Guelfo, Assaff Wunsch, John E. McCray, and Christopher P. Higgins and is being prepared for publication. This paper addresses Hypothesis 4 and investigates the advective transport of PFAA in 1-dimensional column. This included measurement of PFAA breakthrough in various porous media and a comparison of resulting sorptive behavior to equilibrium conditions. The potential for rate-limited sorption was investigated and resulting mass transfer coefficients were used to make intial predictions of the impacts of nonequilbrium PFAA transport on remedial efforts.

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CHAPTER 2

OCCURRENCE AND FATE OF POLY- AND PERFLUOROALKYL SUBSTANCES (PFASS) IN SOIL FOLLOWING THE LAND APPLICATION OF MUNICIPAL BIOSOLIDS

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Abstract

The recent implementation of soil and drinking water screening guidance values for two perfluoroalkyl acids (PFAAs), perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS) by the U.S. Environmental Protection Agency (EPA), reflects the growing concerns regarding the presence of poly- and perfluoroalkyl substances (PFASs) in the natural environment. Previous work has established the potential risk to the environment from the land application of industrially contaminated biosolids, but studies focusing on environmental risk from land application of typical municipal biosolids are lacking. Thus, the present study investigated the occurrence and fate of PFAAs and PFAA precursors from land-applied municipal biosolids by evaluating the levels, mass balance, desorption, and transport of PFAAs and precursors in soils receiving application of municipal biosolids at various loading rates. This study is the first to report levels of PFASs in agricultural soils

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amended with typical municipal biosolids. PFOS was the dominant PFAA in both biosolids (80-219 ng/g) and biosolids-amended soil (2-483 ng/g). Concentrations of all PFAAs and precursors in soil increased linearly with increasing biosolids loading rate. These data were used to develop a model for predicting PFAS soil concentrations in soils amended with typical municipal biosolids using cumulative biosolids loading rates. Mass balance calculations comparing PFASs applied vs. those recovered in the surface soil interval indicated the potential transformation of PFAA precursors. Laboratory desorption experiments indicated that the leaching potential of PFASs decreases with increasing chain length and that previously-derived organic-carbon normalized partition coefficients may not be accurate predictors of the desorption of long-chain PFAAs from biosolids-amended soils. Trace levels of PFASs were also detected in soil cores from biosolids-amended soils to depths of 120 cm, suggesting potential movement of these compounds within the soil profile over time and confirming the higher transport potential for short-chain PFAAs in soils amended with municipal biosolids.

2.1 Introduction

Poly- and perfluoroalkyl substances (PFASs) are environmentally persistent, bioaccumulative, toxic, and widely distributed in the environment [1]. PFAS-based products have a wide variety of uses including nonstick coatings, stain-repellant fabrics, paper packaging products, and firefighting foams [2]. Two specific subclasses of perfluoroalkyl acids (PFAAs), perfluorocarboxylates (PFCAs) and perfluoroalkylsulfonates (PFSAs), have received particular attention in recent years. Because of their widespread use, PFASs have been detected in the influent, effluent, and sludge (biosolids) at municipal wastewater treatment plants (WWTPs) [3–5]. Municipal biosolids may not only contain PFAAs but also a variety of PFAA precursors that could be transformed to PFAAs over time[4, 6]. Some of these precursors, such as 2-(N-ethylperfluorooctane sulfonamido) acetic acid (EtFOSAA), may be transformed to PFSAs [7], while others, such as the fluorotelomer alcohols (FTOHs), may be transformed to PFCAs[8].

As of 2004, 7.2 million dry tons of biosolids were generated in the U.S. each year, and approximately 49% were applied to agricultural lands as fertilizer[9]. Though the land application of biosolids in the U.S. is regulated, no regulations are currently in place with respect to PFASss in biosolids. This issue is coming under increased scrutiny, mainly after a recent event in Decatur, Alabama, where industrially-contaminated biosolids were applied to land used for grazing cattle and growing crops, resulting in PFAS detections in soil, beef, grass, and groundwater from the biosolids-amended fields [10, 11]. Indeed, it was out of growing concern about the potential exposure to PFASs in soil and groundwater that provisional health advisories and residential soil screening guidance values were developed [12, 13]. For example, the U.S. Environmental Protection Agency (EPA) recently issued drinking water provisional health advisories for perfluorooctanoate (PFOA, a PFCA) and perfluorooctane sulfonate (PFOS, a PFSA) of 0.4 μg/L and 0.2 μg/L, respectively[14]. In addition, EPA's residential soil screening guidance values for PFOA and PFOS are 16,000 μg/kg and 6,000 μg/kg, respectively [12]. While PFASs are known to be present in municipal biosolids [4], it remains unclear whether the application of typical municipal biosolids to agricultural soil could pose any potential PFAS-related risks for human and ecological health.

If PFAAs and PFAA precursors in typical municipal biosolids are transferred to biosolids-amended soils, their environmental fate will depend on several processes. PFAA precursors may be transformed to PFAAs over time, while the PFAAs themselves may either accumulate in the surface soil and/or leach into the subsurface. To the best of our knowledge, the potential accumulation and/or leaching of PFAAs and PFAA precursors in soils amended with typical municipal biosolids has not been documented. Additionally, there is no prior work documenting transformation of PFAA precursors in soils amended with typical municipal biosolids, though transformation of FTOHs in soils receiving industrially-contaminated biosolids has been documented [8]. Furthermore, there are no studies investigating leaching of PFAAs or PFAA precursors in soils amended with typical municipal biosolids. Previous work with industrially-contaminated biosolids has suggested the potential for PFAA leaching, particularly for shorter chained PFAAs [15]. Finally, equilibrium partitioning can provide an idea of the leaching potential of organic contaminants, and relevant work has been done investigating equilibrium partitioning of PFASs in spiked sediment-water systems [16]. These data suggest a greater leaching potential for short-chain PFAAs under equilibrium conditions. However, previous work with other organic chemicals in biosolids [17] suggests soil-water partitioning coefficients derived from adsorption experiments do not accurately predict desorption behavior from biosolids, particularly under field conditions. For example, the desorptive release of biosolids-borne chemicals such as triclosan and triclocarban is often incomplete [17]. To this end, desorption data from laboratory batch experiments using field samples of biosolids-amended soils are needed to evaluate the fate and transport of PFASs applied to soils via municipal biosolids, and these data should be compared to observations of leaching in intact soil cores.

The objective of this study was to examine the occurrence and fate of select PFCAs, PFSAs, and PFAA precursors in biosolids-amended soils through a combination of field and laboratory studies. Specifically, we tested whether the repeated application of typical municipal biosolids results in predictable accumulation of PFASs in the biosolids-amended surface soils over time. In addition, concentrations of PFAAs and PFAA precursors applied to soil via municipal biosolids over a three-year period were compared to concentrations measured in the amended soil. The resulting mass balance calculations enabled a first evaluation of the potential formation of PFAAs from PFAA precursors in biosolids-amended soil. Laboratory desorption experiments were completed with field samples of biosolids-amended soils to verify previous observations of higher leaching potential for short-chain PFAAs and to enable evaluation of previously measured adsorption-derived partition coefficients vs. desorption-derived partition coefficients. Lastly, analysis of PFASs in soil cores from fields receiving biosolids was completed to determine if chain-length dependent leaching is also observed in the field.

2.2 Materials and Methods

The following is a sumary of materials and methods utilized in this work.

2.2.1 Materials

Standards of perfluorobutanoate (PFBA), perfluoropentanoate (PFPeA), perfluorohexanoate (PFHxA), perfluoroheptanoate (PFHpA), PFOA, perfluorononanoate (PFNA), perfluorodecanoate (PFDA), perfluoroundecanoate (PFUnA), perfluorododecanoate (PFDoA), perfluorobutanesulfonate (PFBS), perfluorohexanesulfonate (PFHxS), perfluoroheptanesulfonate (PFHpS), PFOS, perfluorodecanesulfonate (PFDS), 2-(N-methylperfluorooctane sulfonamido) acetic acid (MeFOSAA), and EtFOSAA, as well as stable-isotope surrogate standards (Table A.1) were purchased from Wellington Laboratories. Stock solution of these analytes and the surrogate standards were prepared in a 70/30 (v/v) methanol/aqueous ammonium hydroxide (0.01%) solution. Unless otherwise specified, all other chemicals and solvents were of reagent grade and were purchased from Fisher Scientific, Mallinckrodt Chemicals, or Sigma Aldrich.

2.2.2 Characterization of Study Sites

All biosolids and biosolids-amended soils analyzed in this study were provided by the Metropolitan Water Reclamation District of Greater Chicago (MWRDGC). Samples from four series of biosolids-amended soils were examined. General soil types and characteristics are summarized in Table 2.1. Soils were selected to represent a variety of soil types, biosolids loading rates, duration of biosolids application, and time since last biosolids application. First, short-term plots of Soil W (loam) and Soil K (sand) received biosolids applications over three consecutive years at various biosolids loading rates as part of a previously described, field-scale experiment at two farms in Illinois [18]. Samples of the six source biosolids applied to these soils were also analyzed for PFAS content. Second, archived soil cores from a previously characterized [19] site (long-term plots) were selected for plots that have received various cumulative biosolids loading rates. Finally, soil samples were collected from three general fields (Fields 2, 40, and 51) that have received multiple applications of biosolids in varying years [20]. All sites included control plots to which no biosolids were applied, and corn was grown in all fields. The biosolids loading rates used for both the short-term W and K plots encompassed the typical agronomic rates for biosolids applications for these soils, whereas the biosolids loading rates for the long- term application plots represent various worst-case scenarios[18] in which more than 100 years of agronomic biosolids applications were applied within a 33 year window.

Table 2.1: Biosolids-Amended Soil Characteristics

Soil	Soil Type	f_{oc}^{a}	Loading Rates^{b}	Years of Application	Last Application
Short-Term W	Silty Clay Loam	0.041	0-178	3	2006
Short-Term K	Fine Sand	0.011	0-133	3	2007
Long Term Plots	Silt Loam	NM	0-2218	32	2010
General Fields	Silt Loam	0.047	47-1654	1-20	1983-2002

^{a}$f_{oc}$was analyzed for the following loading rates: short-term W at 178 Mg/ha, short-term K at 133 Mg/ha, and general field 2 at 1654 Mg/ha. ^{b}Loading rates are provided in Mg/ha on a dry weight basis. NM = not measured.

2.2.3 Sample Collection

Composite samples of the biosolids applied to the short-term plots (Soils W and K) were collected at the time of biosolids application and stored at -20°C until analysis. Composite soil samples were collected from the long-term plots in fall 2005, short-term W plots in fall 2007, and short-term K plots in spring 2008. All soil samples were sieved through a 2-mm sieve and stored at -20°C until analysis. Further details about sample processing are given elsewhere[18, 19]. Samples collected from the general application fields were collected from 0-15 cm in summer 2010 and shipped to the laboratory on ice. Soil samples used in batch desorption experiments were analyzed by a commercial laboratory for foc by the Walkley Black method. Organic carbon content within each soil varied with the biosolids loading rate, and thus only the foc values relevant to desorption experiments are reported in Table 2.1.

2.2.4 Batch Desorption Experiments

After confirming the presence of PFASs, batch desorption experiments were conducted with soil from a short-term W plot (cumulative biosolids loading rate 178 Mg/ha), a short-term K plot (133 Mg/ha), and Field 2 (1654 Mg/ha). Equilibrium desorption experiments were conducted over 14 days to determine the time necessary for the soil-water mixtures to reach equilibrium, with the resultant data enabling the calculation of desorption-based organic carbon-water partitioning coefficients (K_{oc} values). Results of the equilibrium desorption experiments were used to calculate soil-water distribution coefficients (K_{des}) as follows (2.1):

$$K_{des} = \frac{C_s}{C_w} = \frac{m_s^0 - m_v - m_w}{m_w} * \frac{V_w}{M_{soi}} \tag{2.1}$$

where C_s is the concentration of the analyte in the solid phase, C_w is the concentration of analyte in the aqueous phase, m_s^0 is the mass of analyte in the solid phase before desorption, m_v is the mass of analyte lost to the desorption reactor vial, m_w is the mass of PFAS in the aqueous phase at equilibrium, V_w is the volume of the aqueous phase, and M_{soil} is the mass of soil in the reactor. Resulting K_{des} values were then organic carbon normalized to calculate K_{oc} (2.2):

$$K_{oc} = \frac{K_{des}}{f_{oc}} \tag{2.2}$$

2.2.5 Sample Extraction and Analysis

All solid samples were extracted as received, though all concentrations are reported on an oven-dry weight basis. Soils (50-1000 mg) and biosolids (100 mg) were spiked with surrogate standards and extracted using a procedure modified from a previous study [16]. Cleaned-up extracts were analyzed by liquid chromatography tandem mass spectrometry (LC-MS/MS). All biosolids and biosolids-amended soil samples were extracted and analyzed in triplicate. Aqueous sample preparation and analysis protocols were also modified from a previous study [16]. All biosolids extracts, soil extracts, and aqueous samples were quantified by LC-MS/MS using protocols similar to those previously described [4]. A MDS Sciex Applied Biosystems 3200 Q trap mass spectrometer (MDS Sciex, Ontario) was used to monitor two MRM transitions for each analyte. Quantitation was performed using Analyst® software. The limits of quantitation (LOQs) were analyte, matrix, and run-dependent, but were approximately 0.02-0.5 ng/g in soil and 0.9-9 ng/L in aqueous samples. All values reported are corrected for recovery of the surrogate standards, as appropriate, which were generally greater than 60% for all samples in all matrices. Additional details on sample analysis including eluents, eluent conditions, transitions, and quantitation are provided in Appendix A.

2.2.6 Quality Assurance/Quality Control Measures

Soils and biosolids were extracted in triplicate, desorption reactors were prepared in sets of three, and all analytical results are reported as the average of the three values. Solid and aqueous spike-recovery experiments and sequential extraction experiments were conducted to ensure the validity of the data (Table A.2, Figure A.1). As a result of poor recovery (either under or over recovery) during aqueous spike-recovery experiments, aqueous-phase data for PFBA, PFPeA, PFUdA, PFDoA, MeFOSAA, and EtFOSAA were removed from additional analysis. Finally, control reactors were prepared for desorption experiments to account for losses in the reactors. If losses for an analyte were greater than 10%, then these results were used to calculate m_v for the analyte (see 2.1) to account for losses to the vial when determining K_{des} values. Additional details regarding materials, batch desorption experimental set-up, sample extraction and analysis, and quality assurance/quality control measures are provided in the Supporting Information.

2.3 Results and Discussion

The following summarizes results and provides a discussion of results found in this work.

2.3.1 Occurrence in Biosolids and Biosolids-Amended Soils

Six composite samples of biosolids applied to the short-term plots were collected from 2004 to 2007 and analyzed for the full suite of PFASs. The most abundant PFAAs or PFAA precursors in all six biosolids were PFOS (80-219 ng/g), followed by MeFOSAA (63-143 ng/g), EtFOSAA (42-72 ng/g), and PFOA (8-68 ng/g) (Figure A.2). To facilitate comparison to previously reported concentrations, mean total PFASs (sum of PFOA, PFNA, PFDA, PFUdA, PFDoA, MeFOSAA, EtFOSAA, PFHxS, PFOS, and PFDS) and mean PFOS concentrations were calculated and were 433 ± 121 ng/g and 144 ± 57 ng/g, respectively. Data from this study were compared to data from a previous study that was collected post 2002 when the use of certain PFASs was phased out [4]. Mean, total PFASs and mean PFOS concentrations are not statistically different from the values of 436 ng/g and 124 ng/g, respectively, that were reported in a previous study [4], confirming that the biosolids applied to these soils were representative of typical municipal biosolids.

Soil analysis showed PFASs do occur in soils amended with typical municipal biosolids. As in biosolids, PFOS was the most abundant PFAS detected in the short-term plots (Soils W and K). PFOS concentrations ranged from 2-11 ng/g over the various biosolids loading rates in these soils. Though MeFOSAA was abundant in the applied biosolids, concentrations in the biosolids-amended soils were less than 4 ng/g, suggesting transformation of this PFAA precursor. PFOS was also the most abundant PFAS in the soil samples from the long-term plots and the general application fields. In these soils, PFOS was detected at 5.5-483 ng/g over various biosolids loading rates, with the 5.5 ± 0.4 ng/g PFOS levels from Field 51 (single biosolids application in 1988). Control soils with no biosolids application were also analyzed for all sites. In these samples, any PFASs present were detected at concentrations of approximately 1 ng/g or less, with the exception of PFOS. In the long-term control plots, PFOS was measured to be 22 ± 2 ng/g and 96 ± 4 ng/g. The high background concentration of PFOS in the long-term control plots is likely due to cross-contamination from maintenance activities such as plowing and planting because of the close proximity of these control plots to the plots receiving the highest biosolids applications. There are no physical barriers to separate the control plots from the biosolids-amended plots, and all plots were plowed and planted as a single unit. Atmospheric deposition can be eliminated as a source of the elevated PFOS levels in the long-term control plots since elevated PFOS concentrations are not found in control plots from the short-term W and K sites and the general fields, which are from the same geographic region.

2.3.2 Occurrence with Biosolids Loading Rate

Once occurrence of PFASs in soils amended with municipal biosolids was established, trends of PFAS concentrations in these soils with varying loading rates were examined. This was done using data from the short-term W plots and long-term plots as a cumulative data set, plotting individual PFAS concentrations vs. cumulative biosolids loading rate, and then performing regressions on the cumulative data set (Figure 2.1 and Table A.3). These regressions took the form of (2.3):

$$[PFAS] = m * LR \tag{2.3}$$

where [PFAS] is the individual PFAS concentration (i.e., [PFOS]; ng/g), m is the slope (ng/g per dry Mg/ha), and LR is the cumulative loading rate (Mg/ha). Some variability was observed, but the overall regressions of PFAS concentrations in surface soil vs. cumulative biosolids loading rates were statistically significant ($p < 0.05$) for all PFASs, with the exception of PFBS. Within each soil, PFBS showed increases with loading rate; however when the data sets from the soil types were combined, there was not a consistent increase in soil concentrations with increased biosolids loading rate. As a result, PFBS could not be modeled. Regressions were performed with the y-intercept set to zero since some control plot PFAS concentrations were falsely elevated due to cross contamination, and additional background PFAS concentrations were not available. The results of these regressions confirm that the primary source of PFASs to these soils is the biosolids, as opposed to atmospheric deposition, and that levels of PFASs increase with increased biosolids loading rate.

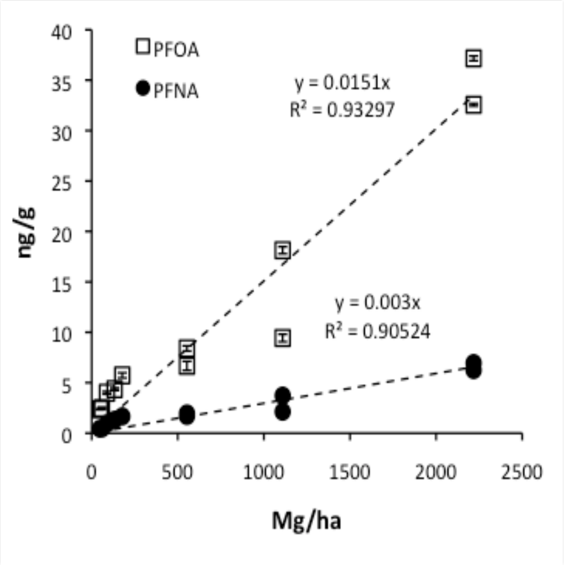

Figure 2.1: Example regressions of measured soil concentration vs. cumulative loading rate for PFOA and PFNA in the short-term W and long-term plots. Regressions and associated statistics for all PFASs are available in the Supporting Information (Table A.3).

Next, PFAS concentrations in the general fields were predicted by incorporating loading rates from the general fields into the linear equations (Table A.3) obtained from the regressions of the short-term and long-term plots. These predicted concentrations were then compared to the PFAS concentrations measured in surface soil samples taken from the general fields (Figure 2.2). The regressions slightly over-predicted concentrations of all PFASs, particularly for the plot amended at a rate of 497 Mg/ha (Field 40), suggesting that some losses of PFASs from the surface soils may have occurred since the last application in 1983. Nonetheless, relatively accurate predictions of soil PFAS levels in the general fields can be made despite the highly variable biosolids applications. However, as all soils and biosolids included in this study are from the same region with presumably similar PFAS levels in the source biosolids, the application of these regressions for predicting PFAS levels in biosolids-amended soils must be done with caution: slight differences in PFAS levels in source biosolids could translate to substantial differences in biosolids-amended soil concentrations, particularly when these differences are integrated over many years. Nevertheless, in the absence of PFAS concentrations in typical municipal biosolids applied to a particular site, these regressions provide a first approximation of expected PFAS levels in soil based on cumulative biosolids loading rates.

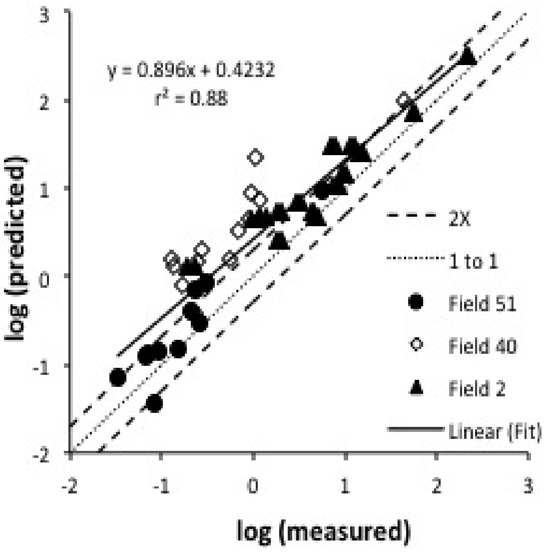

Figure 2.2: Measured concentrations for all PFASs detected in the general fields plotted vs. predicted values for all modeled PFASs using linear regressions derived from the short-term W and long-term plots.

2.3.3 PFAS Fate in Surface Soils

Comparison of PFAS concentrations in source biosolids vs. the amended soils suggested a potential loss of PFAA precursors from the surface soil layer between biosolids application and the time of sample collection. To explore the potential for PFAA precursors to contribute to PFAA concentrations and to examine any increases or decreases in PFAS levels, mass balance calculations were performed to determine how much mass of each PFAS applied in the biosolids was recovered in the short-term W and K plots. A range of expected soil concentrations for each PFAS was determined for each biosolids loading rate using a mean

(± the standard deviation) of the measured concentration of PFAS in biosolids applied at each site over a three-year period, the incorporation depth (0.15 m for short-term W plots, 0.2 m for short-term K plots), the measured loading rates Higgins [18], and the soil bulk density (1.3 g/cm^3short-term W, 1.6 g/cm^3 short-term K). The range of calculated concentrations for each PFAS was then compared to the measured range of concentrations in the short-term W and K plots. Though these calculated concentrations represent only an estimate of the expected soil concentrations, comparison to the measured values can provide an estimate of any significant increases or decreases in PFAS levels relative to what was applied. Complete mass balance results are provided in the Appendix A (Table A.4). In both soils, the biggest increases in PFAS concentrations were observed for PFBS, where, on average, PFBS was ˜300% to ˜2000% of what would be anticipated for the short-term W and K plots based on the applied biosolids. Because PFHxS is used as a surrogate standard for PFBS (Table A.1), standard additions were performed to determine if matrix effects contributed to the significantly elevated PFBS measurements (see Appendix A). Though matrix effects did lead to artificially high soil measurements, they could not entirely account for the elevated levels of PFBS in the short-term W and K plots, strongly suggesting that significant quantities of PFBS were being formed from a PFAA precursor over the short-term. The most notable losses in each soil were of the two PFAA precursors, MeFOSAA and EtFOSAA, where, on average, concentrations were only 23-69% of what was expected. These results further indicate potential transformation of PFAA precursors, though full conversion of these precursors to end product PFAAs was not observed. For example, PFOS, a known transformation product of EtFOSAA (Rhoads et al. [7]) was well within the expected range of concentrations, with average recoveries in Soil W and Soil K plots of 97% and 83%, respectively. Future efforts should focus on temporal monitoring of biosolids-borne PFAAs and PFAA precursors to better understand the transformation rate and formation of any potential intermediates.

2.3.4 Leaching Potential

To understand leaching potential under equilibrium conditions, desorption was examined in soil from the short-term W and K plots as well as from the general fields (Field 2). Aqueous equilibrium, defined as when no statistical differences were observed in aqueous concentrations measured in subsequent time points (up to 14 days), was achieved for all PFASs within the first 24 hours of desorption from the biosolids amended soils (Figure A.3). Losses in control (no solids) vials were used to calculate a fraction of the PFAS associated with the surfaces of a vial when the fraction of the total PFAS mass lost in the control blank was greater than 10%. The remaining PFASs were assumed to remain in the solid phase, and this was verified for a subset of samples by extracting solids at the completion of the desorption experiments (Table A.5). Using these data in conjunction with the measured PFAS mass in the aqueous phase, equilibrium K_{des} values were calculated for all PFASs with detectable aqueous concentrations (2.1). The K_{des} values were normalized to f_{oc} for each biosolids-amended soil to calculate K_{oc} values (2.2, Table S6). Desorption-derived K_{oc} values from the short-term W and K plots and the general fields were used to calculate an average log K_{oc} value for each PFAS (Table 2.2). Similar to previous studies (Higgins and Luthy [16], log K_{oc} values showed a general increase with chain length, indicating greater leaching potential of short-chain PFASs under equilibrium conditions (Table 2.2 and Table A.6). Values from this study are also similar to those reported previously (Higgins and Luthy [16]) (Table 2.2), with the exception of PFDA and PFOS, which were approximately one half to one order of magnitude greater. The disagreement between previously measured K_{oc} values for PFOS and PFDA but not the shorter chain-length PFAAs suggests that desorption of longer-chain length PFAAs may be particularly slow. These data call into question the application of the previously determined adsorption K_{oc} values (Higgins and Luthy [16] for predicting the transport of PFASs in biosolids-amended soils as adsorption-derived K_{oc} values may over predict the leaching potential of longer chain-length PFAAs such as PFOS and PFDA in biosolids-amended soils.

Table 2.2: K_{oc} results vs. previous studies

Analyte	Log K_{oc}	StDev	Log K_{oc} Prev. Work[a]
PFHxA	1.91	0.39	N/A
PFHpA	2.19	0.65	N/A
PFOA	2.31	0.35	2.06
PFNA	2.33	0.31	2.39
PFDA	3.17	0.14	2.76
PFHxS	2.70	0.38	N/A
PFOS	3.34	0.27	2.57

[a] Log K_{oc} values determined in previous studies of PFAA sorption (Higgins and Luthy [16].

2.3.5 Leaching Under Field Conditions

Laboratory batch desorption experiments with field samples demonstrated higher leaching potential for short-chain PFAAs as compared to long-chain PFAAs. This finding was confirmed in soil cores, which reflect the actual leaching of PFASs in the field. Analysis of soil cores from the long-term plots showed that levels of PFASs decreased with depth regardless of the biosolids loading rates (Figure 2.3 and Figure A.4). However, PFASs were detected in the bottom depth interval at 120 cm. Data previously reported for these plots showed similar trends for triclocarban, triclosan, and PBDEs (Xia et al. [19]). This previous report concluded that detection of these relatively hydrophobic chemicals in the deeper layers of these soil cores suggests facilitated transport (e.g. via preferential flow paths) may have occurred (Xia et al. [19]). However, patterns of PFAS concentrations in deeper layers suggests that leaching is likely responsible for the transport of PFASs in these cores. First, levels of PFASs in the core samples from the control plots (no biosolids amendment) were relatively consistent with depth, with the exception of PFOS. As previously mentioned, PFOS was detected in high concentrations in the surface control samples, presumably due to cross contamination with plots receiving biosolids application. Second, statistically significant correlations of soil concentration vs. loading rate were observed for some PFASs (including PFOA and PFOS) in the bottom layer of the soil cores. Finally, similar to the trends recently reported for soil cores from the Decatur site (Washington et al. [15]), the ratios of PFAS concentration in the surface soil to PFAS concentration in the lowest depth interval show an overall decrease with increasing chain length, indicating greater transport of the short-chain PFASs (Figure 2.4). These data strongly suggest leaching of PFASs from the biosolids application zone to a depth, in some cases, of 120 cm. However, as expected from the batch desorption studies, the longer chain-length PFAAs appear to be much less mobile than the shorter chain-length PFAAs.

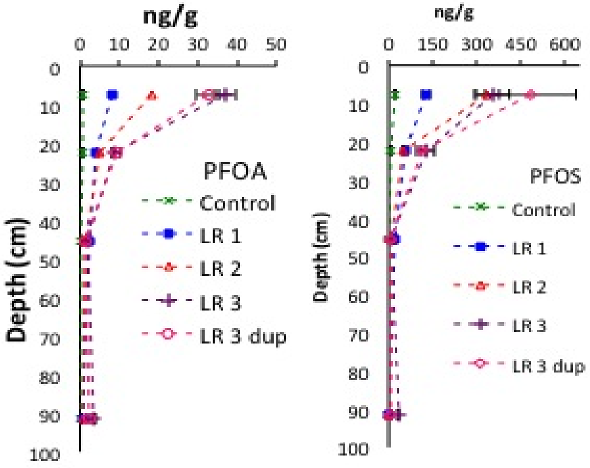

Figure 2.3: Concentrations of PFOA and PFOS with depth in the long-term plots at various loading rates. Control = 0 Mg/ha, LR 1 = 553 Mg/ha, LR 2 = 1109 Mg/ha, and LR 3 and LR 3 dup = 2218 Mg/ha (on dry weight basis).

2.3.6 Implications

To better understand the environmental significance of these data, it is useful to further examine the results in comparison to the recently outlined provisional health advisory (PHA) values and residential soil screening guidance values. No soil concentrations measured in this study exceeded the residential soil screening guidance values, which were designed for protection against direct exposure to soil. However, soil screening standards for the protection of groundwater have not yet been developed; therefore, it is illustrative to calculate whether

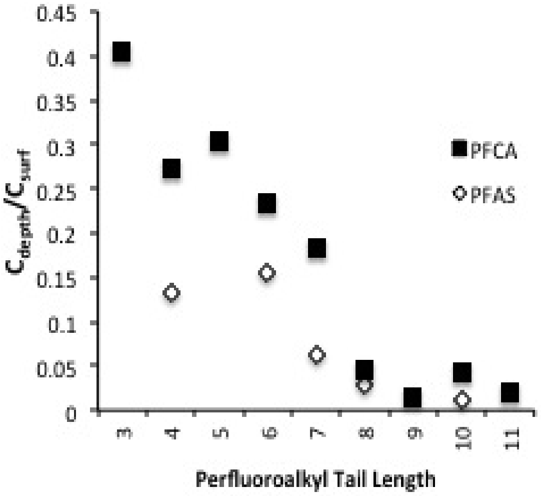

Figure 2.4: The ratios of surface concentration (C_{surf}) to concentration in the bottom soil core depth interval (60-120cm, C_{depth}). Ratios represent an average of the ratios calculated for the long term plots for each biosolids loading rate.

measured soil concentrations have the potential to lead to groundwater exceedances of the PHAs for PFOS and PFOA. These calculations are extremely conservative, as there is likely substantial dilution of soil pore water in the subsurface. Equilibrium pore water concentrations for the short-term W and K plots at multiple biosolids loading rates were estimated using K_{oc} values from this study, f_{oc} values from this and previous work (Higgins [18]), and measured soil PFOA and PFOS concentrations. These calculations indicate the PHA for PFOA would be exceeded in the short-term W pore water at loading rates of 89 and 178 Mg/ha and in the short-term K pore water at 44 and 133 Mg/ha. Soil pore-water PFOS concentrations would also exceed the PHA in Soil K plots at 44 and 133 Mg/ha. The cumulative loading rates of 89 Mg/ha (Soil W) and 178 Mg/ha (Soil K) represent an agronomic rate of biosolids application over a five year period. Understanding that these estimates represent a worst-case scenario that does not account for dilution, these results indicate that the risk of groundwater impact from biosolids–borne PFASs is uncertain and will depend heavily on soil type and PFAS concentrations in biosolids. Once PFASs are introduced to the environment, two of the primary concerns for human health are the potential for contamination of water and food. This study focused on the potential for contamination of water from the application of typical municipal biosolids to agricultural fields. Collectively, the data in this study suggest that though the risk to groundwater is uncertain, transport of PFASs from soils amended with municipal biosolids is possible. However, there may be limitations to this transport, particularly for the long-chain PFASs. Further work is needed to determine the risk to food from land application of municipal biosolids, though plant uptake of PFASs from industrially-contaminated biosolids has been documented (Yoo et al. [11]. Given the current movement towards increased regulation of PFASs, particularly PFOS and PFOA, this study emphasizes the importance of gaining an increased understanding of the fate and transport of PFASs in soils amended with typical municipal biosolids.

2.4 Acknowledgements

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CHAPTER 3

SUBSURFACE TRANSPORT POTENTIAL OF PERFLUOROALKYL SUBSTANCES ACIDS AT AQUEOUS FILM-FORMING FOAM (AFFF)-IMPACTED SITES

A paper published in *Environmental Science & Technology.*

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Abstract

Subsurface transport potential of a suite of perfluoroalkyl acids (PFAAs) was studied in batch sorption experiments with various soils and in the presence of co-contaminants relevant to aqueous film-forming foam (AFFF)-impacted sites. Specifically, PFAA sorption to multiple soils in the presence of nonaqueous phase liquid (NAPL) and non-fluorinated AFFF surfactants was examined. This study is the first to report on sorption of perfluorobutanoate (PFBA) and perfluoropentanoate (PFPeA) (Log K_{oc}= 1.88 and 1.37, respectively) and found that sorption of these compounds does not follow the chain-length dependent trend observed for longer chain-length PFAAs. Sorption of PFBA was similar to that of perfluorooctanoate (PFOA; Log K_{oc}=1.89). NAPL and non-fluorinated AFFF surfactants all had varying impacts on sorption of longer chain (>6 CF2 groups) PFAAs. The primary impact of NAPL was observed in low foc soil (soil A) where Freundlich n-values increased when NAPL was present. Impacts of non-fluorinated AFFF surfactants varied with surfactant and soil. The anionic surfactant sodium decyl sulfate (SDS) illicited PFAA chain-length dependent impacts in two negatively-charged soils with varying f_{oc}. In soil A, Kd values for perfluoroheptanoate

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(PFHpA) increased 91% with SDS, whereas values for perfluorodecanoate (PFDA) increased only 28%. An amphoteric surfactant, n,n-dimethyldodecylamine n-oxide (AO), had the most notable impact on PFAA sorption to a positively-charged soil (soil C). In this soil, AO oxide significantly increased sorption for the longer chain PFAAs (i.e., 528% increase in K_d for PFDA). Changes in sorption caused by SDS and AO may be due to mixed hemimicelle formation, competitive sorption, or changes to PFAA solubility. Short-chain PFAA behavior in the presence of NAPL, SDS, and AO was again notable. Co-contaminants generally increased the sorption of these compounds to all soils. Log Kd values of PFBA in soil A increased 85%, 372%, and 32% in the presence of NAPL, SDS, and AO, respectively. Use of K_d values to calculate retardation factors (R_f) of PFAAs demonstrates the variability of co-contaminant impacts on PFAA transport. Whereas NAPL and non-fluorinated surfactants decreased the sorption of perfluorooctanesulfonate (PFOS) at lower PFOS concentrations (1 µg/L), they led to increases in sorption at higher PFOS concentrations (500 µg/L). These results demonstrate that PFAA groundwater transport will depend on the solid phase characteristics as well as PFAA concentration and chain length. Detailed site-specific information will likely be needed to accurately predict PFAA transport at AFFF-impacted sites.

3.1 Introduction

Perfluoroalkyl acids (PFAAs) have been the focus of many recent studies due to their widespread distribution in the environment, toxicity, and potential for bioaccumulation [1, 2]Lau et al. [1], Conder et al. [2] PFAAs have been used in a variety of products including nonstick coatings, stain-repellants, paper packaging, and aqueous film-forming foams (AFFF) [3]. Used in fighting fuel fires, AFFF is often utilized by fire-fighting facilities, the hydrocarbon industry, and the military [4]. Repeat use of AFFF to extinguish fires at fire protection training areas (FPTAs) has led to the presence of PFAAs in groundwater at µg/L to mg/L levels [5–7]. The U.S. Environmental Protection Agency recently implemented provisional health advisories for perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS) in drinking water of 0.4 and 0.2 µg/L, respectively [8]. Because of high PFAA groundwater levels at FPTAs, it is important to understand factors controlling the transport of PFAAs in the saturated zone. If PFAAs are released to groundwater through AFFF use, interactions with aquifer sediment is likely the primary process impacting transport. Previous work has studied sorption of PFAAs to sediment, biosolids, and mineral surfaces [9–11], but data are limited with respect to the conditions likely present at many AFFF-impacted FPTAs.

AFFF formulations are complex, proprietary, and often include solvents and both fluorinated and hydrocarbon surfactants [5, 12]. Transport of PFAAs in groundwater at FPTAs may thus be impacted by other AFFF components and by co-contaminants released during training exercises, such as fuels or chlorinated solvents, which may exist as non-aqueous phase liquids (NAPLs). Previous work has investigated sorption of PFOS to NAPL-contaminated soil and in the presence of hydrocarbon surfactants [13, 14]. To the best of our knowledge, behavior of multiple PFAAs in the presence of NAPL or hydrocarbon surfactants specific to AFFF has not been documented.

Multiple mechanisms may influence PFAA sorption at AFFF-impacted FPTAs (Figure 3.1)[15], The presence of multiple PFAAs may lead to competitive sorption amongst PFAAs. Previous work showed no competition when multiple PFAAs were present below 1 µg/L [9], but competition at higher concentrations applicable to AFFF-impacted FPTAs has not been investigated. Fuels or chlorinated solvents may have a varied effect on sorption. Trichloroethylene (TCE), selected as a model NAPL for this study, has been documented in groundwater at FPTAs along with fuel components such as benzene, toluene, ethylbenzene, and xylenes [16, 17]. These components may compete with PFAAs for sorption sites, but when present at high enough concentrations to exist as a NAPL, may also act as an additional sorbent [18, 19]. For example, NAPL led to increases in sorption of both polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), and in some cases these compounds had a higher affinity for NAPL than for soil organic carbon [18, 19]. Previous work found PFOS sorption increased in the presence of crude oil [13], but behavior of other PFAAs in the presence of other NAPLs is uncertain, especially given their hydrophobic and oleophobic nature. Hydrocarbon surfactants in AFFF that may also be present in groundwater include anionic sodium decyl sulfate (SDS) and amphoteric n,n-dimethyldodecylamine n-oxide (AO) [20, 21]. These surfactants may have varied effects on PFAA sorption. Sorption of atrazine increased in the presence of a nonionic surfactant and decreased in the presence of cationic and anionic surfactants [22]. PFOS sorption has been shown to increase in the presence of a cationic surfactant and decrease when an anionic surfactant was present [14]. To the best of our knowledge, the impacts on PFAA sorption of non-fluorinated surfactants specific to AFFF remain unexplored.

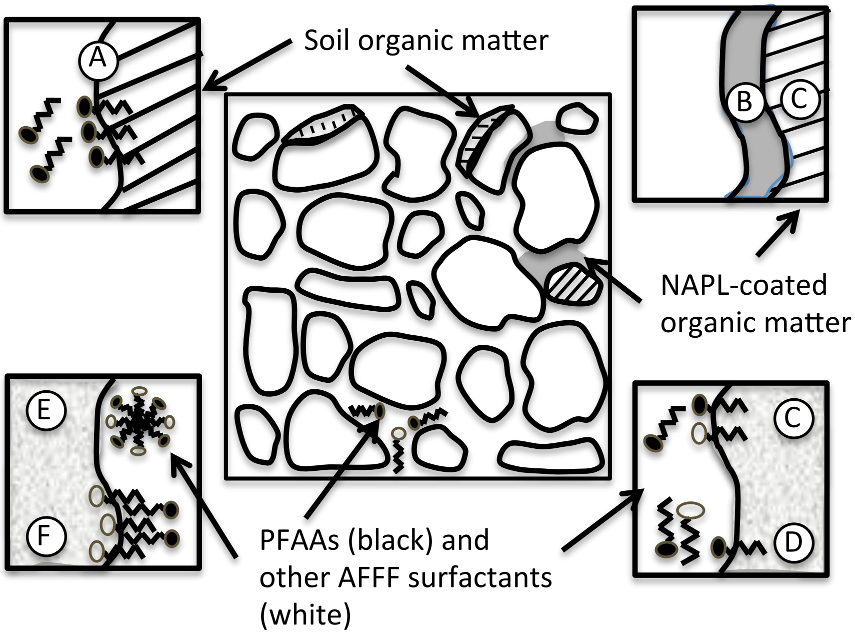


Figure 3.1: Figure 1. A conceptual model of the processes that may impact PFAA sorption at AFFF-impacted sites. A.) Competitive sorption among PFAAs; B.) NAPL as a sorbent; C.) Co-contaminant interference at PFAA sorption sites; D.) Hydrocarbon surfactant-enhanced PFAA solubility. E.) Hydrocarbon surfactant/PFAA mixed hemimicelles increasing sorption; and F.) Hydrocarbon surfactants as a sorbent.

The objective of this work was to determine the subsurface transport potential of PFAAs by studying sorption in mixed PFAA and co-contaminant systems using batch studies. We tested sorptive behavior of perfluoroalkyl carboxylates (PFCAs) and perfluoroalkane sulfonates (PFSAs) in single-PFAA vs. mixed-PFAA systems to examine competitive effects.

PFAA sorption was studied in soils amended with NAPL, and in systems containing representative non-fluorinated AFFF surfactants. Conceptual models were developed to provide potential explanations for the observed changes in PFAA sorption. Lastly, results of this study were used to make initial predictions of relative advective transport of PFAAs.

3.2 Materials and Methods

The following is a summary of materials and methods used in this work.

3.2.1 Materials

Calibration standards of perfluorobutanoate (PFBA), perfluoropentanoate (PFPeA), perfluorohexanoate (PFHxA), perfluoroheptanoate (PFHpA), PFOA, perfluorononanoate (PFNA), perfluorodecanoate (PFDA), perfluoroundecanoate (PFUnA), perfluorobutanesulfonate (PFBS), perfluorohexanesulfonate (PFHxS), and PFOS, 1H,1H,2H,2H-pefluorooctane sulfonate (6:2 FTSA), and 1H,1H,2H,2H-pefluorodecane sulfonate (8:2 FTSA) as well as stable-isotope surrogate standards (Table B.1) were purchased from Wellington Laboratories. Spiking solutions for all experiments were prepared from standards of PFCAs and PFSAs purchased from Sigma-Aldrich as well as 6:2 FTSA and 8:2 FTSA provided by 3M Co. The hydrocarbon surfactants SDS and AO were purchased from Alfa Aesar. Stock solution of calibration standards, spiking standards (purity-corrected), surfactants (purity-corrected) and surrogate standards were prepared in a 70/30 (v/v) methanol/aqueous solution. Unless otherwise noted, all experiments utilized a spiking solution containing all 13 chemicals. Unless otherwise specified, all other chemicals were of reagent grade and were purchased from Fisher Scientific, Mallinckrodt Chemicals, or Sigma Aldrich.

Solid phases used in this study were selected to represent a variety of geochemical and physical characteristics (Table B.2). A loamy sand (A) and loam (B) were purchased from Agvise Laboratories, and a sandy clay loam (C) was donated. Soil C likely exhibits a net positive charge due to high iron oxide content (Table B.2). All soils were dry sieved (2mm) prior to use. To study NAPL impacts on PFAA transport, some experiments utilized soils amended with TCE as a model NAPL. To ensure TCE was present as NAPL, 1 mL of TCE was added to 15 g of soil to achieve a TCE concentration of ˜100 g/kg and stirred vigorously prior to use. Artificial groundwater (AGW) was made by modifying deionized water with ions typically found in groundwater and was used as the aqueous phase for all experiments (Table B.3).

3.2.2 Batch Sorption Experiments

Batch Sorption Experiments. Five-point sorption isotherms were measured in soils A, B, and C with initial aqueous concentrations (C_w^i) of 0.5-1000 µg/L of each PFAA. Batch reactors were prepared in 50 mL polypropylene centrifuge tubes with 15 g of soil and 40 mL of AGW, spiked with the PFAA mix, and equilibrated on a shaker table for 10 days based on previous studies [9, 10]. To determine if PFAAs sorbed competitively, 5-point isotherms were repeated in soils A and B with PFOS or PFOA only and the single-solute isotherms compared to those measured in the PFAA mix. To determine NAPL impacts on PFAA sorption, aliquots of soils A and B were amended with TCE as described above, and 5-point isotherms repeated in the amended soil. To determine impacts of non-fluorinated AFFF surfactants on PFAA sorption, 5-point isotherms with the PFAA mix were repeated in soils A, B, and C with the addition of 100 mg/L of either SDS or AO. These surfactants were selected because of of their presence in some AFFF formulations [20, 21] To better understand the effects of SDS and AO on PFAA sorption, 4-point SDS isotherms were measured in soils A and B with initial aqueous concentrations of 0.5-100 mg/L. Similar isotherms are not available for AO because of matrix interference during liquid chromatography tandem mass spectrometry (LC-MS/MS) analysis.

To elucidate on PFAA sorptive behavior in the presence of NAPL, NAPL-water sorption experiments were completed. These experiments were conducted with TCE and dodecane (DD). DD was selected to determine if PFAA NAPL-water distribution varied with NAPL type. For these experiments, NAPL and AGW were placed into 50 mL glass centrifuge tubes with a NAPL-water ratio of 0.25 mL/mL and spiked to a Cwi of 500 µg/L with PFAA mix.

Reactors were placed on a shaker table for three days based on previous work [19]. At the end of the equilibration period, reactors were allowed to sit for 30-minutes prior to aqueous phase sampling.

3.2.3 Sample Extraction, Preparation, and Analysis

Aqueous samples were analyzed directly via LC-MS/MS. The solid phase of all sorption reactors was extracted and resulting extracts analyzed for PFAAs via LC-MS/MS. All aqueous preparation (Table B.4), solid extraction (Table B.5), and analytical protocols were modified from previous studies [9, 10]. An Applied Biosystems 3200 mass spectrometer (MDS Sciex) was used to monitor two transitions for each analyte. Quantitation was performed using Analyst. Limits of quantitation were analyte, matrix, and run-dependent but were approximately 0.02-0.5 ng/g in soil and 2-9 ng/L in aqueous samples. All values reported are corrected for recovery of surrogate standards, which were generally greater than 60% for all samples and matrices.

3.2.4 Quality Assurance/Quality Control

All sorption reactors were prepared in triplicate, and the solid phase from all reactors was extracted and analyzed. Aqueous and solid phase analytical results are reported as the average of the three values. Method performance for solid phase samples is well documented[10, 23], though additional spike recovery experiments were completed for soil modified with NAPL (Table B.6). Additionally, control reactors were prepared for all sorption experiments to account for losses in the reactor. Separate control experiments were completed for glass and polypropylene reactors. If losses for an analyte were greater than 10%, control (no solids) results were used to calculate the mass of PFAA lost to the reactor. Finally, mass balances of PFAA mass recovered in the aqueous phase, solid phase, and reactor were completed and generally showed 70-130% recovery (Table B.7). If average mass recovered on any single isotherm point exceeded 130%, that point was excluded from the isotherm. Mass balances less than 70% were measured for PFDA and PFUnA and are thought to result from underestimation of PFAA mass lost to the reactor. Because of this and because all solid and aqueous concentrations were measured directly, these analytes were still considered to facilitate examination of chain-length dependent trends. As a result of consistent over-recovery in the mass balance, 6:2 FTSA and 8:2 FTSA were removed from analysis. Additional details regarding materials, experimental setup, sample preparation and analysis, and quality assurance/quality control measures are provided in the Supporting Information.

3.3 Results and Discussion

The following summarizes results and provides a discussion of results found in this work.

3.3.1 PFAA Sorption

In some cases, PFAA sorption was found to be non-linear; therefore PFAA sorption isotherms were fit with the Freundlich equation (r^2 >0.95, Table B.8, 3.1):

$$C_s = K_f C_w^n \tag{3.1}$$

where C_s is the concentration in the soil, K_f is the Freundlich sorption coefficient, and n describes isotherm linearity. Nonlinearity is thought to arise because there are multiple types of sites that have different sorption free energies. The linear portion of the isotherm implies constant free energy of sorption [24]. In this study, values for n were 0.7-1.1 (Table B.9), consistent with previous studies [9]. Because sorption of some PFAAs was nonlinear and to facilitate comparison of sorption between PFAAs and soils, concentration-specific solid-water distribution coefficients (K_d values; L/kg) were calculated for each PFAA and soil at two aqueous concentrations. Interpolated values were calculated at a concentration of 5 nM as done in prior work to facilitate comparison of results [9] and at a concentration of 0.35 mg/L to represent differing trends at the upper end of the isotherm at concentrations more typical of AFFF-impacted sites (i.e. 18 to 6570 µg/L) [5]. K_d values at 5 nM were normalized to f_{oc} and averaged to obtain concentration-specific K_{oc} (L/kg_{oc}) values. Consistent with previous work [9], K_d values increased with increasing f_{oc} (Figure B.1), confirming the importance of organic matter interactions in PFAA sorption. Where available, K_{oc} values (Table B.10) compared well with prior work and also increase with increasing PFAA chain length [9]. Exceptions to this trend were observed for PFBA and PFPeA, as will be discussed. In single vs. mixed PFAA systems, minor competitive effects were observed for PFOA and PFOS in soil A only (Figure B.2), suggesting competitive effects amongst PFAAs may be a factor in low f_{oc} soils. Overall competitive effects were considered to be minor, and all remaining experiments were conducted with the full mixture of analytes.

Previous work observed a ˜0.55 log unit increase in K_d per addition of each CF_2 group to the fluorocarbon tail based on K_d measurements for PFCAs with 7 CF_2 groups (C7) to C10 PFCAs[9]. This study included regressions of K_d values with chain length for C3 to C10 PFCAs in soils A and B and found similar Log K_d increases of 0.45 (± 0.04) and 0.51 (± 0.04) per CF_2 group in soils A and B, respectively, for C5 to C10 PFCAs (Figure 3.2). C3 and C4 PFCAs, however, did not follow this trend. Regressions of C7-C9 PFCA K_d values vs. chain length in soil C yielded a slope of 0.46 (± 0.01). Small deviations from this slope were observed for C5-C6 in the soil C; however, C3 and C4 PFCAs were again exceptions to the trend. Sorption of these compounds was much higher than would be expected based on extension of chain length-Log K_d regressions. As both solid and aqueous phase concentrations were measured and mass balances of PFBA and PFPeA in the soil, aqueous phase, and reactor were 109-111% (Table B.7) for all isotherms, it is very unlikely that these large deviations resulted from experimental artifacts.

The chain length-K_d relationship indicates the importance of van der Waals effects (e.g. hydrophobic effects) in PFAA sorption, so exceptions observed in PFBA and PFPeA suggest a different mechanism may be relatively more important for shorter chain length PFAAs. For example, ion exchange may play a relatively more important role for these PFAAs. In fact, K_d values for PFPeA and PFHxA were statistically higher in positively charged Soil C (f_{oc}= 0.008) than in negatively charged Soil A (f_{oc}= 0.017, Figure B.1). Another possibility is that there is a subset of sorptive sites in organic matter available only to smaller molecules (i.e., a steric effect). Previous work studying the absorbtion of cyclohexanes and equivalent n-alkanes from air found absoption of cycohexanes to be higher due, in part, to steric factors [25]. If this were true, K_d values would be higher for smaller PFAAs and, in fact, Log K_d values do decrease with increasing size from C3 to C5 PFCAs before increasing for C6 and higher PFCAs. It is important to note anomalous behavior, as recent PFAA production has moved from long-chain (>7 CF_2 groups) PFAAs such as PFOS to short-chain PFAAs [26–28], which were widely believed not to undergo significant sorption. These results suggest non-neglibible sorption of these compounds does occur. Further mechanistic studies, such as those conducted by Tulp et al. [29], of sorption of these short chain PFAAs to organic matter are needed to confirm and explain this behavior.

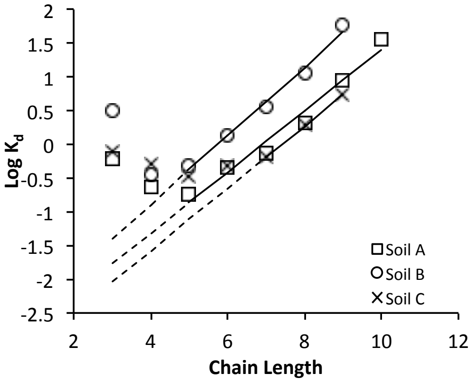
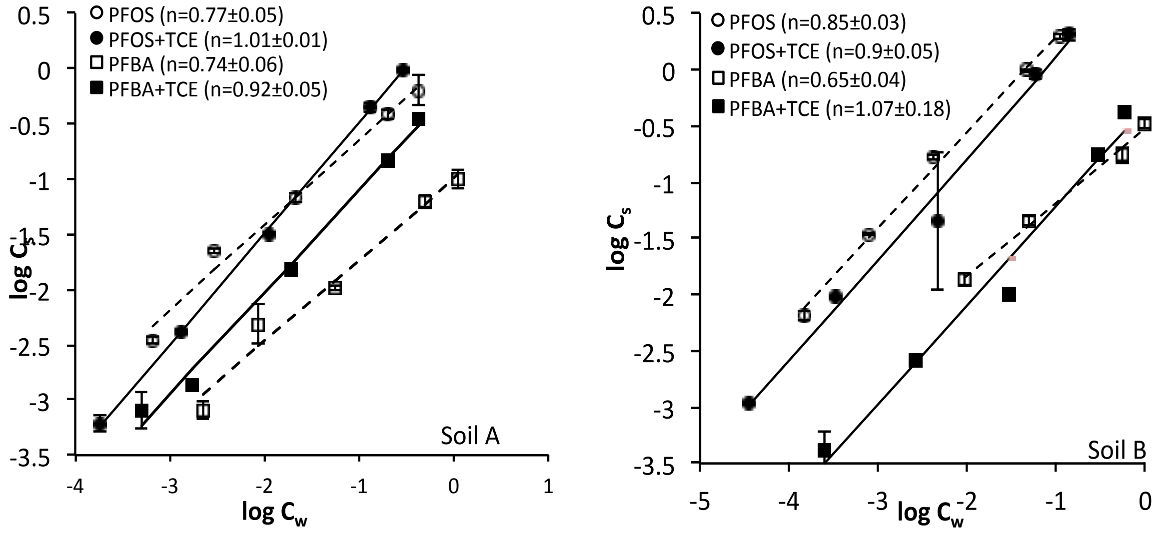


Figure 3.2: Log K_d values for PFCAs of varying chain length in A, B, and C soils. Solid lines are regressions of chain length vs. Log K_d ($r^2 > 0.95$) for C5-C10 (soils A and B) or C7-C9 (soil C) PFCAs. Slopes of the solid lines are 0.45 (± 0.04), 0.51 (± 0.04), and 0.46 (± 0.01) for the A, B, and C soils, respectively. Dashed lines are extrapolations of the regressions to the smaller chain lengths.

3.3.2 Impacts of NAPL

Behavior of PFAAs in the presence of NAPL was investigated by measuring PFAA sorption in both A and B soils amended with TCE (Figure 3.3, Table B.8). The impacts of NAPL on PFAA sorption varied between PFAAs and soils. In soil A (f_{oc}= 0.017), the presence of NAPL generally led to an increase in isotherm linearity (Table B.8) and thus a concentration-dependent effect on sorption. Sorption was unimpacted or slightly decreased at lower PFAA concentrations and increased at higher concentrations (Figure 3.3). PFBA, PFPeA, and PFHxA were exceptions to this trend. Sorption of these compounds increased across the entire concentration range when TCE was present (Figure 3.3, Figure B.3). In soil B (f_{oc}= 0.045), sorption was unchanged or decreased in the presence of NAPL (Figure 3.3). PFBA, PFPeA, and PFHxA were again exceptions. For these compounds, sorption again increased over all or part of the concentration range (Figure 3.3, Figure B.3).



(a) (b)

Figure 3.3: Sorption of PFBA (squares) and PFOS (circles) in the presence (closed symbols) and absence (open symbols) of TCE to soils A and B. Solid lines are fitted Freundlich isotherms for closed symbols and dashed lines are fitted Freundlich isotherms for open symbols. Error bars represent relative error in triplicate measurements of C_s.

Multiple factors may influence PFAA sorption in the presence of NAPL [19]. Previous work with PAHs and PCBs indicated an increase in sorption when oil is present above the critical separate phase concentration (CSPC), which is the concentration (C_{NAPL}) where oil will exist as a NAPL, typically at 1000-3000 mg/kg [19, 30]. The exact CSPC is dependent on the soil f_{oc} because a NAPL will only form if the soil organic carbon is saturated with NAPL components: more NAPL is required in systems with higher f_{oc} [19]. CSPCs typically occur at approximately 15% of oil in organic carbon (w/w)[19]. Based on an f_{oc} of 1.7% for soil A, the CSPC would be approximately 255 mg/kg, which is approximately 400 times lower than the C_{NAPL} employed here. Above the CSPC, NAPL may serve as an additional sorbent either by bulk partioning of PFAAs into NAPL or to the NAPL-water interface [19, 30]. NAPL may also reduce sorption by blocking access to organic matter sorption sites [19, 30]. A combination of these mechanisms may explain the varied effects of NAPL on PFAA sorption. PFAA sorption to soil A without NAPL was low (i.e. PFOS Log K_d=0.72) and in some cases fairly nonlinear (i.e. PFOS n=0.77±0.05; Table B.8) suggesting different types of organic matter sorption sites are available, including high affinity sites in the lower end of the isotherm and lower affinity sites in the upper end. In the lower end of soil A isotherms, PFAA sorption in the presence of NAPL was unchanged or slightly decreased, suggesting PFAAs either had access to an adequate number of high affinity sites or, in some cases, were blocked from sorption sites by NAPL. In the upper end of the isotherms, small increases in sorption were observed when TCE was present and isotherm linearity generally increased (i.e. PFOS n=1.01±0.01; Table B.8). Consistent with the lower f_{oc} of soil A, these data suggest NAPL acted as a sorbent and increased the number of sorption sites at high concentrations of PFAAs.

Sorption of PFAAs to soil B without NAPL was stronger (i.e. PFOS Log K_d=1.54) than to soil A, consistent with its higher f_{oc}. Addition of TCE to soil B caused no change or decreases in PFAA sorption, with only minor changes in linearity (i.e. PFOS+TCE n=0.85±0.03 vs 0.90±0.05 without TCE). Where PFAA sorption was unchanged by NAPL, an adequate number of higher affinity sorption sites were likely still present. Decreases in sorption were chain-length dependent, with the magnitude of sorptive decreases increasing from C7 to C9 PFCAs, and were likely the result of TCE blocking access to organic matter sorption sites in soil B. This suggests that blocking of sorption sites by NAPL has more of an impact on stronger sorbing PFAAs. These results are consistent with higher f_{oc} of soil B. Because higher affinity sorption sites were more abundant in this soil and isotherms fairly linear, NAPL provided no additional capacity as a sorbent and in fact sometimes reduced the sorptive capacity of the soil, likely through blocking of organic matter sites.

As with sorption in the absence of NAPL, changes in sorption of short-chain PFAAs in the presence of TCE were unexpected. Sorption of PFBA, PFPeA, and PFHxA generally increased over the entire concentration range in soils A and B (Figure 3.3, Figure B.3). Previous work found affinity of smaller PAHs for weathered oils was higher than for larger PAHs, and similar results were found for PCBs [18, 19]. The authors hypothesized a steric effect wherein smaller molecules were better able to fit into the complicated oil matrix [18, 19]. Therefore, it is possible that trends observed in sorption of PFBA, PFPeA, and PFHxA to TCE are a steric effect, though TCE is a pure phase NAPL not subject to change during weathering. Some have proposed that sorption when unweathered NAPL is present can be described as the linear sum of sorption to the soil and sorption to NAPL as follows (3.2) [19]:

$$K_d = f_{oc}K_{oc} + f_{NAPL}K_{NAPL} \tag{3.2}$$

where f_{NAPL} is the fraction of NAPL in the soil and K_{NAPL} is the NAPL-water partition coefficient. Moreover, sorptive losses to different kinds of unweathered NAPLs should be similar, suggesting K_{NAPL} values will be consistent among varying NAPL types [19, 31]. This study measured single-point K_{NAPL} values in NAPL-water batch systems for both DD and TCE (Table B.11). Overall, sorption of PFAAs to NAPL appears to have a chain-length dependent trend; however the trend is somewhat unclear for C5-C8 PFAAs (Figure B.4). Additionally, K_{NAPL} values for TCE and DD were not statistically different, suggesting NAPL type may not be a determining factor in PFAA NAPL sorption. K_{NAPL} values for TCE and DD were used with K_{oc} values to calculate predicted K_d values for PFCAs in soil A at aqueous PFAA concentrations of 0.35 mg/L, where sorptive increases were observed in the presence of TCE (Figure B.5). In general, equation 3.2 under predicted sorption in the presence of NAPL. Many values were within a factor of two of those measured; however K_{NAPL} values under predicted sorption of long-chain PFAAs by an order of magnitude or more. These results suggest that even though NAPL is present as a separate phase in these systems, pure NAPL-water partitioning cannot be used to predict sorptive increases of PFAAs in soil A.

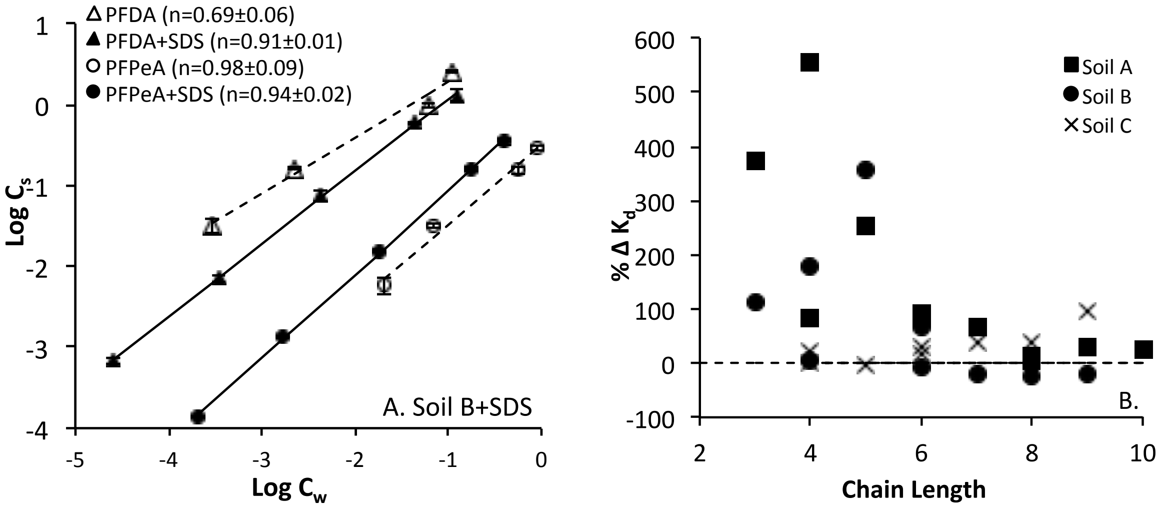
Previous work reported Log K_{NAPL} values of 4.16 L/kg for PFOS in crude oil using equation 2 at a PFOS concentration of 5µg/L [13]. Though this would account for any soil-NAPL-water interactions, it is much higher than the Log K_{NAPL} of -0.18 L/kg for TCE measured herein. If equation 2 is solved for K_{NAPL} , the resulting values are higher than those measured in water-NAPL systems. For example, at aqueous PFAA concentrations of 0.35 mg/L, the calculated PFOS Log K_{TCE} value is 2.0 L/kg. Though this is still lower than values reported for crude oil, this value is more consistent with what was observed previously. NAPL or soil type may help explain additional differences between the two studies. While this study found similarities in PFAA sorption to DD and TCE, it should be noted that crude oil and NAPLs present in the environment are often complex mixtures that change composition with weathering, and some organic contaminants have a higher affinity for weathered vs. unweathered NAPL [18, 19]. Overall, PFAA transport in subsurface environments with NAPL may not depend primarily on NAPL type, but rather soil f_{oc}.

3.3.3 Impacts of SDS

PFAA isotherms were measured in soils A, B, and C in the presence of 100 mg/L SDS, results were fit with the Freundlich isotherm, and K_d values interpolated at PFAA concentrations of 0.35 mg/L (Table B.8). In the presence of SDS, PFAA sorption was essentially unchanged in soil C (Figure 3.4, Figure B.6), and the impacts of SDS on PFAA sorption were chain length-dependent in soils A and B (Figure 3.4, Figure B.6). In soils A and B, SDS caused increases in PFAA sorption in short-chain PFAAs such as PFPeA. These increases diminished in magnitude with increasing chain-length such that there was no change in sorption for some compounds such as PFOA, and decreases in sorption were observed with SDS for the largest PFAAs such as PFDA (Figure 3.4).

SDS may influence PFAA sorption in multiple ways. Even at concentrations below the CMC, surfactants and organic compounds may have a partition-like interaction between nonionic portions of the surfactant and organic compounds [22, 32]. These interactions may take place between the organic compound and surfactant in solution, leading to an increase in apparent solubility and a decrease in sorption. This has been observed with DDT and trichlorobenzene in the presence of multiple nonionic surfactants and with PFOS in the presence of the anionic surfactant sodium dodecylbenzene sulfonate [32, 33]. At concentrations of about 0.001-0.01 of the CMC, surfactants may also form hemimicelles near a solid surface [24], which, when coupled to sorbate interactions with surfactants (including mixed hemimicelle formation), may lead to increases in apparent sorption of the sorbate [22]. Surfactants may also decrease sorption if they compete for sorption sites.

SDS led to increases in sorption of PFBA, PFPeA, PFHxA, PFHpA, and PFBS in the A and B soils as well as PFOA in the B soil. Because SDS was present at concentrations where hemimicelle formation is possible, increases in sorption may be due to mixed hemimicelle formation with SDS. SDS had no effect on, and in some cases decreased, sorption of long-chain PFAAs in A and B soils. Specifically, sorption decreased for PFNA, PFDA, and PFOS. Sorption of PFHxS in soil A and PFOA and PFHxS in soil B was unchanged. This study did not directly measure PFAA solubility in the presence of SDS; however preliminary control experiments with PFAAs and varying concentrations of SDS (i.e., no soil) implied little impact of SDS on aqueous PFAA concentrations (Figure B.8). Hemimicelle formation with SDS may play a role in sorptive increase of short-chain PFAAs, but it is possible that formation of mixed hemimicelles with SDS is not favorable for larger PFAAs due to increased oleophobicity of the larger fluorocarbon tail. Finally, semi-quantiative SDS sorption isotherms indicate a log K_{oc} for SDS of approximately 5 vs. 2.8 for PFOS (Figure B.7), so it is possible SDS outcompetes stronger-sorbing, long-chain PFAAs. Where sorption was unchanged, it is likely that multiple competing processes result in no net change to overall PFAA affinity for the soil. Such was likely for soil C, for which no changes in PFAA sorption were observed with SDS. Soils A and C have similar f_{oc}, so similar changes to sorption with SDS might be expected; however, soil C is positively charged, which may lead to increased importance of electrostatic effects. For example, the anionic sulfonate group of SDS may interact electrostatically with the soil C surface, such that sorption is a combination of interactions with organic matter and the positive soil C surface. This combination of mechansims may dilute SDS distribution in the soil matrix and reduce potential for hemimicelle formation. These results indicate nonfluorinated, anionic AFFF components may have a chain-length dependent impact on PFAA transport and, importantly, may slow transport of relatively more mobile PFAAs in negatively charged soils. The degree of impact will vary with soil f_{oc}.



(a)

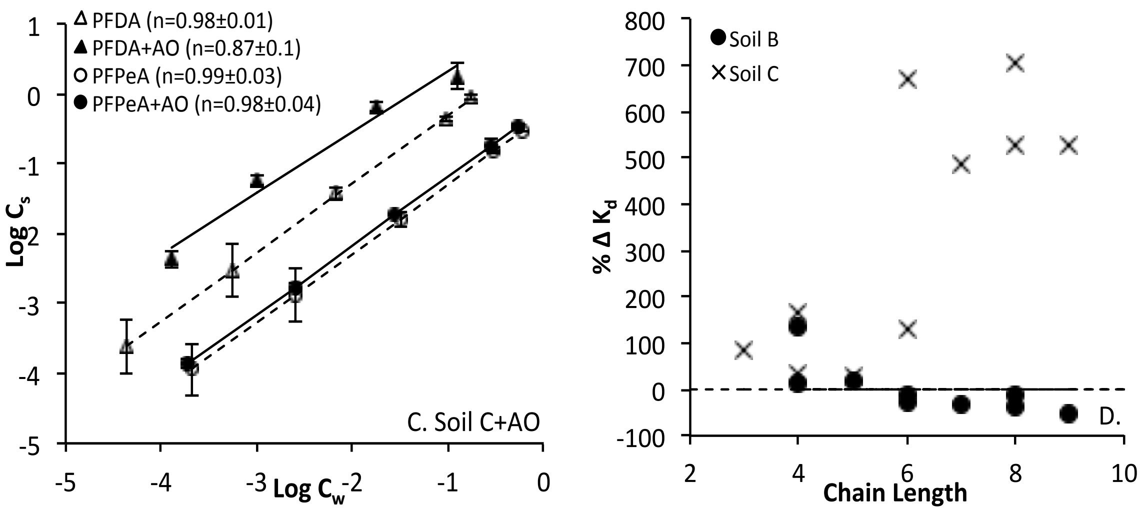
(b)

Figure 3.4: A.) Sorption of PFPeA (circles) and PFDA (triangles) in the presence (closed symbols) and absence (open symbols) of SDS to soil B. B.) The percent change in K_d values between systems with no SDS and 100 mg/L SDS vs. PFAA chain length in soils A, B, and C. In all isotherms, solid lines are fitted Freundlich isotherms for closed symbols and dashed lines are fitted Freundlich isotherms for open symbols, and error bars represent relative error in triplicate measurements of C_s.

3.3.4 Impacts of AO

PFAA sorption was also measured in soils A, B, and C in the presence of 100 mg/L AO, results were fit with the Freundlich isotherm, and K_d values interpolated (Table B.8). Addition of AO led to sorption increases for PFPeA and PFHxA in soils A and B. Addition of AO did not lead to significant changes to sorption of the remaining PFAAs in soil B, excepting PFBA where effects were concentration dependent and PFDA, where a decrease in sorption was observed (Figure 3.5, Figure B.9). In soil A, concentration-dependent changes to sorption of all remaining PFAAs were observed when AO was added (Figure B.9). In soil C, chain-length dependent effects were observed (Figure 3.5). PFBA and PFPeA sorption was unchanged, but increases in sorption were observed for the longer-chain PFAAs.

As with SDS, AO may influence PFAA sorption via changes to solubility, hemimicelle formation, or competitive sorption. Aqueous PFAA measurements in control (no soil) reactors with PFAA and varying amounts of AO were used to understand AO-PFAA interactions in solution. As the aqueous concentration of AO increased, aqueous PFAA concentrations decreased, with larger differences observed for longer chain length PFAAs (Figure B.10). This implies a greater affinity of longer-chain PFAAs for interfaces when AO is present. If this mechanism was the dominant process impacting PFAA sorption to AO-contaminanted soils, sorption would likely increase with increasing PFAA chain length in the presence of AO. This was observed in soil C, suggesting amphoteric AO does not interact with a positive surface in a manner that elicits competitive sorption effects. As mentioned previously, matrix interference during analysis prevented the evaluation of AO K_{oc} values and thus its competitive potential. Competition, however, would not completely explain changes in PFAA sorption observed in soils A and B with AO. Concentration-dependent effects in soil A suggest that, similar to NAPL, AO is outcompeting PFAAs for higher energy sorption sites at the lower end of the isotherm. However, at the upper end of the isotherm, sorbed AO may create an environment favorable for PFAA sorption, possibly through formation of mixed hemimicelles. This would explain increases in linearity of PFAA isotherms (Table B.8) and increases in sorption of PFAAs in the upper end of the isotherm where lower affinity sites are the only remaining sites in soil A. This effect is likely not apparent in soil B due to the higher f_{oc} and greater number of high affinity sites available for sorption. Collectively, these data suggest that amphoteric AFFF surfactants could have a varied effect on groundwater transport of PFAAs depending on PFAA chain length as well as surface charge and soil f_{oc}.



(a) (b)

Figure 3.5: A.) Sorption of PFPeA (circles) and PFDA (triangles) in the presence (closed symbols) and absence (open symbols) of AO to soil C. B.) The percent change in K_d values between systems with AO and 100 mg/L AO vs. PFAA chain length in soils B and C. In all isotherms, solid lines are fitted Freundlich isotherms for closed symbols and dashed lines are fitted Freundlich isotherms for open symbols, and error bars represent relative error in triplicate measurements of C_s.

3.4 Implications

Impacts of co-contaminants on groundwater transport potential of PFAAs at AFFF-impacted sites are quite complex and not easily generalized. They may depend on such factors such as f_{oc}, PFAA chain length, PFAA concentration, and solid phase surface charge. To illustrate this potential variability, K_d values were used to calculate retardation factors (R_f) for soil A at two PFAA concentrations (1 and 500 $\mu g/L$, Table 3.1) as follows (3.3):

$$R = 1 + \frac{\rho_b}{\theta} K_d \tag{3.3}$$

where ρ_b is the soil bulk density (1.14 g/cm^3) and θ is the porosity (0.53) [24]. R_f provide an indication of contaminant transport relative to groundwater with a value of one indicating conservative transport. In the absence of co-contaminants, PFAA transport is expected to be chain-length dependant, as observed in previous studies at sites receiving land application of PFAA-containing municipal biosolids [10, 34], with the exception of PFBA and PFPeA. The R_f values for the smallest PFAAs generally increase in the presence of TCE, SDS, or AO, indicating that these co-contaminants may reduce smaller PFAA groundwater transport. For other PFAAs, the effect of co-contaminants on R vary based on the PFAA concentration. R_f values for PFOS at 1 $\mu g/L$ decrease when TCE is present, though the opposite is seen at PFOS concentrations of 500 $\mu g/L$, where R_f values increase when TCE is present. Similar trends are observed with SDS and AO. Various mechanisms may be responsible for sorptive changes, and until these mechanisms are better understood, it may be necessary to have a detailed understanding of site characteristics to predict PFAA transport. Further work is also needed to understand impacts to PFAA transport when multiple co-contaminants are present under nonequilibrium conditions. Given the complex nature of PFAA and co-contaminant interactions and the recent push towards regulation, these results emphasize the need for additional research on subsurface transport of PFAAs.

3.5 Acknowledgements

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Table 3.1: Soil A R_f for select PFAAs in the presence and absence of co-contaminants.

	R 1 $\mu g/L$	R+TCE $1\mu g/L$	R+SDS $1\mu g/L$	R+AO 1 $\mu g/L$	R 500 $\mu g/L$	R+TCE 500 $\mu g/L$	R+SDS 500 $\mu g/L$	R+AO 500 $\mu g/L$
PFBA	2.67	4.06	2.75	3.17	1.33	2.91	2.69	3.83
PFPeA	1.67	4.06	3.58	1.89	1.25	2.57	2.69	3.52
PFHxA	1.52	1.64	3.26	1.52	1.39	2.04	2.35	2.77
PFHpA	2.26	1.75	2.68	1.58	1.77	2.08	2.50	2.63
PFOA	3.18	4.27	3.36	1.73	2.06	2.70	2.80	4.40
PFNA	7.54	6.40	4.40	3.40	2.99	3.73	3.33	6.39
PFDA	32.82	18.80	11.58	10.14	5.42	9.45	7.14	18.13
PFBS	3.34	2.78	3.46	2.53	1.72	2.43	2.37	3.70
PFHxS	4.25	2.93	3.76	2.75	1.95	2.71	2.83	4.21
PFOS	18.47	9.54	9.08	12.15	5.27	9.95	5.63	10.58

Concentrations of 1 and 500 $\mu g/L$ refer to the aqueous concentration of PFAA modeled. R is the retardation factor. R+ is the retardation factor in the presence of the respective co-contaminant.

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CHAPTER 4

TRANSPORT POTENTIAL OF PERFLUOROALKYL ACIDS (PFAAS) AT AFFF-IMPACTED SITES: 1-DIMENSIONAL COLUMN STUDIES

A paper being prepared for publication

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Abstract.

One-dimensional (1-D) advective transport of a suite of perfluoroalkyl acids (PFAAs) was studied with miscible displacement experiments in a variety of solid phases under conditions relevant to aqueous film-forming foam (AFFF)- impacted sites. Specifically, 1-D column transport of PFAAs in soils, aquifer sediment, and sand were studied under a variety of flow rates at concentrations relevant to those detected at AFFF-impacted fire protection training areas (FPTAs) to determine if advective transport can be described by an equilibrium assumption. Previous batch studies suggested that PFAA transport would be chain-length and organic carbon (f_{oc}) dependent for longer chain (>6 CF_2) compounds. Low flow column experiments (0.032-0.067 cm/min) confirmed behavior with chain length but trends with foc were unclear indicating possible nonequilibrium conditions. Previous work showed anomalous behavior of perfluorobutanoate (PFBA) and perfluoropentanoate (PFPeA; log K_{oc} = 1.88 and 1.37 respectively) wherein equilibrium sorption partition coefficients (K_{deq}) were similar to that of perfluorooctanoate (PFOA; log K_{oc}=1.89). This anomalous behavior was confirmed under advective conditions. Log Koc values measured for PFBA, PFPeA, and PFOA in one soil were 1.5, 1.3, and 1.5 respectively. Measured column sorption coefficients

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(Kdcol) were smaller than batch equilibrium sorption coefficients (K_{deq}) for some PFAAs and solid phases further suggesting potential for nonequilibrium conditions. Flow interruption of high-flow columns (0.48-0.70 cm/min) confirmed rate-limited sorption of PFAAs under advective conditions. Kinetic parameters obtained from low flow experiments yielded mass transfer coefficients of 2.53x 10-8 to 4.68 x 10-3 min^{-1}; however rates were both velocity and organic carbon dependent. Rates decreased with increasing velocity suggesting rate-limited behavior (e.g. tailing) will be exaggerated at lower flow rates. Rates increased with decreasing f_{oc} suggesting that molecular diffusion into the organic matter matrix is at least partially responsible for rate-limited behavior. Rate-limited behavior may also reflect the impacts of pore diffusion particularly in low foc solid phases. The results of this work show that using an equilibrium assumption to model groundwater transport of PFAAs may lead to poor estimates of plume size and travel time for some PFAAs and in some solid phases. This has important implications as the scientific and regulatory community moves towards risk assessment and remediation of these compounds.

4.1 Introduction

Perfluoroalkyl acids (PFAAs) have a wide variety of uses including nonstick coatings, stain-repellants, paper packaging, and aqueous film-forming foams (AFFF) [1]. Used in fighting fuel fires, AFFF is often utilized by fire-fighting facilities, the hydrocarbon industry, and the military[2]. Because of their widespread environmental distribution, and potential for toxicity and bioaccumulation [3, 4], PFAAs are the subject of increased study, and the U.S. Environmental Protection Agency has issued provisional health advisories for perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS) in drinking water of 0.4 and 0.2 µg/L, respectively [5]. Repeat use of AFFF at fire protection training areas (FPTAs) has led to comparatively high occurrence of PFAAs in groundwater at $\mu g/L$ to mg/L levels [6–8], so it is important to understand transport of these compounds in the saturated zone. Interactions with aquifer sediment via sorption will be fundamental in determining the fate of PFAAs in groundwater. Previous work has focused on equilibrium sorption studies of

PFAAs to sediment, biosolids, and mineral surfaces and under conditions specifically relevant to AFFF-impacted FPTAs [9–12]; however studies are limited with respect to advective PFAA transport.

AFFF formulations can include solvents, fluorinated surfactants, and hydrocarbon surfactants that may be released during fire training exercises along with other potential co-contaminants such as fuel components and chlorinated solvents [6, 13]. Equilibrium sorption of PFAAs under conditions relevant to AFFF-impacted facilities has been studied. Though results of these studies may be used to make initial predictions of groundwater transport, PFAA behavior may differ in an advective transport scenario particularly as ideal, equilibrium conditions may not apply. To the best of our knowledge, there are no prior studies determining the extent to which equilibrium PFAA behavior translates to an advective scenario.

In ideal transport, sorption is presumed to be instantaneous under the assumption that it occurs at much faster rates than the residence time of groundwater [14]. However, sorption and desorption can be rate-limited [14]. Various mechanisms have been proposed to explain this behavior, including interactions with organic matter [15]. Rate-limited transport is sometimes characterized by early breakthrough and/or tailing of compounds in column breakthrough curves (BTCs). Flow interruption column experiments are useful in making a definitive determination of rate-limited sorption [16]. These are miscible displacement experiments during which flow with the solute of interest is pumped through a column, stopped for a period of time to allow conditions to progress towards sorbate-sorbent equilibrium, and then resumed [16]. Flow interruption experiments are also often conducted at high porewater velocities to experimentally exaggerate any kinetic effects. If aqueous concentrations decrease during the stop flow period, this can indicate physical or chemical nonequilibrium. Bromide tracer tests are used to verify the absence of physical nonequilibrium in the column such that drops in concentration should confirm ongoing (e.g. rate-limited) sorption.

The objective of this work was to further the understanding of transport behavior of perfluoroalkyl carboxylates (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs) in groundwater by investigating advective transport in 1-dimensional (1-D) column transport experiments and comparing the results to previous equilibrium sorption studies. We conducted low flow column experiments at environmentally relevant pore-water velocities to determine if previously measured batch equilibrium data could be used to accurately describe PFAA transport. Flow interruption experiments were completed at higher pore water velocities to determine if rate-limited sorption impacted PFAA transport. Results of flow interruption and low flow experiments were used to determine mass transfer coefficients describing rate-limited transport. Lastly, the results of this study were used to make initial predictions of the implications to remediation of PFAAs.

4.2 Materials and Methods

The following is a summary of the materials and methods used in this work.

4.2.1 Materials

Calibration standards of perfluorobutanoate (PFBA), perfluoropentanoate (PFPeA), perfluorohexanoate (PFHxA), perfluoroheptanoate (PFHpA), PFOA, perfluorononanoate (PFNA), perfluorodecanoate (PFDA), perfluorobutanesulfonate (PFBS), perfluorohexanesulfonate (PFHxS), and PFOS, as well as stable-isotope surrogate standards (Table 4.1) were purchased from Wellington Laboratories. Spiking solutions for all experiments were prepared from standards of PFCAs and PFSAs purchased from Sigma-Aldrich. Stock solution of calibration standards, spiking standards (purity-corrected), and surrogate standards were prepared in a 70/30 (v/v) methanol/aqueous solution. Unless otherwise noted, all experiments utilized a spiking solution containing all 10 PFAAs. Potassium bromide was used as a nonreactive tracer. Unless otherwise specified, all other chemicals were of reagent grade and were purchased from Fisher Scientific, Mallinckrodt Chemicals, or Sigma Aldrich.

Table 4.1: PFAAs and surrogate standards used in this study

Analyte	Molecular Weight	Tail Length	Surrogate Standard
PFBA	213.03	3	$[^{13}C_4]$PFBA
PFPeA	263.04	4	$[^{13}C_3]$PFPeA
PFHxA	313.05	5	$[^{13}C_2]$PFHxA
PFHpA	363.05	6	$[^{13}C_4]$PFHpA
PFOA	413.06	7	$[^{13}C_4]$PFOA
PFNA	463.07	8	$[^{13}C_5]$PFNA
PFDA	513.08	9	$[^{13}C_2]$PFDA
PFBS	299.09	4	$[^{18}O_2]$PFHxS
PFHxS	399.11	6	$[^{18}O_2]$PFHxS
PFOS	499.12	8	$[^{13}C_4]$PFOS

Solid phases used in this study were selected to represent a variety of geochemical and physical characteristics (Table 4.2). A loamy sand (A) and loam (B) were purchased from Agvise Laboratories and have been used by the authors in previous batch equilibrium sorption studies [10]. An alluvial aquifer sediment (C) was also used. In addition, three sands of varying grain sizes were used. The silica sand size ranges were 0.841 to 1.68 mm (12/20), 0.595 to 0.841 mm (20/30), and 0.297 to 0.420 mm (40/50) (Accusands, Unimin Corp., Ottawa, MN), and have been previously characterized [17]. Soils A and B were air dried and sieved (2mm) prior to use in columns. Column aqueous phase was artificial groundwater (AGW) made by modifying deionized water with ions typically found in groundwater and was used as the aqueous phase for all experiments (Table 4.3).

4.2.2 Column Design

All column experiments were conducted in 2.5 X 15 cm (No. 42400-2515) and 2.5 X 5 cm (No. 420400-2505) Kontes ®, glass chromatography columns with a fritted, glass bed support in the influent end of the column. Columns were packed in 1cm increments. Each increment was vortexed and tamped to establish uniform column properties.

Table 4.2: Summary of PFAA experimental conditions

Solid Phase	f_{oc}^{1}%	Sand %	Silt %	Clay%	ρ_b (g/cm^3)	pH	K (mg/kg)	Ca (mg/kg)	Mg (mg/kg)	Na (mg/kg)	H (mg/kg)	Fe^2 (g/kg)	Al^2 (g/kg)
Loamy Sand	1.7	81	1	9	1.14	6.1	319	1084	171	11	33	2.21	0.93
Loam	4.5	33	42	25	0.92	7.8	888	4418	607	14	21	6.14	1.67
[1]Walkley-Black [2]Citrate-Bicarbonate-Dithionite (CBD) extractable NM = not measured													

Glass wool and 1 mm glass beads were used as additional bed support at each end of the column to stabilize column packing material and establish uniform influent distribution across the bed during column operation. Following packing, columns were saturated with CO_2 to remove residual air and subsequently saturated with AGW in up-flow mode. After the completion of all column experiments, Br- tests were repeated to ensure that column properties remained consistent throughout the duration of the experiments.

Table 4.3: Composition of artificial groundwater

Component	Concentration (mg/L)	Concentration (mM)
$MnSO_4 \bullet H_2O$	1	0.01
Na_2SO_4	180	1.27
$NaCl$	113	1.93
$NaHCO_3$	40	0.48
HCl	pH to 6.5	N/A

Column bulk density and porosity were determined gravimetrically (Table 4.4). Columns were attached to an Ismatec ®, high accuracy peristaltic pump. All columns were operated in up-flow mode and column influent/effluent samples were collected from 3-way valves installed at each end of the column (Table 4.3).

4.2.3 Bromide Tracer Tests

Nonreactive bromide (Br-) tracer tests were completed to determine hydrodynamic transport conditions (Table 4.5) in all columns and probe the potential for physical nonequilibrium in flow interruption columns. Br- was measured with a Cole-Parmer Br- combination electrode connected to a Thermo Orion 420 A+ pH/mV/ORP meter. Bromide breakthrough curves were fit as described below. Br- solutions were prepared in AGW and injected into columns until relative concentrations (C/C_0) of the effluent reached one. In some cases, Br- tests were conducted at higher pore water velocities than subsequent PFAA experiments since hydrodynamic properties should be independent of flow rate.

Table 4.4: Summary of PFAA experimental conditions

Column	Packing Material	Column Length (cm)	Darcy Velocity (cm/min)	Pore Water Velocity (cm/min)	Bulk Density (g/cm^3)	Porosity	Experiment Type
1	Soil A	5	0.031	0.053	0.99	0.58	Low flow
2	Soil B	5	0.020	0.032	0.76	0.63	Low flow
3	Soil C	5	0.020	0.045	1.34	0.45	Low flow
4	40/50	5	0.031	0.067	1.45	0.46	Low flow
5	Soil A	15	0.286	0.476	0.99	0.60	Flow interruption
6	Soil C	15	0.286	0.697	1.44	0.41	Flow interruption
7	40/50	15	0.286	0.664	1.42	0.43	Flow interruption

For low flow experiments, columns were subsequently flushed with AGW until Br- concentrations returned to background levels. For flow interruption experiments, flow was discontinued for a period of 24-hrs to determine if C/C_0 would change during the stop flow period, indicative of physical nonequilibrium (Table 4.6). After flow interruption, Br- input was continued for approximately one pore volume after which columns were flushed with AGW to reach background Br- levels.

Table 4.5: Summary of Br- experimental conditions

Column	Influent Br- Concentration (mg/L)	Darcy Velocity (cm/min)	Pore Water Velocity (cm/min)	Longitudinal Dispersivity (cm)	Bromide Mass Recovery
1	95.2	0.102	0.176	0.543	97%
2	95.2	0.112	0.178	0.162	92%
3	95.2	0.112	0.249	0.078	104%
4	95.2	0.102	0.222	0.067	106%
5	519.7	0.286	0.476	0.325	100%
6	519.7	0.286	0.697	0.192	110%
7	519.7	0.286	0.664	0.272	103%

Table 4.6: Design of flow interruption experiments

Experimental Step	Br-	PFAA
Initial pulse	to C/C_0=1	to C/C_0=1
Stop flow period	24 hrs	36 hrs
Post interruption pulse	to C/C_0=1	to C/C_0=1
AGW flush	to C/C_0=1	to C/C_0=1

4.2.4 PFAA Column Tests

Two types of column experiments were utilized in this study to investigate PFAA transport. Low flow column experiments (columns 1-4) were utilized to study PFAA transport at environmentally relevant groundwater flow conditions. Flow interruption experiments (columns 5-7) were used to determine the impact of rate-limited sorption on PFAA transport (Table 4.6). Column influent consisted of a PFAA mixture (each PFAA at a nominal concentration of 5 µg/L) prepared in AGW. Depending on solid phase type, a pulse of 19-37 pore volumes of spiked AGW was injected at varying flow rates (Table 4.4) into columns 1-4 for low flow experiments. Pulses of 18-23 pore volumes of spiked AGW were injected into columns 5-7 at a Darcy velocity of 0.29 cm/min (Table 4.4) after which flow was stopped for a period of 36 hrs. Following the flow interruption period, an additional 3-4 pore volumes of spiked AGW were injected into columns. Injection volumes for all experiments were selected to ensure that the entire suite of PFAAs reached effluent C/C_0=1. Following injection of spiked AGW, all columns were then flushed with AGW until PFAA concentrations returned to background.

4.2.5 Sample Preparation and Analysis

Column influent and effluent samples were collected manually in 2.0 mL polypropylene, microcentrifuge tubes. Tubes were weighed prior to and after sample collection to determine the exact volume of sample collected. An additional aliquot of isopropanol was then added to comprise 9% of the aqueous volume in the tube. Prior to sample preparation, samples were centrifuged (Fisher Scientific, accuSpin Micro 17) at 17,000 relative centrifugal force (RCF) for 30 minutes. An aliquot of sample was then used to prepare a 1500 µL final sample for analysis in an autosampler vial. Autosampler vials contained 1350 μL of column effluent and 150 μL of 70/30 containing 0.3 ng surrogate standard (Table 4.1). Samples were analyzed directly via liquid chromatography tandem mass spectrometry (LC-MS/MS) using methods modified from previous studies [10, 12, 18]. An Applied Biosystems 3200 mass spectrometer (MDS Sciex) was used to monitor two transitions for each analyte. Quantitation was performed using Analyst software (AB Sciex). Limits of quantitation were analyte, matrix, and run-dependent but were approximately 2-9 ng/L. All values reported are corrected for recovery of surrogate standards, which were generally greater than 60% for all samples and matrices.

4.2.6 Data Analysis

Breakthrough curves (concentration vs. time) for Br- and PFAAs were fit with a numerical solution to the advective-dispersive equation (ADE) using HYDRUS-1D [19]. Longitudinal dispersivities were determined from inverse fits of bromide tracer tests and utilized when modeling breakthrough of PFAAs. HYDRUS 1-D was used in both inverse and forward modeling of PFAA transport. Column sorption coefficients (K_{dcol}, L/kg) were obtained by inverse fits of PFAA breakthrough curves and were compared to equilibrium sorption coefficients (K_{deq}, L/kg). K_{deq}, L/kg for Soils A and B were calculated based on Freundlich sorption coefficients (K_f) and linearity values (n) collected in previous work that utilized the same soils [10]. The range of aqueous concentrations (C_w) detected in each column was used to predict solid phase concentrations (C_s) as follows (4.1):

$$C_s = K_f C_w^n \tag{4.1}$$

Resulting C_s values and measured C_w values were used to calculate concentration-specific K_{deq} values as follows (4.2):

$$K_d = \frac{C_s}{C_w} \tag{4.2}$$

For Soil C, K_{deq} were not available; however it is assumed that since organic carbon content is the primary factor influencing PFAA sorption when organic matter is present that Soil C K_{deq} values could be approximated using K_{oc} values measured in Soil A. Aqueous concentrations from column 3 were coupled with K_f and n values for Soil A to calculate a range of K_{deq} values. These were then normalized to the f_{oc} of Soil A to calculate concentration-specific organic carbon partition coefficients (K_{oc}) values as follows (4.3):

$$K_{oc} = \frac{K_{deq}}{f_{oc}} \tag{4.3}$$

These K_{oc} values were then multiplied by the f_{oc} of Soil C to estimate K_{deq} values for that solid phase. K_{deq} for 40/50 sand were obtained from single-point K_d measurements made at an initial C_w of 20 $\mu g/L$ using methods described in previous work [12]. Column and equilibrium K_d values were used to calculate linear retardation factors for both equilibrium (R_{eq}) and column (R_{col}) scenarios using the following equation (4.4):

$$R = 1 + \frac{K_d \rho_b}{\theta} \tag{4.4}$$

where ρ_b is soil bulk density and θ is porosity.

Flow interruption and low flow BTCs that exhibited rate-limited sorptive behavior were fit with a 2-site sorption model that assumes sorption sites can be divided into two fractions, and which is incorporated into the ADE [20]. Sorption (C_s, mg/kg) onto type-1 sites (C_s^e) is assumed to be instantaneous and sorption onto type-2 sites (C_s^k) is assumed to be time-dependent. For type-1 and type-2 sites respectively (4.5, 4.6):

$$C_s^e = fC_s = fK_dC_w \tag{4.5}$$

$$C_s^k = (1-f)C_s = (1-f)K_dC_w \tag{4.6}$$

where f is the fraction of sorption sites assumed to be at equilibrium with the solute. The sorption rate for type-1 sites is assumed to be linear and instantaneous and can be described as follows (4.7):

$$\frac{\partial C_s^e}{\partial t} = f\frac{\partial C_s}{\partial t} \tag{4.7}$$

Sorption onto type-2 sites is assumed to be a first order rate process (4.8):

$$\frac{\partial C_s^k}{\partial t} = k[(1-f)K_dC_w - C_s^k \tag{4.8}$$

where k is the first order rate constant (min^{-1}). The only difference in the application of this model to flow interruption vs. low flow data is that HYDRUS-1D modeling of flow interruption data incorporated a time period during which no advective processes occurred.

4.2.7 Quality Assurance/Quality Control

To ensure that the hydrodynamic properties were not altered during PFAA experiments, bromide tracer tests were repeated after the completion of column experiments and resulting BTCs fitted using parameters obtained in the initial tracer tests to ensure that these parameters still described transport within the column. Method of moments analysis was used to calculate mass recovery of all bromide (Table 4.5) and PFAA BTCs (Table 4.7).

Table 4.7: Mass recoveries from PFAA column experiments

Analyte	Column 1	Column 2	Column 3	Column 4	Column 5	Column 6	Column 7
PFBA	105%	102%	100%	97%	110%	101%	101%
PFPeA	106%	98%	105%	102%	113%	103%	107%
PFHxA	101%	105%	96%	104%	109%	105%	94%
PFHpA	103%	103%	94%	107%	107%	98%	99%
PFOA	95%	105%	95%	104%	112%	110%	102%
PFNA	109%	98%	92%	104%	108%	101%	93%
PFDA	92%	66%	97%	106%	108%	97%	92%
PFBS	99%	103%	99%	105%	107%	94%	97%
PFHxS	103%	96%	105%	102%	109%	98%	96%
PFOS	92%	72%	105%	100%	109%	94%	100%

4.3 Results and Discussion

The following summarizes results and provides a discussion of results found in this work.

4.3.1 Low Flow PFAA Transport

Equilibrium studies of PFAA groundwater transport potential indicate that PFAA retardation should be chain-length dependent for longer chain ($\geq$C6) PFAAs and should increase with increasing f_{oc} [9, 12]. Overall chain-length dependent trends were observed in all low flow column experiments, with the largest PFAAs such as PFDA showing the strongest retardation, but the trend was somewhat unclear for PFHxA, PFHpA, and PFOA (Figure 4.1, 4.8, Table 4.8). Breakthrough of these compounds was sometimes simultaneous, implying that nonequilbrium transport may impact their transport. During equilibrium studies, short-chain PFAAs ($<$C6) did not follow chain-length dependent trends in Soils A or B, indicating that other factors such as steric and ion exchange effects may play a role in their sorption [12]. Similar exceptions were observed in Soil A during column studies (Table 4.8, Table 4.8). Equilibrium studies of PFAA groundwater transport potential also indicate that retardation should increase with increasing solid phase f_{oc} for long-chain PFAAs [9, 12]. Breakthrough curves of PFNA, PFDA, and PFOS in Soils A-C showed breakthrough that was dependent on f_{oc} (**??**, Table 4.8, Table 4.8). Smaller compounds did not show a trend with f_{oc}

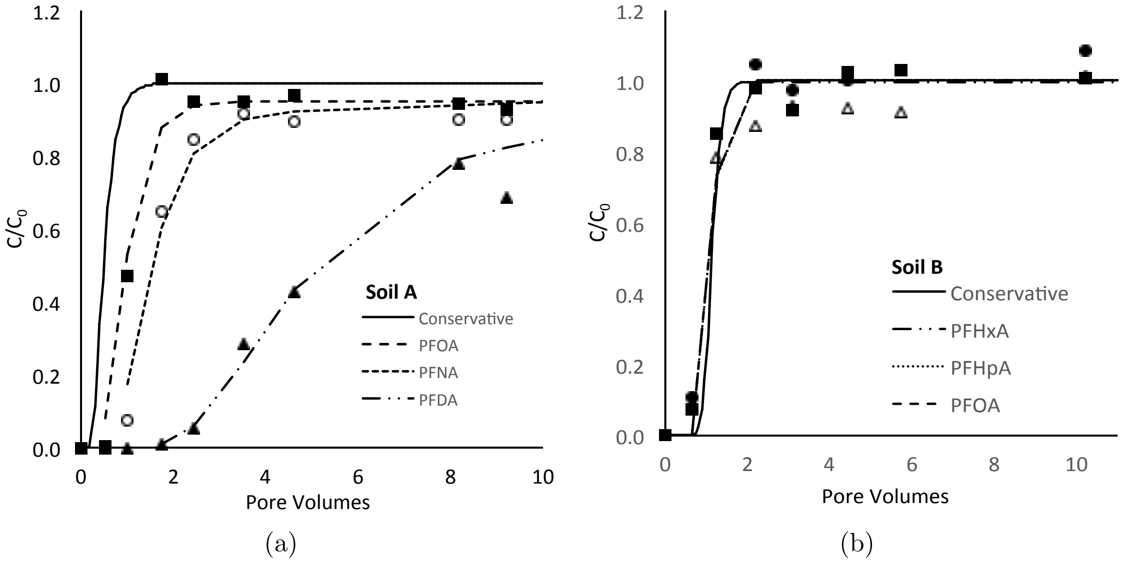


Figure 4.1: Breakthrough of PFOA (solid squares), PFNA (open circles), and PFDA (solid triangles) in Soil A (f_{oc}=0.017) and PFHxA (closed circles), PFHpA (open triangles), and PFOA (solid squares) in Soil B (f_{oc}=0.045). The conservative (solid line) case represents a compound with no sorption (i.e., bromide), and dashed lines are model fits of the whole breakthrough curve though only the approach to C/C_0 is shown so that chain-length dependent behavior can be seen.

K_{deq} were compared to K_{dcol} to determine if equilibrium conditions describe 1-D PFAA advective transport (Table 4.8 Table 4.8). In Soil A, PFBA, PFPeA, PFHxA, and PFHpA Kdcol values were within the range of Kdeq values expected based on aqueous concentrations within the column, indicating that the equilibrium assumption is appropriate (Figure 4.3). K_{dcol} values of the remaining PFAAs were smaller than expected, resulting in early breakthrough relative to equilibrium conditions (Figure 4.3). Similarly, in Soils B and C, all K_{dcol} values were smaller than K_{deq} values. In some cases K_{dcol} values in these solid phases were not statistically different from zero. In Soils A through C, low K_{dcol} values are likely indicative of nonequilibrium transport conditions that cannot be predicted by assuming equilibrium

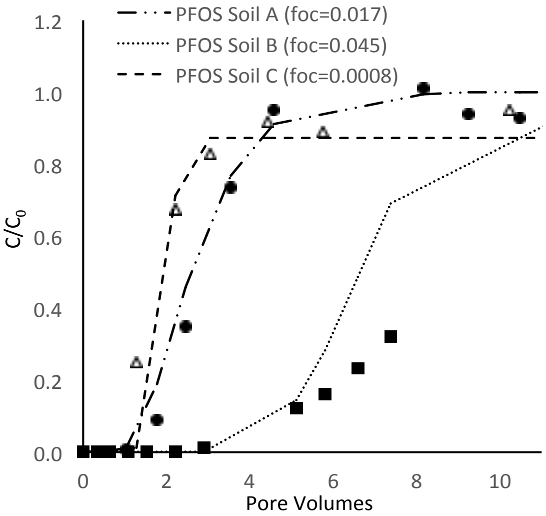


Figure 4.2: Breakthrough of PFOS in Soil A (solid circles), Soil B (solid squares), and Soil C (open triangles). Dashed lines are model fits of the whole breakthrough curve though only the approach to C/C_0 is displayed to enable observation of foc -dependent behavior.

Table 4.8: Summary of equilibrium and column K_d values

a

	Soil A^1			Soil B^1		
Analyte	K_{deq}	K_{dcol}	$\pm$	K_{deq}	K_{dcol}	$\pm$
PFBA	0.44-1.8	0.59	0.071	2.2-15	0.00078	0.0066
PFPeA	0.21-0.39	0.31	0.10	0.35-0.39	0.0000066	0.13
PFHxA	0.18-0.25	0.34	0.047	0.43-1.2	0.000044	0.0043
PFHpA	0.41-0.79	0.63	0.076	1.1-2.9	0.000037	0.0051
PFOA	0.70-1.41	0.49	0.072	3.3-6.8	0.068	0.020
PFNA	2.0-5.3	0.74	0.049	11-27	1.3	0.039
PFDA	9.2-45	2.9	0.28	63-220	8.8	0.37
PFBS	0.64-2.1	0.29	0.041	2.0-5.3	0.0000049	0.0
PFHxS	0.88-3.5	0.32	0.040	5.3-25	0.35	0.088
PFOS	4.5-23	2.4	0.11	31-100	4.4	0.22

Table 4.8

b

	Soil C^2			40/50					
Analyte	K_{deq}	K_{dcol}	±	K_{deq}	±	K_{dcol} LF	±	K_{dcol} FI	±
PFBA	0.023-0.078	0.000045	0.004	0.18	0.015	0.60	0.078	0.13	0.025
PFPeA	0.010-0.017	0.000047	0.005	0.25	0.013	0.61	0.081	0.13	0.037
PFHxA	0.0089-0.011	0.000022	0.002	0.21	0.0023	0.63	0.083	0.13	0.026
PFHpA	0.020-0.028	0.00056	0.01	0.19	0.0016	0.63	0.083	0.14	0.031
PFOA	0.035-0.062	0.00029	0.006	0.19	0.020	0.61	0.056	0.13	0.036
PFNA	0.11-0.27	0.041	0.01	0.26	0.028	0.60	0.056	0.20	0.030
PFDA	0.51-0.93	0.27	0.02	0.41	0.036	0.59	0.042	0.42	0.046
PFBS	0.031-0.083	0.0000013	0.0	0.20	0.0010	0.89	0.091	0.13	0.022
PFHxS	0.044-0.010	0.00015	0.003	0.19	0.013	0.89	0.070	0.14	0.027
PFOS	0.24-0.79	0.22	0.03	0.25	0.013	0.61	0.039	0.32	0.028

K_{deq}=equilibrium K_d values. LF=Low flow. FI=Flow Interuption. K_{dcol}=column K_d values. $^1K_{deq}$ ranges calculated based on the range of aqueous concentrations detected using K_f, n values from previous work [12]. $^2K_{deq}$ values calculated using K_f, n values for Soil A for the appropriate range of aqueous concentrations and normalizing to f_{oc}. $^3K_{deq}$ values were single point measurements made using methods described in previous work [12]; values were measured in triplicate so standard deviation is provided. K_{dcol} values and standard errors are from fits of column BTCs.

transport. In 40/50 sand, K_{dcol} values were higher than K_{deq}. Sand K_{deq} are single-point K_{deq} measurements collected at aqueous PFAA concentrations of 20 $\mu g/L$, which is higher than the ˜5 $\mu g/L$ used in column experiments. Single point K_{deq} measurements collected at a single concentration do not account for nonlinearity that may be apparent in isotherms. If nonlinearity was a factor, K_{deq} measurements at higher aqueous concentrations would likely be smaller than those measured at lower aqueous concentrations because the slope in the upper portion of nonlinear isotherms is lower. Therefore, high K_{dcol} values may reflect potential isotherm nonlinearity. High K_{dcol} values coupled with low equilibrium PFAA sorption to solid phases with no f_{oc} [9], indicate that transport of PFAAs in 40/50 sand can likely be described with an equilibrium assumption.

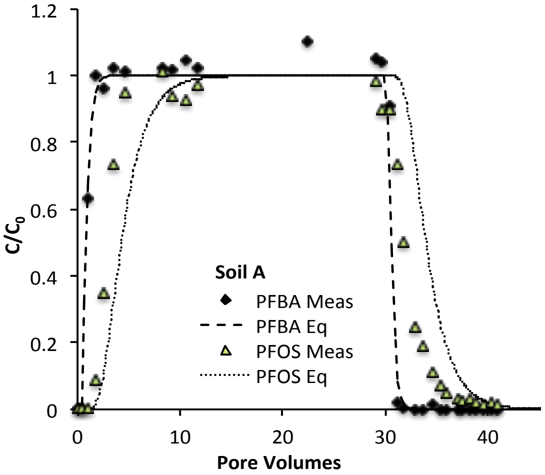
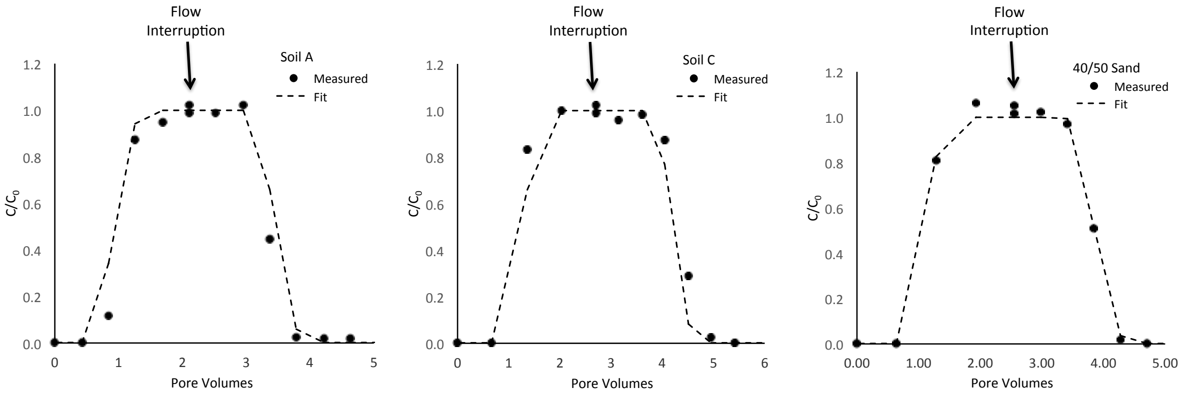


Figure 4.3: Predicted equilibrium and measured breakthrough of PFBA and PFOS in Soil A

4.3.2 Flow Interruption Experiments

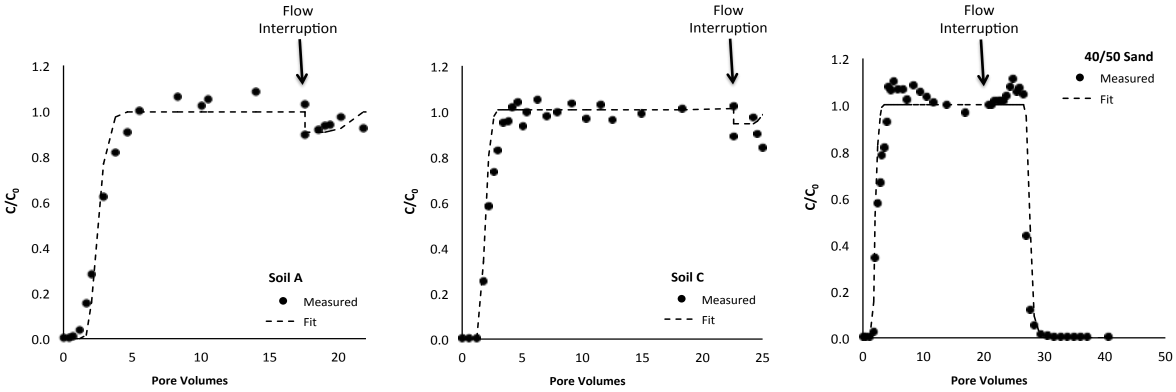
Nonideal transport may be caused by several factors including nonlinear and rate-limited sorption [14]. In this study, nonlinear sorption has been addressed by use of concentration-specific K_{deq} values that account for isotherm nonlinearity. Rate-limited sorption can have various impacts on BTCs including early breakthrough and tailing [14] as was observed for compounds where $K_{deq} > K_{dcol}$ (Table 4.8, Table 4.8, Figure 4.3). In the present study, flow interruption experiments were completed with Soils A, C, and 40/50 sand to investigate the impact of rate-limited sorption on advective PFAA transport (Table 4.6). Prior to initiation of PFAA tests, flow interruption experiments were completed with Br-. Because Br- is a nonreactive tracer, any changes in Br- concentration during the flow interruption period are indicative of physical nonequilibrium, such as diffusive mass transfer between mobile and immobile regions, within the column [16]. Physical nonequilibrium was not observed in any of the flow interruption Br- experiments; therefore any concentration drops observed in subsequent PFAA flow interruption experiments should be solely due to rate-limited sorption (Figure 4.4).



(a) (b) (c)

Figure 4.4: Flow interruption Br- tracer tests for Soil A, Soil C, and 40/50 sand

Decreases in PFAA concentrations during the stop flow period were observed for PFOA, PFNA, PFDA, PFBS, PFHxS, and PFOS in Soil A and PFNA, PFDA, and PFOS in Soil C (Figure 5), indicating that rate-limited sorption impacted transport of these compounds during flow interruption experiments, as suggested by low K_{dcol} values, early breakthrough, and tailing observed in low flow column experiments. A comparison of K_{deq} and K_{dcol} values suggests that rate-limited sorption also impacts PFBA, PFPeA, PFHxA, PFHpA, and PFOA in Soil C and that a drop in concentration should have occurred during the stop flow period. It is possible that because K_{deq} values in this solid phase are so low, decreases in C_w during the stop flow period were not detectable. It is also possible that an experimental design artifact masked potential concentration drops, as will be discussed. Low flow column data indicated that PFAAs were likely in equilibrium with 40/50 sand. The flow interruption period had no impact on PFAA concentrations in the 40/50 sand, which is consistent with equilibrium conditions (Figure 4.5).



(a) (b) (c)

Figure 4.5: Flow interruption data and model fits for PFOS in Soils A, C and 40/50 sand. Model fits in Soils A and C were obtained using a 2-site transport model whereas 40/50 model fits were obtained using an equilibrium model.

4.3.3 Determination of Mass Transfer Coefficients

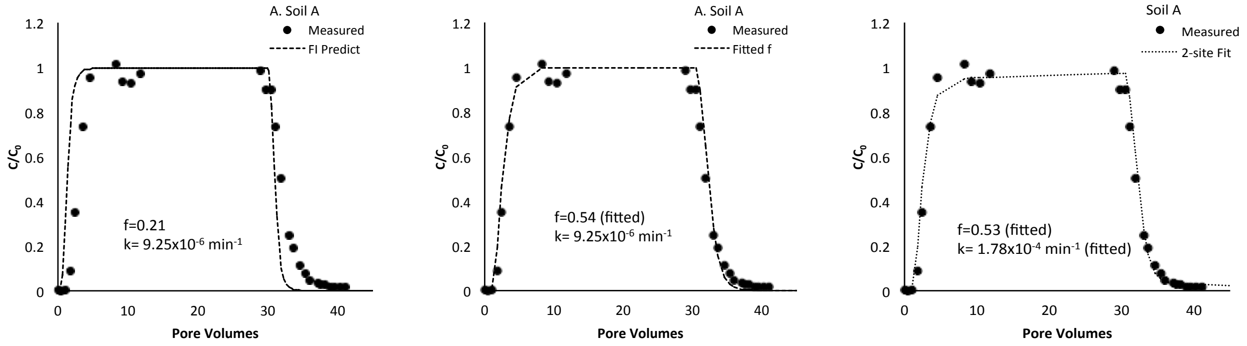
In addition to qualitatively confirming the occurrence of rate-limited sorption, another benefit of flow interruption experiments is that changes in C_w during the stop flow period can be modeled to obtain quantitative kinetic f and k values associated with the process. These values reflect the fraction of sites (f) that reach instantaneous equilibrium and the mass transfer coefficient (k) (4.5, 4.6, 4.7, 4.8). Ideally f and k values can then be applied to experiments conducted at lower pore water velocities [16]. Where drops in C/C_0 occurred, BTCs for flow interruption experiments in Soils A and C (Columns 5 and 6) were fit using K_{deq} in the 2-site sorption transport model to obtain f and k values (Figure 4.5, Table 4.9). Model fits to BTCs of flow interruption data for Soils A and C would not converge on a solution that adequately captured both the drop in C/C_0 during the stop flow period and tailing of compounds. Because tailing may be impacted by experimental factors such as increased compound exposure time to the solid phase during the stop flow period, the elution portion of these BTCs was removed from inverse modeling efforts, and fits focused on obtaining f and k from drops in C/C_0 during flow interruption (Figure 4.5, Table 4.9). Values for k ranged from 7.40 x 10^{-6} min^{-1} (PFHxS, Soil A) to 6.03 x 10^{-3} min^{-1} (PFOA, Soil C).

Flow interruption data for 40/50 sand did not demonstrate a drop in C/C_0 during the stop flow period or exhibit tailing. The lack of rate-limited processes in the sand implies that conditions in these columns should be at equilibrium. Flow interruption data for 40/50 sand were fit with an equilibrium assumption to ensure that K_{dcol} were greater than or equal to K_{deq}, as would be consistent with equilibrium conditions (Figure 4.5, Table 4.8, Table 4.8). Equilibrium model fits to 40/50 flow interruption data yielded Kdcol values greater than or equal to Kdeq values for all PFAAs, confirming equilibrium transport even at high pore water velocities (Table 4.8, Table 4.8).

Table 4.9: Summary of f and k values measured in this study

	Soil A (f_{oc} = 0.017)				Soil B (f_{oc}=0.045)		Soil C (foc=0.0008)			
Analyte	FI f	FI k	LF f	LF k	LF f	LF k	FI f	FI k	LF f	LF k
PFBA	N/A	N/A	N/A	N/A	7.81E-04	2.91E-07	N/A	N/A	3.13E-02	3.83E-03
PFPeA	N/A	N/A	N/A	N/A	7.81E-05	3.18E-06	N/A	N/A	1.56E-02	3.25E-03
PFHxA	N/A	N/A	N/A	N/A	2.93E-02	1.73E-04	N/A	N/A	4.22E-03	4.33E-04
PFHpA	N/A	N/A	N/A	N/A	3.91E-03	3.04E-06	N/A	N/A	1.17E-02	2.14E-03
PFOA	2.42E-04	2.10E-05	7.13E-01	8.85E-05	2.10E-02	2.53E-08	N/A	N/A	1.56E-03	1.63E-04
PFNA	9.00E-02	3.36E-05	3.70E-01	2.20E-04	1.18E-01	8.68E-06	1.07E-01	6.03E-03	2.79E-01	4.35E-03
PFDA	1.50E-01	1.75E-05	2.91E-01	1.80E-04	1.36E-01	4.71E-06	6.79E-01	4.84E-05	3.25E-01	3.03E-03
PFBS	7.73E-04	1.57E-05	4.45E-01	1.74E-04	2.66E-06	4.71E-06	N/A	N/A	3.13E-02	2.31E-04
PFHxS	4.05E-04	7.40E-06	5.00E-01	2.93E-06	6.70E-02	8.77E-08	N/A	N/A	5.04E-03	1.28E-05
PFOS	2.14E-01	9.52E-06	5.28E-01	1.78E-04	1.53E-01	3.07E-05	9.34E-01	9.75E-04	9.83E-04	4.68E-03
FI=Flow interruption. LF= Low flow. k in units of min^{-1}										

Flow interruption f and k values were used to forward model the low flow experiments to determine if they could adequately predict PFAA transport at lower pore water velocities. Flow interruption f and k values predicted earlier breakthrough and did not match tailing in low flow experiments as compared to measured data (Figure 4.6). However, assuming that k is a constant, k values were able to predict low flow BTCs when f was allowed to be a fitted parameter (Figure 4.6). This would imply that the fraction of type 1 sites is dependent on velocity as will be discussed further below. Alternatively it is possible that k varies with velocity. To evaluate this potential the low flow BTCs were inversely fit with the 2-site transport model to determine f and k values for all PFAAs for which K_{dcol} values reflected a potential for nonequilibrium (Figure 4.6, Table 4.9). Factors that may impact f and k are discussed further below.



(a) (b) (c)

Figure 4.6: Measured low flow PFOS BTC in Soil A with predicted BTC using flow interruption (FI Predict) f and k to forward model measured values, with flow interruption k value and fitted f (Fitted f), and with 2-site sorption transport model fit (2-site Fit) to obtain f and k values from low flow data.

4.3.4 Factors Impacting PFAA Mass Transfer

Modeling of flow interruption and low flow data showed potential variations in f and/or k values with pore water velocity. The experimental designs of flow interruption and low flow experiments were different, so it is not possible to directly compare their f and k values from full BTCs. However, outside of differences in velocity, when considering only the breakthrough side of the BTCs, the experimental conditions were the same. Thus, to enable comparisons of results under different pore water velocities, BTCs of both sets of data from the initial breakthrough were fit with the 2-site sorption transport model for Soil A to obtain f and k values (Table 4.10). Values of k are higher under low flow vs. high flow conditions, sometimes by an order of magnitude or more. Previous researchers have found that values for k can vary with pore water velocity [21]. Essentially the authors hypothesize the rates are directly related to diffusion coefficients and diffusion lengths that may vary with time [21]. The authors do not definitively state what the trends of diffusion coefficients and lengths will be with time; however in their data set values of k decrease with decreasing pore water velocity, which is the opposite of what was observed in this study.

It is also worthy to note that it was possible to get reasonable model fits of low flow PFOS data in Soil A using nearly identical values of f and values of k that were more than an order of magnitude different (Figure 4.6). Model fits using f=0.54 and k=9.25×10^{-6} min^{-1} and f=0.53 and k=1.78×10^{-4} min^{-1}. Forward modeling using these parameters yields similar BTCs until tailing begins to occur using the lower rate constant. This tailing occurs at extremely low concentrations that may be below the LOQs obtained in this study; therefore it is possible that inadequate capturing of tailing in measured data is leading to apparent differences in k that are an artifact of the experimental conditions: if more tailing had been captured during low flow experiments, model fits of k would be lower.

There is the potential that values of f vary with velocity as well. As flow rates decrease, hydraulic residence times increase and many models assume an inverse relationship between pore water velocity and the validity of the equilibrium assumption [21]. It is possible that this would be reflected in the fraction of sites that are type 1 sites leading to increases in f at lower pore water velocities. Fitted values of f in this study increase with decreasing pore water velocity (Table 4.10). However as previously mentioned, it is possible that more tailing occurred than was captured in measured data. If additional tailing was captured, estimates of k would likely change, and it is possible that resulting estimates of f would also change. Because of the uncertainty associated with this experimental artifact it is difficult to determine with any certainty the exact causes of the observed differences in f and k values with pore water velocity.

Table 4.10: Summary of k values measured at high and low flow

Analyte	High flow f	High Flow k	Low flow f	High flow f
PFOA	4.77E-05	1.54E-04	7.53E-01	4.64E-05
PFNA	8.93E-02	1.56E-04	4.05E-01	4.05E-04
PFDA	1.41E-01	4.36E-05	4.17E-01	2.77E-04
PFBS	3.91E-05	5.00E-07	3.45E-01	4.13E-04
PFHxS	4.47E-03	6.25E-06	5.00E-01	1.00E-05
PFOS	2.29E-01	1.31E-06	5.86E-01	1.32E-04

Values of f and k obtained by fitting 2-site sorption model to flow interruption model to flow interruption (high flow) and low flow low flow experiments from breakthrough to C/C_0=1

Rate-limited behavior in contaminant transport is generally attributed to processes related to diffusive mass transfer, specifically intraparticle and intrasorbent diffusion [22, 23]. Intraparticle diffusion is related to aqueous molecular diffusion within microporous particles [22, 23], whose pore surfaces may or may not be organic matter. Diffusion is slowed because of interactions with the pore surfaces, pore tortuosity, pore diameter, and dead end pores.23 In contrast, intrasorbent diffusion proposes diffusion through the organic matter matrix as the rate-limiting step [22, 23]. Low flow rate constants measured in this study decreased with increasing organic carbon content (Table 4.9), indicating that intraparticle diffusion into the organic matter matrix is likely at least partially responsible for the rate-limited behavior of these compounds in solid phases containing organic carbon. As intraparticle diffusion may also involve organic matter interactions inside pore walls, it is possible that both intraparticle and intrasorbent diffusion impact rate-limited behavior of PFAAs. Additionally, rate-limited behavior was observedin Soil C, which has extremely low organic carbon content. It is possible that in this solid phase, intraparticle diffusion may be a relatively more important process. Rate-limited behavior was not observed in the 40/50 sand, which also has little or no organic carbon, though it is possible this solid phase did not contain the pore structure that would lead to intraparticule diffusion.

4.4 Implications

Groundwater modeling efforts require an estimation of contaminant retardation in the subsurface. Such estimates are often made utilizing Kd measurements made in batch equilibrium studies. This study shows that use of equilibrium K_d values may be appropriate when predicting transport of some PFAAs in some solid phases. Regardless of the uncertainty surrounding f and k values, flow interruption experiments confirm that rate-limited processes also apply, particularly for longer-chain PFAAs and in porous media with appreciable organic carbon content and/or a potential for pore diffusion, as rate-limited processes even apply in aquifer sediments with extremely low organic carbon (e.g. Soil C). A failure to consider rate-limited processes can have implications in both risk assessment and remediation scenarios, since it may impact factors such as bioavailability and estimates of remedial effectiveness [23]. An illustrative example of the importance of this can be made when considering a simple pump and treat scenario for the remediation of PFOS. Though in situ treatments are largely considered favorable over ex situ methods, to date, no in situ methods have been found that are effective in the treatment of PFOS. Therefore pump and treat may be one of the only viable options for treating this compound, and because of its strong sorption relative to other PFAAs, it is useful to consider the potential impacts of rate-limited sorption to this treatment technology. A simple 1-D pump and treat scenario was simulated for both equilibrium and rate limited scenarios (Table 4.11, Figure 4.7). Concentrations at an extraction well were predicted over a 200-day pumping period assuming that groundwater was initially at equilibrium with the solid phase. In an equilibrium scenario, PFOS concentrations reach concentrations less than the PHA of 200 ng/L after 85 days (Figure 4.7). In a rate-limited scenario, concentrations do not decrease below regulatory levels until approximately 125 days (Figure 4.7). Understanding of rate-limited processes is therefore important in estimates of time and cost for remediation. Additional research may be needed to better understand how the slow fraction and mass transfer coefficients are impacted by velocity or with other factors such as concentration or sorption hysteresis. This study shows that equilibrium conditions will not adequately predict PFAA transport and that a complete understanding of the transport of these compounds will involve additional studies of their behavior under advective conditions.

Table 4.11: Pump test conditions

Parameter	Value
Aquifer size (1-D)	100 m
Pump time	200d
Porosity	0.43
Bulk Density (g/cm^3)	1.5
Longitudinal dispersivity (m)	0.1
K_d (L/kg)	2
f_{oc}	0.007
Darcy velocity (m/d)	4.5
Initial [PFOS] ($\mu g/L$)	4.7
f	0.25
k (min^{-1})	0.18

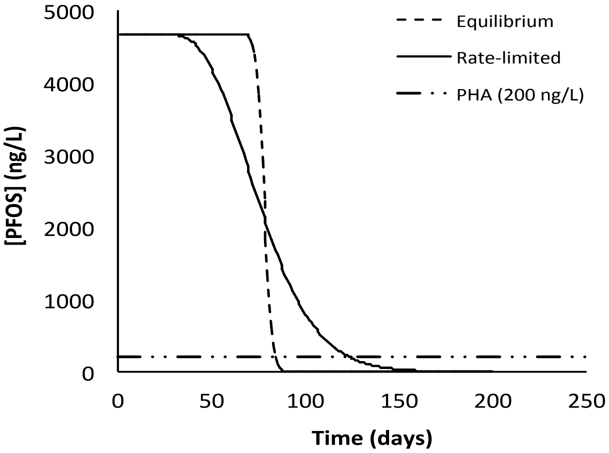


Figure 4.7: Estimates of PFOS transport for a pump and treat scenario under equilibrium and rate-limited conditions.

4.5 Acknowledgements

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CHAPTER 5
CONCLUSIONS

Whether released to the environment through biosolids application, use of aqueous film-forming foam (AFFF), or via other potential sources, an understanding of perfluoroalkyl substance (PFAS) fate and transport in the environment is crucial due to their persistent, bioaccumulative, and potentially toxic nature Lau et al. [1], Conder et al. [2]. The objective of this work was to initiate an understanding of the subsurface fate and transport of PFASs through a series of batch equilibrium and 1-dimensional (1-D) column studies targeted at biosolids-amended soils and AFFF-impacted facilities.

5.1 Summary of Findings

A summary of the findings is presented below by research hypotheses.

5.1.1 Hypothesis 1

Hypothesis 1: A combination of laboratory and field studies of soils amended with municipal biosolids will demonstrate chain length-dependent transport potential of PFASs.

PFASs have been measured in municipal biosolids, but levels of these compounds present in biosolids destined for land application remain unregulated in the United States. PFAS impact to groundwater from land application of industrial biosolids has been documented Washington et al. [3], Yoo et al. [4] so it is important to understand if impact may also occur from municipal biosolids. A suite of biosolids-amended soils, source biosolids, and soil cores was used to look at the mass balance, occurrence, occurrence as a function of biosolids loading rate, desorption, and leaching of PFASs. Specific findings from this work include:

- PFAS concentrations in the source biosolids were not statistically different from concentrations measured in previous studies Higgins et al. [5]. Concentrations of PFASs were measured in the biosolids-amended soils with perfluorooctane sulfonate (PFOS) being the most abundant at 2-483 ng/g over various biosolids loading rates. The relative abundance of the PFOS precursor 2-(N-methylperfluorooctane sulfonamido) acetic acid (MeFOSAA) in biosolids vs. biosolids-amended soils suggests the potential for this compound to have been transformed to PFOS once biosolids were applied.

- The occurrence of PFASs in biosolids-amended soils was investigated with respect to the associated biosolids loading rate. Linear regressions of PFAS soil concentration vs. biosolids loading rate showed a statistically significant relationship between loading rate and [PFAS] for most compounds studied. Linear regressions of these relationships were used to predict biosolids concentration at a separate site and a comparison of predicted vs. measured values found that the regressions yielded reasonable approximations of [PFAS] in biosolids-amended soils.

- Mass balance calculations of PFASs applied vs. recovered were completed to determine any significant increases or decreases in PFAS levels relative to what was applied. Perfluorobutane sulfonate (PFBS) recovery was approximately 300-2000% of expected, while precursors MeFOSAA and 2-(N-ethylperfluorooctane sulfonamido) acetic acid (EtFOSAA) were only 23-69% of expected. Both of these findings suggest transformation of precursors, though it is not expected that transformation of MeFOSAA and EtFOSAA, are directly related to formation of PFBS.

- Desorption experiments were used to study the leaching potential of PFASs from biosolids-amended soils. Log K_{oc} values were reported for compounds with $\geq$6 CF2 groups (long chain) and showed increasing sorption with increasing chain length. Log K_{oc} values for desorption were similar to those previously reported for batch sorption experiments Higgins and Luthy [6] with the exception of PFDA and PFOS. In the current study, log K_{oc} values of these compounds were higher, suggesting that desorption of these compounds may be slower than would be predicted by equilibrium sorption values.

- Analysis of soil cores from biosolids-amended soil sites showed detectable concentrations of PFASs at the bottom depth interval of the cores (120 cm). Differences in PFAS concentrations in the surface vs. the depth interval suggest higher transport potential of short chain PFASs, confirming laboratory desorption experiments.

5.1.2 Hypothesis 2

Hypothesis 2: The sorption of PFASs to soil and aquifer material will behave consistently with that previously observed in sediment at low concentrations (ng/L-$\mu g/L$); however sorption in the $\mu g/L$-mg/L range will be increasingly non-linear. Overall, transport will be chain-length dependent with transport potential inversely related to PFAS chain length.

- Batch sorption isotherms were completed in multiple solid phases with initial aqueous concentrations as high as 1 mg/L for a suite of perfluoroalkyl acids (PFAAs). PFAA isotherms were nonlinear, and Freundlich n-values were 0.7-1.1, consistent with previous studies Higgins and Luthy [6]. Where available for comparison, log K_{oc} values were consistent with previous work Higgins and Luthy [6]. Except for PFBA and PFPeA, log K_{oc} values increased with increasing chain length and f_{oc}.

- PFBA and PFPeA, for which sorption had not been measured in previous studies, were important exceptions to trends with chain length. Sorption of these compounds was an order of magnitude or more higher than expected based on sorption-chain length relationships. This suggests that sorption mechanisms such as ion exchange or steric effects play a relatively more important role for sorption of these smaller PFAAs.

5.1.3 Hypothesis 3

Hypothesis 3: Sorption of PFASs will increase in the presence of non aqueous phase liquid (NAPL), and the tendency of dissolved phase co-contaminants to

impact PFAS transport through competitive sorption will vary based on the cosolute and sorbent type. Cosolvency effects will not be observed for the co-contaminants proposed for this research.

- Batch isotherms were measured for a suite PFAAs in in two soils (f_{oc} of 1.7 and 4.5%) amended with NAPL, and NAPL was found to have a varying impact on sorption. The primary effect of NAPL was observed in the low foc soil where Freundlich n-values increased when NAPL was present for long chain PFAAs. In the high f_{oc} soil, impacts were chain-length dependent with sorption decreasing for the largest PFAAs (e.g. PFOS, PFDA).
- NAPL led to increases in sorption of PFBA and PFPeA in both soils, again showing anomalous behavior and potential steric effects related to these compounds.
- Batch isotherms were measured for PFAAs in the presence of the anionic hydrocarbon surfactant sodium decyl sulfate (SDS). In general, effects of SDS on PFAA sorption were chain length dependent. Increases in sorption were noted for the smallest compounds and these increases diminished in magnitude with increasing chain length such that there was no change in sorption for the largest PFAAs.
- Batch isotherms were measured for PFAAs in the presence of the amphoteric surfactant n,n-dimethyldodecylamine n-oxide (AO). The most notable impact to sorption was in a positively charged soil in which sorption increased with increasing PFAA chain length.
- As with NAPL, sorption of PFBA and PFPeA tended to increase in the presence of SDS and AO.
- Changes in sorption in the presence of SDS and AO may be due to hemimicelle formation, competitive sorption, and/or changes in apparent PFAA solubility in the presence of these compounds.

5.1.4 Hypothesis 4

Hypothesis 4: Due to potential nonequilibrium conditions, transport parameters determined in spiked laboratory batch experiments may not adequately describe PFAS transport in an advective scenario. However overall trends such as chain-length and f_{oc} dependent transport will still apply.

- Column studies in multiple solid phases were used to understand 1-D advective transport of PFAAs. Overall breakthrough of PFAAs in columns was chain-length dependent. Exceptions included PFBA and PFPeA which broke through later than expected, confirming anomalous behavior observed in batch sorption experiments

- Trends of PFAA breakthrough with organic carbon content of the solid phase were unclear. Only the largest PFAAs (e.g. PFOS, PFDA) showed trends of increasing retardation with increasing chain length. Smaller PFAAs did not show a trend with f_{oc} indicating possible nonequilibrium with the solid phase.

- Comparison of equilibrium sorption (K_{deq}) with column sorption (K_{dcol}) values showed that ideal transport conditions applied for PFAAs in sand and for smaller PFAAs in low f_{oc} (1.7%) soil. However for larger PFAAs and in soils with higher f_{oc} nonequilibrium transport conditions were observed, likely due to rate-limited sorption.

- Flow interruption experiments showed drops for some PFAAs during stop flow periods, confirming rate-limited, 1-D advective transport.

- Mass transfer coefficients describing rate-limited PFAA sorption were obtained from column breakthrough data. These data were somewhat insensitive to the k value applied, which may indicate that additional breakthrough curve tailing would need to be captured in order to narrow the range of applicable mass transfer coefficients. Rates decreased with increasing solid phase f_{oc}. This may be related to intraparticle diffusion into the organic matter matrix Brusseau et al. [7], Pignatello and Xing [8].

5.2 Contributions to Conceptual Framework

Provisional health advisories (PHAs) have been developed by the USEPA for concentrations of PFOA and PFOS in drinking water using results of studies showing varying toxicological impacts, including effects to the mammalian liver and endocrine systems USEPA [9]. PHAs were developed in response to detectable concentrations of PFAAs in drinking water at a site in Decatur, AL that had received land application of industrial biosolids. PHAs for PFOA and PFOS are 0.4 and 0.2 $\mu g/L$, respectively, and in 2009 the USEPA collected surface water and private water well samples at the Decatur site that were found to exceed these limits Washington et al. [3]. Concentrations of PFOA and PFOS in surface and groundwater samples at AFFF-impacted facilities have also been documented above the PHAs Moody et al. [10]. These examples provide documentation of risk from exposure to PFAAs and illustrate the importance of understanding their subsurface fate and transport. Because PFAAs are resistant to degradation, sorption is one of the primary processes that will control their fate and transport once released to the environment. This study focuses on sorption of PFAAs under equilibrium and advective scenarios using conditions specific to the release of PFASs through land application of municipal biosolids and use of AFFF; however, the findings have relevance to PFAA transport regardless of the method of release.

Studies of PFAA transport potential in sorption, desorption, and 1-D column experiments all confirm the chain-length dependent transport potential of long chain PFAAs found in previous studies Higgins and Luthy [6]. This was confirmed in sorption studies in spiked systems (Table B.10) and in desorption experiments with field-collected, biosolids-amended soils (Table 2.2). Soil cores collected in the vadose zone of a biosolids-amended soil test facility also show chain-length dependent transport (Figure 2.4), indicating that this behavior may also apply in unsaturated systems. Exceptions to this trend may be observed when kinetic limitations apply and for short-chain (< 6 CF2 groups) PFAAs as discussed below.

Another important factor influencing PFAA transport is the organic carbon content of the solid phase. Long chain PFAA sorption increases with increasing organic carbon content as identified in this study (Chapters 2-4) and in prior work Higgins and Luthy [6]. This is important to consider when developing a conceptual framework for PFAA transport since PFAAs released to the environment will move through various zones with differing f_{oc}. PFAAs in the source zone may be exposed to solid phases with relatively high f_{oc}, and this may be even more relevant at biosolids application sites. This increased f_{oc} may reduce the tendency for PFAAs to move from the source zone as was reflected by mass balance calculations of PFAA recovery in biosolids-amended soils (Table A.4). Saturated zone f_{oc} is likely to be lower than that encountered in the source zone, which will increase the transport potential of long chain PFAAs relative the source zone. Trends with f_{oc} were apparent in batch sorption (Figure B.1) and 1-D column experiments (**??**). Important exceptions again include short chain PFAAs and when kinetic limitations apply.

As mentioned, short chain PFAAs exhibited anomalous behavior relative to the long chain compounds. Specifically, the degree of sorption was much higher than what would be expected based on chain-length dependent, hydrophobic (e.g. van der Waals) effects as observed in both equilibrium (Figure 3.2) and 1-D column (Table 4.8) experiments. Additionally, there was no trend of increasing sorption with increasing f_{oc} (Figure B.1). This anomalous behavior indicates that a different mechanism is relatively more important to sorption of short chain PFAAs, and this is potentially attributable to either ion exchange or steric effects. These trends are an important consideration for transport predictions, since industry has decreased manufacturing and use of long chain PFAAs in favor of the short chain compounds DuPont [11], Dynax Corporation [12].

Equilibrium desorption experiments with biosolids-amended soils yielded some PFAA K_{oc} values that were higher than what had previously been observed in the literature Higgins and Luthy [6], suggesting that desorption is kinetically limited (Chapter 2). 1-D flow interruption experiments confirmed rate-limited behavior during advective transport (Figure 4.5), determined mass transfer coefficients (Table 4.9), and showed that kinetic behavior was related to intraparticle diffusion into solid phase f_{oc} (Table 4.9). In some cases nonequilibrium conditions caused by rate-limited interactions with the solid phase lead to advective PFAA transport that deviated from chain length (Figure 4.1) and f_{oc} dependent trends. Therefore, a comprehensive conceptual framework of PFAA transport in saturated systems will need to include a rate-limited consideration, particularly for higher f_{oc} solid phases.

The fluorochemical load in both biosolids and AFFF may be largely comprised of PFASs outside of the PFAAs that were the primary focus of this work. For example, recent studies identified the presence of anionic, cationic, and zwitterionic surfactants with varying fluoroalkyl tail lengths in 7 different AFFF formulations Place and Field [13]. While perfluoroalkyl sulfonates (PFSAs) are present in older AFFF formulations, perfluorocarboxylates (PFCAs) were not detected in any AFFF formulation Place and Field [13]. A comprehensive analysis of the PFAS load in biosolids has not been completed; however, PFASs such as MeFOSAA and EtFOSAA, along with a fluorochemical class known as fluorotelomer alcohols have been identified in municipal and industrial biosolids and amended soils Yoo et al. [4], Higgins et al. [5]. Recent studies have suggested that some of these PFASs are precursors to the end point PFAAs included in this study McGuire, Meghan E. et al. [14], and results in this study suggested the potential for transformation of MeFOSAA and EtFOSAA as well as the production of PFBS in biosolids-amended soils (Table A.4). Regardless of the pathway of release, it is important to consider that the initial PFAS composition in the source zone may consist of precursors that can serve as an additional source of the more persistent PFAAs in the environment.

5.3 Suggestions for Future Work

Results of this work substantially expand understanding of the subsurface fate and transport of PFASs, but they have also highlighted areas where it would be useful to target future research.

- Results of the work with biosolids and biosolids-amended soils showed the potential for transformation of precursors in biosolids. Specifically the increase in concentrations of PFBS and decreases in precursors MeFOSAA and EtFOSAA provide evidence that transformation occurs. Future efforts should focus on temporal monitoring of biosolids-borne PFASs and precursors to better understand the transformation pathways, rates, and any potential intermediates that may form.

- Work with biosolids-amended soils showed a potential for leaching of PFASs from the surface soil interval; however no corresponding aqueous data were available. To better determine the impact of biosolids-borne PFASs comprehensive field studies including groundwater investigations should be completed.
- Work with the equilibrium sorption of PFASs revealed anomalous behavior of short chain PFASs such as PFBA and PFPeA. Because industry is moving towards production of smaller PFASs, additional work should be completed to better understand the mechanisms controlling sorption of these compounds.
- Though this work targeted conditions applicable to AFFF-impacted sites; all systems included in equilibrium sorption and 1-D column studies were spiked systems. Because the conditions at AFFF-impacted facilities may vary greatly and may contain any number of co-contaminants not included in this study, a next logical step would be to conduct additional experiments with field-collected AFFF-impacted soil and groundwater.
- This work verified that rate-limited sorption impacts transport of PFAAs at the 1-D scale and provided mass transfer coefficients associated with that process. However, these mass transfer coefficients ranged over several orders of magnitude and vary with organic carbon content. It remains to be seen whether they would vary with PFAA concentration. Additional work to try and determine which factors are most crucial in determining mass transfer coefficients and whether these rates can be predicted (e.g. by organic carbon-rate relationships) would be useful.

- Lastly, 1-D transport represents the simplest case of advective transport. It now becomes crucial to determine how these results translate to larger and multiply dimensioned scales, as the end goal is to be able to understand PFAS transport at the field scale.

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APPENDIX A - SUPPORTING INFORMATION: OCCURRENCE AND FATE OF PERFLUORINATED COMPOUNDS IN SOIL FOLLOWING LAND APPLICATION OF BIOSOLIDS

A.1 Materials and Methods

Table A.1: PFCs and surrogate standards used in this study

Analyte	Surrogate Standard
PFBA	[$^{13}C_4$] PFBA
PFPeA	[$^{13}C_4$] PFBA
PFHxA	[$^{13}C_2$] PFHxA
PFHpA	[$^{13}C_2$] PFHxA
PFOA	[$^{13}C_4$] PFOA
PFNA	[$^{13}C_5$] PFNA
PFDA	[$^{13}C_2$] PFDA
PFUnA	[$^{13}C_2$] PFUnA
PFDoA	[$^{13}C_2$] PFDoA
MeFOSAA	[$^{2}D_3$] N-MeFOSAA
EtFOSAA	[$^{2}D_5$] N-EtFOSAA
PFBS	[$^{18}O_2$] PFHxS
PFHxS	[$^{18}O_2$] PFHxS
PFHpS	[$^{18}O_2$] PFHxS
PFOS	[$^{13}C_4$] PFOS
PFDS	[$^{13}C_4$] PFOS

A.1.1 Desorption Experiments

For the equilibrium experiments, three sets of triplicate reactors were prepared for each soil type by transferring soil and synthetic fresh water [15] with 1 g/L of sodium azide to a 50 mL polypropylene tube to achieve a 1:10 soil-water ratio (r_{sw}, Soils W and K) or a 1:20 r_{sw} (Field 2). These r_{sw} values were selected for each soil to ensure aqueous PFC concentrations would remain within the standard linear calibration curve for direct injection aqueous analysis. Reactors were vortexed and placed on a shaker table for the duration of the experiment. For the equilibrium desorption study, one reactor from each triplicate set was sampled at each time point such that each reactor was sampled every fourth time step. Three triplicate sets of reactors were prepared for each soil to provide triplicates for each sampling time point. Prior to sampling, the vials were centrifuged at 2,700 rpm for 20 min, a 675 μL sample of the aqueous phase removed, and a replacement aliquot of 675 μL of clean synthetic freshwater was added to each reactor. Reactors for Soil W and Soil K were sampled at 1 hr, 2 hr, 6 hr, 12 hr, 24 hr, and then every subsequent 24 hrs for 14 days. Reactors for Field 40 were sampled at 15 min, 30 min, 45 min, 1 hr, 6 hr, 12 hr, 24 hr, and then every subsequent 48 hrs for 14 days. All reactors were sampled on day 14. At the completion of the 14-day desorption equilibrium experiments, the aqueous phase was removed and the solid phase from a subset of reactors was extracted to determine residual fraction of PFCs in the solid phase and to enable the completion of mass balance calculations. (Table A.5)

A.1.2 Soils and Biosolids Extractions

Moisture content of each sample was separately measured by drying overnight in an oven at 105°C to enable reporting of the results on an oven-dry dry weight basis. Samples were weighed into 50 mL polypropylene conical tubes. An aliquot containing 2 ng of each surrogate standard was added to each tube immediately prior to extraction. A solvent mixture of 99:1 (v/v) methanol and ammonium hydroxide was employed for each extraction. Seven mL of the solvent mixture was added to each tube prior to vortexing and placement of each tube in a heated (30°C) sonication bath (Fisher Scientific FS110H, Pittsburg, PA) for one hour. Each tube was subsequently removed and placed on a shaker table (VWR 5000 STD 120V, West Chester, PA) for two hours. The samples were then centrifuged (Eppendorf 5810, Hamburg, Germany) at 2,700 rpm for 20 minutes (1467 RCF), and the extract was decanted into a clean, glass 20-mL scintillation vial. This procedure was repeated twice for a total of three extraction cycles. The combined extract was then evaporated to dryness under nitrogen (Organomation Associates Inc. N-EVAP 112, Berlin, MA) and reconstituted with 700 μL of 99:1 (v/v) methanol and acetic acid. The reconstituted extract was transferred to a microcentrifuge tube containing 20-40 mg of ENVI-Carb (Supelco Inc., Bellefante, PA), vortexed by hand for thirty seconds, and centrifuged (Fisher Scientific, accuSpin Micro 17) at 17,000 RCF for 30 minutes. An aliquot of each cleaned extract (105 μL) was transferred to an autosampler vial containing 1,350 μL of Milli-Q water (Millipore, Billerica, MA) and 45 μL of dilution water (0.01% ammonium hydroxide in Milli-Q water). Autosampler vials were then vortexed by hand for thirty seconds prior to analysis by liquid chromatography tandem mass spectrometry (LC-MSMS).

A.1.3 Aqueous Sample Preparation

Aqueous phase samples from batch desorption experiments were prepared by transferring 675 μL of aqueous sample into a microcentrifuge tube with 675 μL of optima methanol and a 150 μL aliquot of 70/30 solution containing 0.3 ng of each surrogate standard. Microcentrifuge tubes were vortexed for thirty seconds and centrifuged at 17,000 RCF for 30 minutes. A volume of 1,300 μL of the prepared sample was then transferred to an autosampler vial for direct injection LC-MS/MS analysis.

A.1.4 LC-MS/MS Analysis

Chromatography was performed using an aqueous ammonium acetate (10 mM) and methanol (10mM) gradient delivered at a flow rate of 800 μL/min by an Agilent LC system (Agilent 1200) Binary pump controlled by an Agilent 1200 series Instant Pilot controller (Santa Clara, CA). Samples and standards were injected (1 mL) by a CTC Analytics LEAP Technologies autosampler onto a 50 mm x 4.6 mm Gemini C18 column (3-micron particle size, Phenomenex, Torrance, CA) equipped with a C18 Guard Column and Guard Cartridge (Higgins Analytical). For analysis of soil extracts, initial eluent conditions were 50% methanol and 50% water. The percent methanol was ramped to 95% over 4 min, held at 95% over 4 min, ramped down over 1.5 min, and held at 50% for 2.5 min. For analysis of aqueous samples, initial eluent conditions were 5% methanol and 95% water. The percent methanol was ramped to 60% over 0.75 min, ramped to 100% over 4 min, held at 100% over

3 min, ramped down to 5% over 0.5 min, and held at 5% for 1.75 min. A MDS Sciex Applied Biosystems 3200 Q trap mass spectrometer (MDS Sciex, Ontario) operating in negative electrospray ionization scheduled multiple reaction monitoring (MRM) mode was employed for sample analysis. Two MRM transitions were acquired for all analytes. The monitored transitions were analyte dependent and are the same or similar to those used previously [5]. For PFCAs, these transitions correspond to decarboxylation transitions, while the monitored PFAS transitions were the formation of the FSO_3^- ion (m/z = 99). Quantitation was performed using Analyst®, with all calibration curves having r^2 values greater than 0.99 and the accuracy of each calibration point within 30% of its expected value.

Optimal instrumental source parameters were determined and are as follows: ionspray voltage -4,000 V, curtain gas flow 35 arbitrary units (au), nebulizer gas flow 60 au, turbo gas flow50 au, medium collision gas flow, and source temperature 650 °C. Zero air provided by a Parker-Balston Source 5000 Zero Air Generator (Haverhill, MA) was used for the nebulizer and drier gas, and nitrogen was used as the curtain and collision gas.

A.1.5 Quality Assurance/Quality Control

To account for variations in the samples, all soils and biosolids were extracted in triplicate and all desorption reactors were prepared in sets of three. In all cases, analytical results are reported as the average of the three values. If one of the three values was below detection then the average value was reported as below detection.

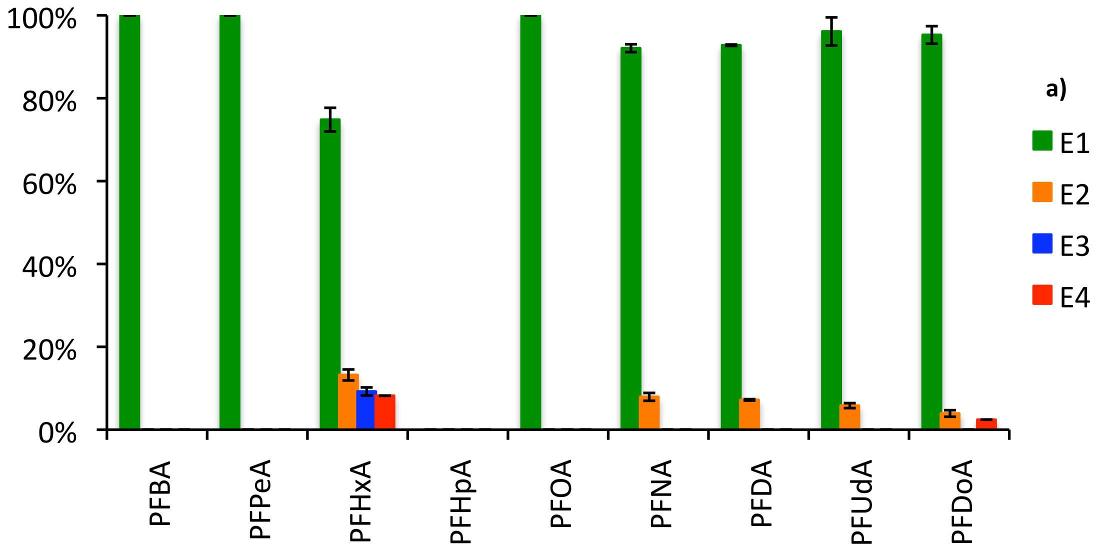
To determine the effectiveness of the soil/biosolid extraction method, soils and biosolids were spiked with a known amount of PFC stock standard solution (Table A.2). Similarly, spike recovery experiments were conducted with aqueous phase samples to determine any potential loss of PFCs during sample preparation. To further ensure that three extractions were sufficient to recover PFCs from soils and biosolids, triplicate samples from each matrix were subjected to four sequential extractions, with each extract analyzed separately. The amount of mass recovered in the fourth extraction was less than 5% in all cases except PFHxA (8%) in biosolids (Figure A.1(a), Figure A.1(b), Figure A.1(c), Figure A.1(d)). To determine the effectiveness of the soil/biosolid extraction method, soils and biosolids were spiked with a known amount of PFC stock standard solution. The extraction method recovered 69% (PFNA) to 153% (PFDS) of PFCs (Table A.1).

Similarly, spike recovery experiments were conducted with aqueous phase samples to determine any potential loss of PFCs during sample preparation. Synthetic fresh water spiked with a known amount of PFC stock standard solution and PFC internal standard solution was placed in either 50 mL polypropylene tubes or microcentrifuge tubes and subsequently transferred to autosampler vials to test for losses to each type of container. Recoveries from 50 mL tubes were 77-95%, with the exceptions of the longer chain length PFCAs (PFUdA and PFDoA) and the PFOS precursors (MeFOSAA and EtFOSAA), for which the recoveries were 32-58%. Additionally, over-recovery of PFBA (174%) and PFPeA (271%) was evident, reflecting an unsatisfactory analytical bias for these PFCs. As a result, aqueous-phase data for PFBA, PFPeA, PFUdA, PFDoA, MeFOSAA, and EtFOSAA were removed from additional analysis. Recoveries of all other analytes from spiked microcentrifuge tubes were 85-103%.

Finally, control reactors were prepared for desorption experiments by preparing synthetic freshwater with a known amount of the PFC stock standard solution and PFC surrogate standard solution in a 50 mL polypropylene tube with no solid phase. These reactors were placed on the shaker table sampled on the final day. If losses for an analyte were greater than 10%, then these results were used to calculate m_v for the analyte (see 2.1) to account for losses to the tube when determining K_{des} values.

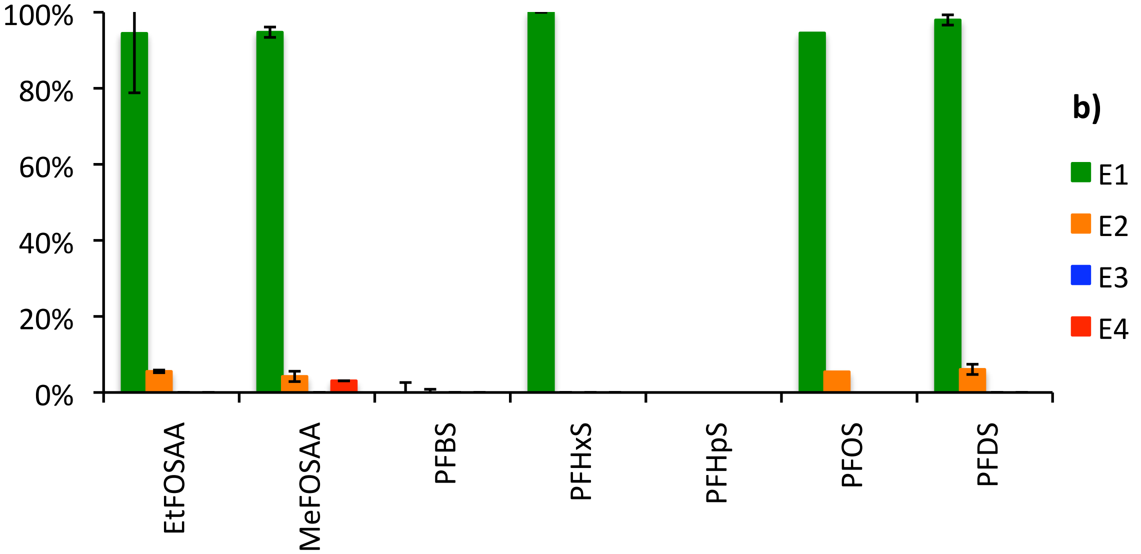
Table A.2: Biosolids and biosolids ammended soils spike recovery results

Analyte	% Recovery from Biosolids	STDEV	% Recovery from Soil	STDEV
PFBA	92%	3%	101%	6%
PFPeA	125%	4%	115%	11%
PFHxA	99%	2%	105%	7%
PFHpA	101%	3%	99%	10%
PFOA	101%	3%	114%	3%
PFNA	69%	3%	73%	3%
PFDA	84%	1%	89%	3%
PFUnA	100%	2%	101%	10%
PFDoA	95%	2%	101%	10%
MeFOSAA	101%	8%	98%	14%
EtFOSAA	108%	12%	118%	13%
PFBS	144%	3%	131%	8%
PFHxS	104%	1%	102%	8%
PFHpS	118%	3%	117%	8%
PFOS	95%	3%	85%	6%
PFDS	153%	35%	96%	4%



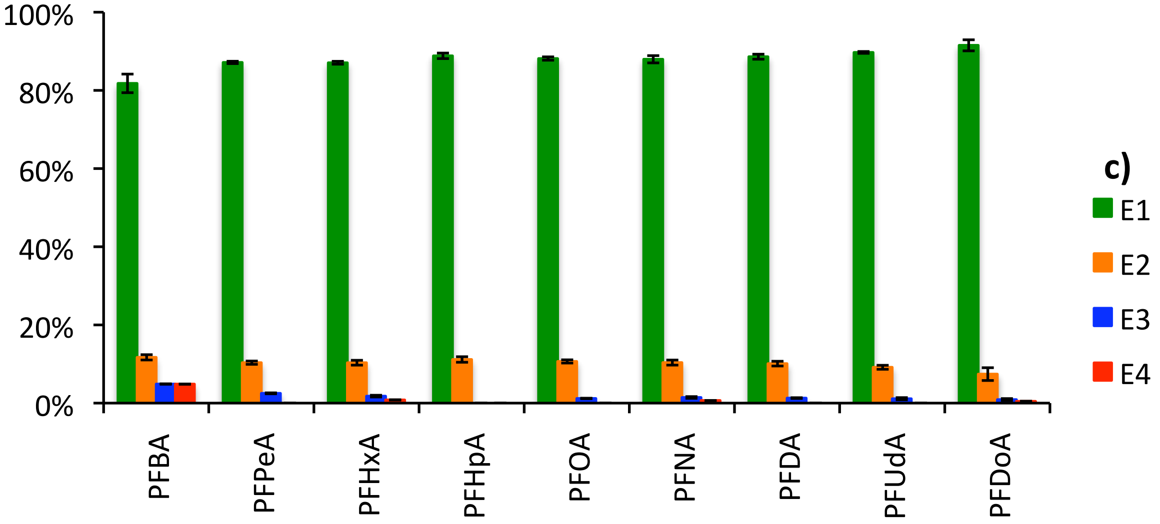
(a)

Figure A.1



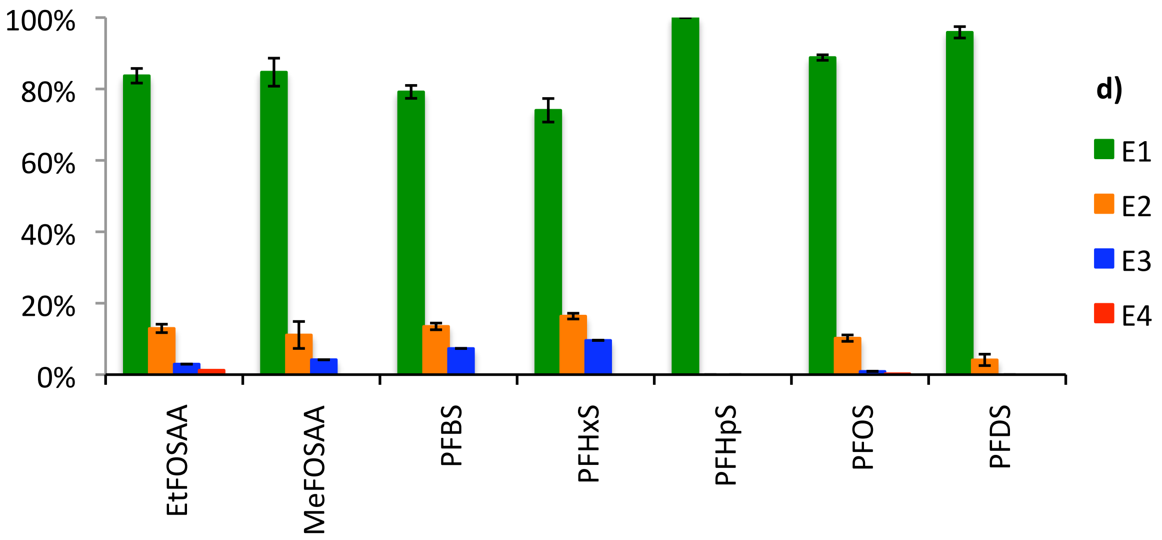
(b)

Figure A.1



(c)

Figure A.1



(d)

Figure A.1: Results of extraction efficiency experiments in biosolids (a-b) and soils (c-d). Reflects the percentage of each PFC recovered in each extraction in a sequence of four extractions. E1=extraction 1, E2=extraction 2, E3=extraction 3, and E4=extraction 4

A.2 Results and Discussion

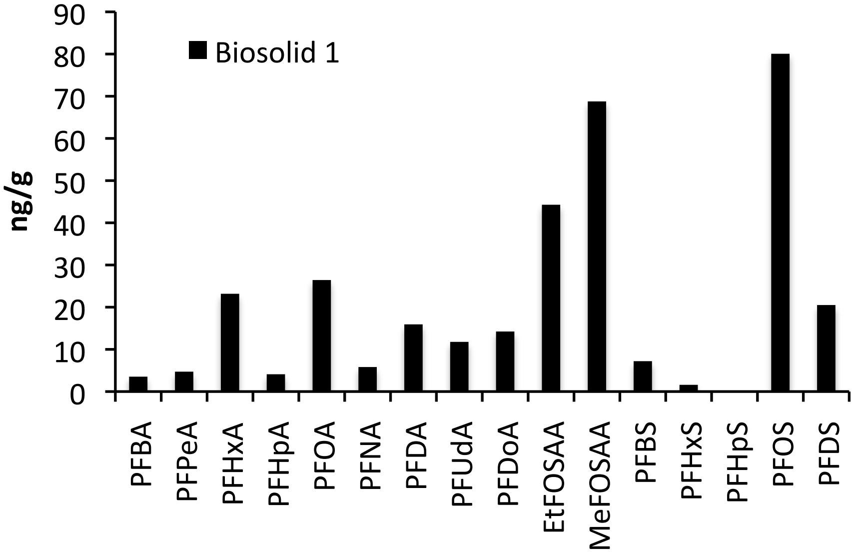
The following sections provide supporting information to results and the discussion of results found in this work.

A.2.1 Biosolids Occurrence

PFC occurrence was measured in the six source biosolids used in this study (Figure A.2(a), Figure A.2(b), Figure A.2(c), Figure A.2(d), Figure A.2(e), Figure A.2(f)).

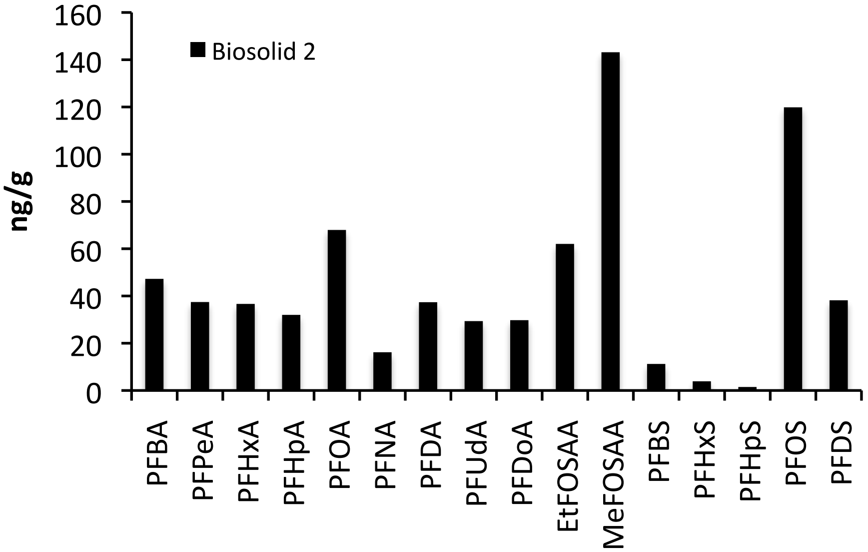
A.2.2 Standard Additions

This study employed the PFHxS stable isotope as a surrogate standard for PFBS (Table A.1). The use of PFHxS as a surrogate standard for PFBS may contribute to potential enhanced recovery of PFBS in biosolids amended soils due to differential matrix effects in the soils and biosolids. To evaluate potential matrix effects, standard additions for PFBS were performed in Soils W and K at the highest loading rates and in the source biosolid for



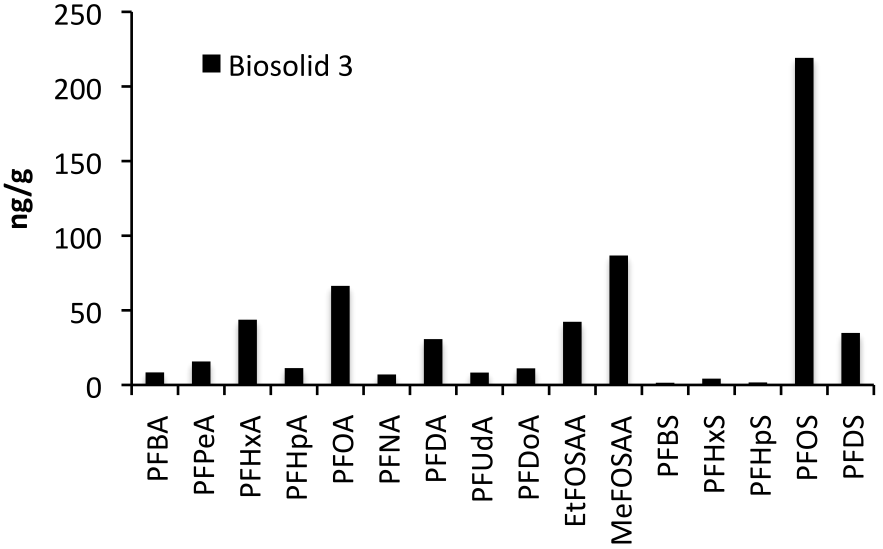
(a)

Figure A.2



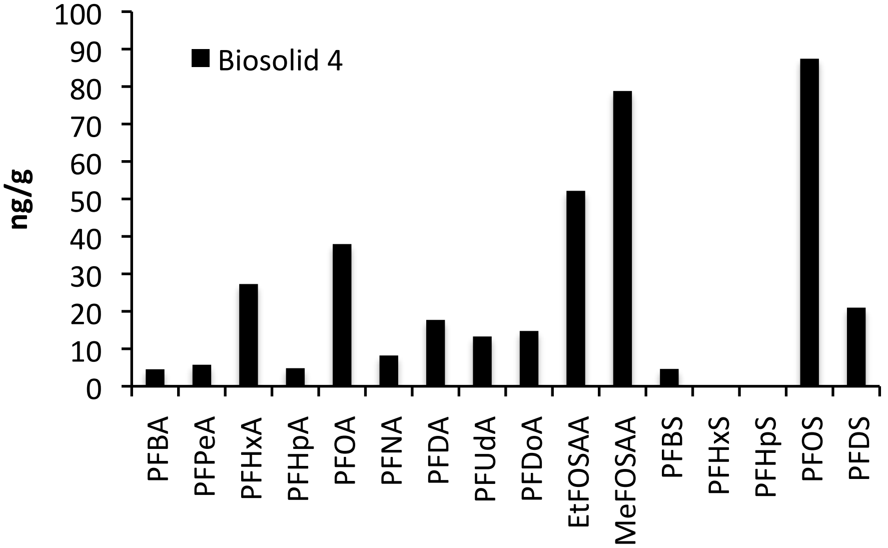
(b)

Figure A.2



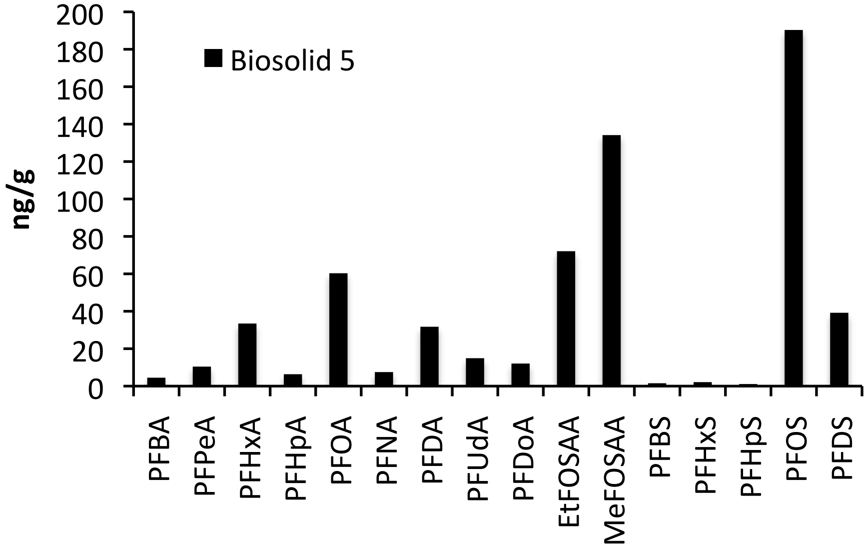
(c)

Figure A.2



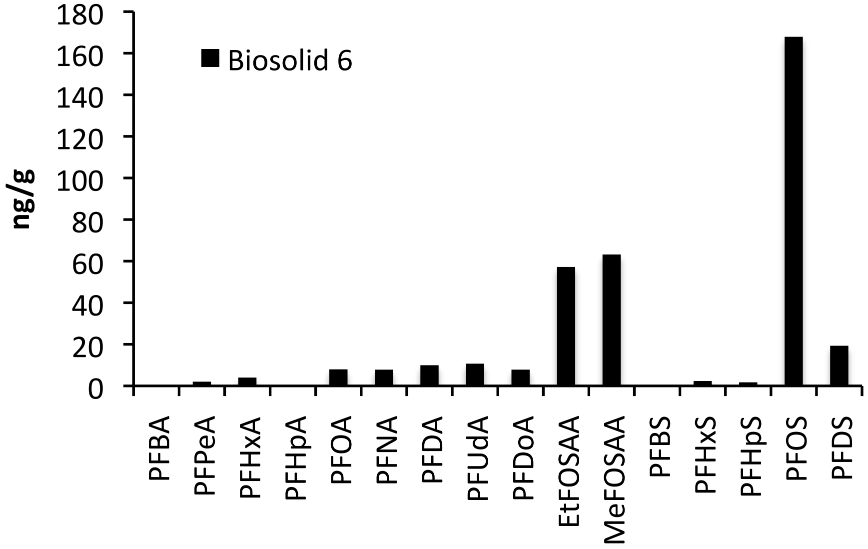
(d)

Figure A.2



(e)

Figure A.2



(f)

Figure A.2: Occurrence of PFCs in six source Biosolids for short-term W and K Soils each soil that had the lowest measured PFBS concentration.

Standard additions showed no difference in instrument response for PFBS calibrations performed in solvent, soil extracts, or biosolids extracts. However, instrument response for PFHxS differed between the matrices, with additional signal suppression of PFHxS in soil extracts when compared to biosolids extracts. This indicates that matrix effects were different between PFBS and PFHxS and also between soils and biosolids, potentially leading to analytical bias. Because of the use of PFHxS as a surrogate standard for PFBS, the suppressed recovery of PFHxS in soil indicates that measured PFBS soil concentrations are slightly enhanced. Results confirm this, as the concentrations of PFBS in the subset of soil samples (determined directly using PFHxS as the surrogate standard) were approximately 1.5-2.5 times higher than those obtained by standard addition. Using the PFBS soil concentrations determined by standard addition, mass balance recoveries of PFBS in Soils W and K were recalculated for the two highest loading rates. In Soil W, recovery of PFBS was adjusted from 450% to 185% with use of standard addition PFBS concentrations, and PFBS recovery in Soil K was adjusted from 2500% to 1600%. These data suggest that while matrix effects are partially responsible for the higher PFBS recovery observed in the soils, there were still significant increases in PFBS in the soils when compared to what was applied via the biosolids.

A.2.3 Occurrence with Biosolids Loading Rate

Table A.3and Table A.4 summarize occurrence and mass balance of PFASs with biosolids loading rate.

Table A.3: Results of linear regressions of soil concentrations with loading rate

Analyte	Slope	±	Y-intercept[1]	r^2
PFBA	0.001	0.0001	0	0.65*
PFPeA	0.003	0.0003	0	0.86*
PFHxA	0.003	0.0003	0	0.84*
PFHpA	0.003	0.0002	0	0.92*
PFOA	0.015	0.0009	0	0.94*
PFNA	0.003	0.0002	0	0.94*
PFDA	0.009	0.0004	0	0.97*
PFUdA	0.003	0.0002	0	0.95*
PFDoA	0.006	0.0003	0	0.96*
EtFOSAA	0.018	0.0013	0	0.92*
MeFOSAA	0.018	0.0013	0	0.86*
PFBS	0.000	0.0003	0	0.26
PFHxS	0.004	0.0003	0	0.94*
PFHpS	0.002	0.0001	0	0.96*
PFOS	0.198	0.0153	0	0.90*
PFDS	0.044	0.0020	0	0.96*

*Indicates a significant ($p<0.05$) relationship between loading rate and PFC concentration.

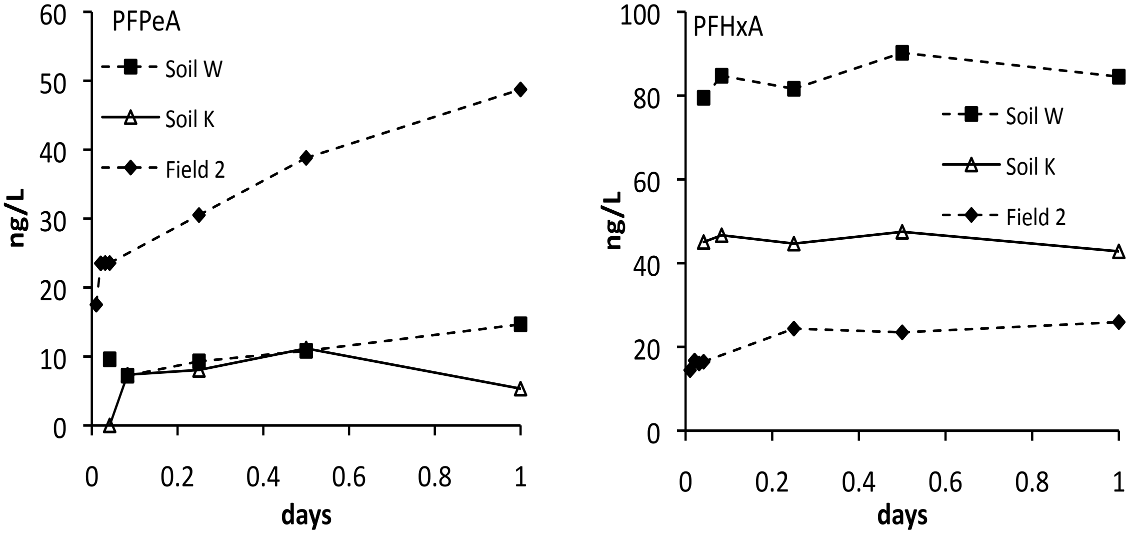
[1] Y-interecepts for all cumulative regressions were forced to equal zero because PFC concentrations in plots receiving no biosolids are assumed to be zero.

Table A.4: Mass balance results of actual vs. calculated soil PFC concentrations

	Soil W		Soil K	
Analyte	% Recovery	±	% Recovery	±
PFBA	51%	11%	151%	14%
PFPeA	152%	43%	282%	38%
PFHxA	69%	18%	48%	18%
PFHpA	139%	39%	282%	39%
PFOA	110%	10%	125%	17%
PFNA	118%	29%	231%	93%
PFDA	125%	38%	301%	39%
PFUdA	78%	32%	169%	20%
PFDoA	115%	52%	316%	28%
PFTrDA	<LOQ	<LOQ	128%	22%
EtFOSAA	64%	5%	69%	12%
MeFOSAA	23%	4%	69%	15%
PFBS	322%	104%	2228%	365%
PFHxS	99%	13%	97%	70%
PFHpS	103%	67%	96%	N/A
PFOS	97%	39%	86%	26%
PFDS	97%	44%	44%	25%

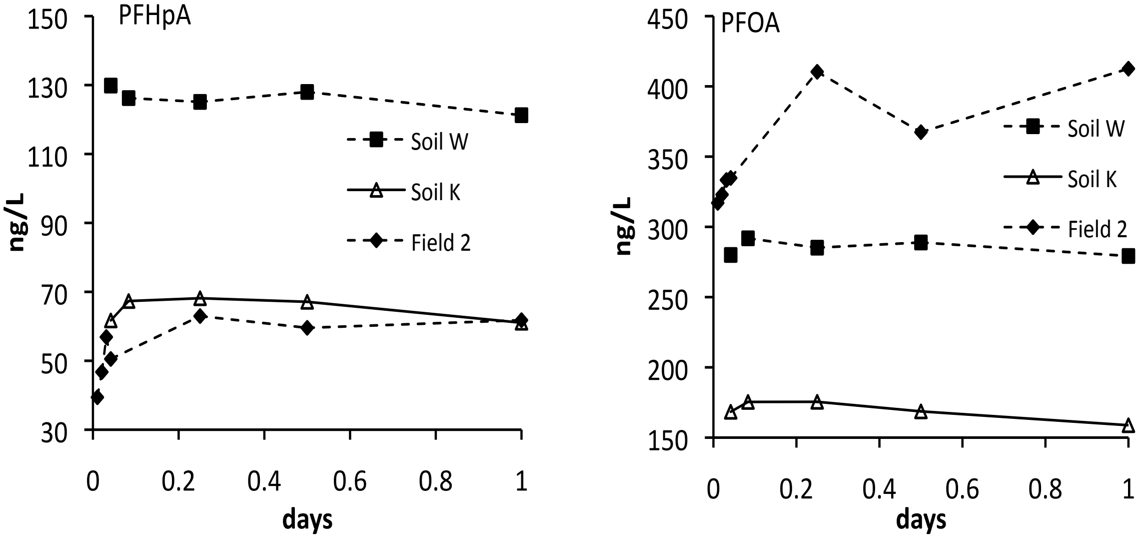
A.2.4 Desorption Equilibrium

Batch desorption experiments showed that aqueous equilibrium, defined as when no statistical differences were observed in aqueous concentrations measured in subsequent time points (up to 14 days), was achieved for all PFCs within the first 24 hours of desorption from the biosolids amended soils (Figure A.3, Figure A.3, Figure A.3, Figure A.3, Figure A.3)



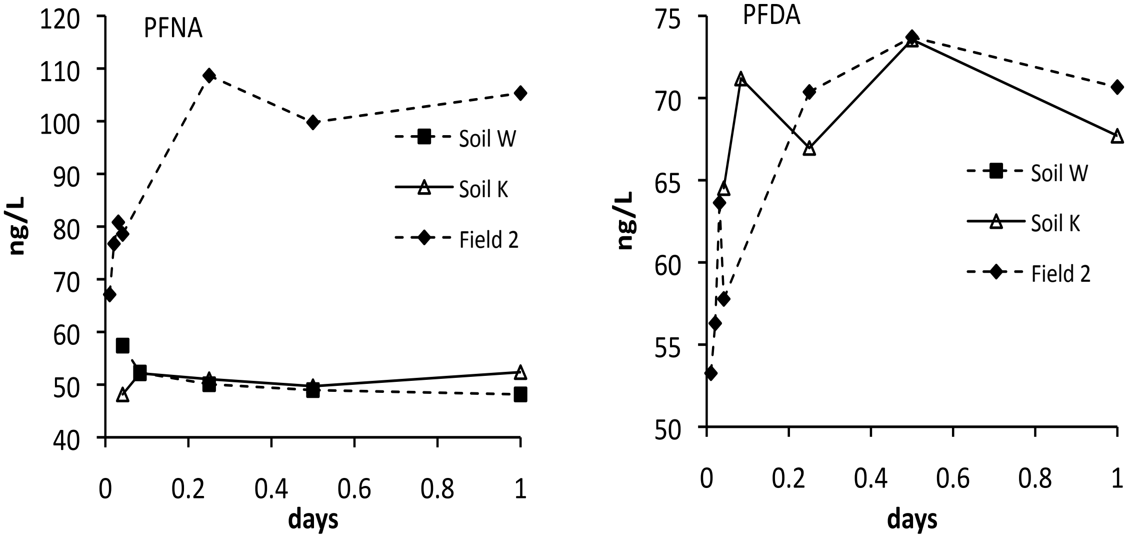
(a) (b)

Figure A.3



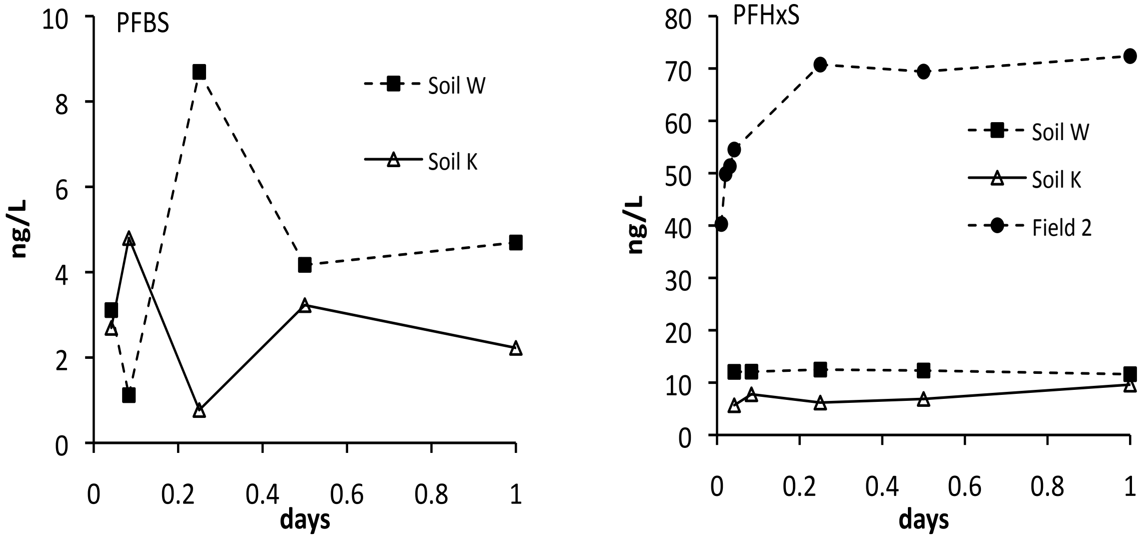
(c) (d)

Figure A.3



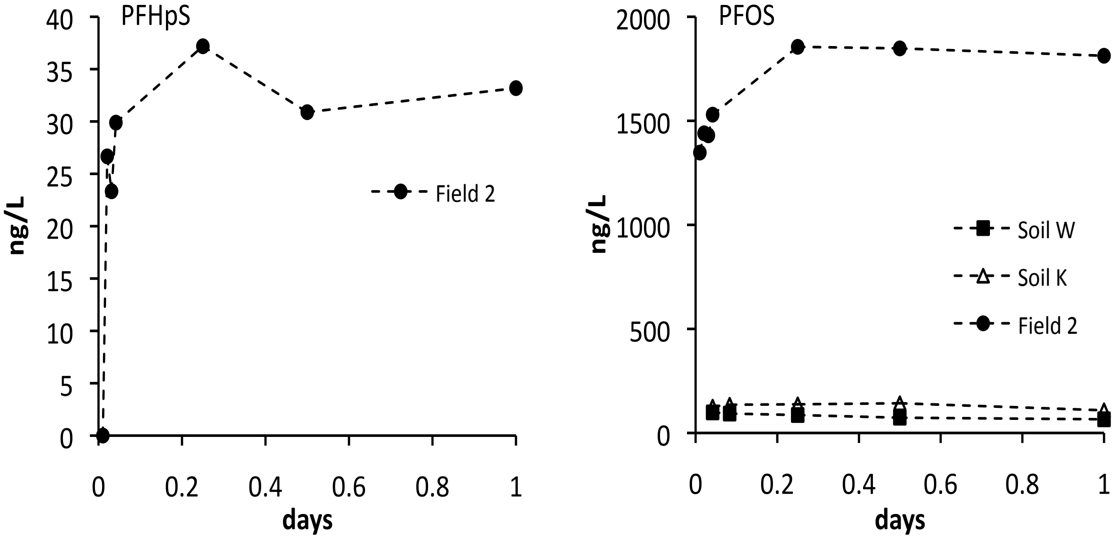
(e) (f)

Figure A.3



(g) (h)

Figure A.3



(i) (j)

Figure A.3: Desorption equilibrium of PFCs from Soil W, Soil K, and Field 2. If a soil is not included in a plot, then this indicates that aqueous concentrations for that particular PFC were below detection in equilibrium experiments with the excluded soil. If a PFC is not included, then it was below detection for equilibrium experiments with all soils. Data beyond 24 hrs are not shown as the slope of the measured aqueous concentrations vs. time was not statistically different ($p < 0.05$) from zero after the initial 24 hrs.

Table A.5: Total aqueous plus total solid phase recovery of PFCs in equilibrium desorption reactors.

Analyte	Recovery Soil W	STDEV	Recovery Soil K	STDEV	Recovery Field 2	STDEV
PFHxA	100%	5%	106%	11%	123%	25%
PFHpA	82%	4%	85%	11%	128%	19%
PFOA	103%	9%	100%	5%	86%	9%
PFNA	100%	8%	105%	9%	105%	3%
PFDA	93%	6%	85%	1%	100%	8%
PFBS	110%	21%	97%	30%	N/A	N/A
PFHxS	65%	6%	N/A	N/A	84%	8%
PFHpS	N/A	N/A	N/A	N/A	102%	6%
PFOS	113%	8%	102%	7%	91%	5%
PFDS	N/A	N/A	N/A	N/A	N/A	N/A

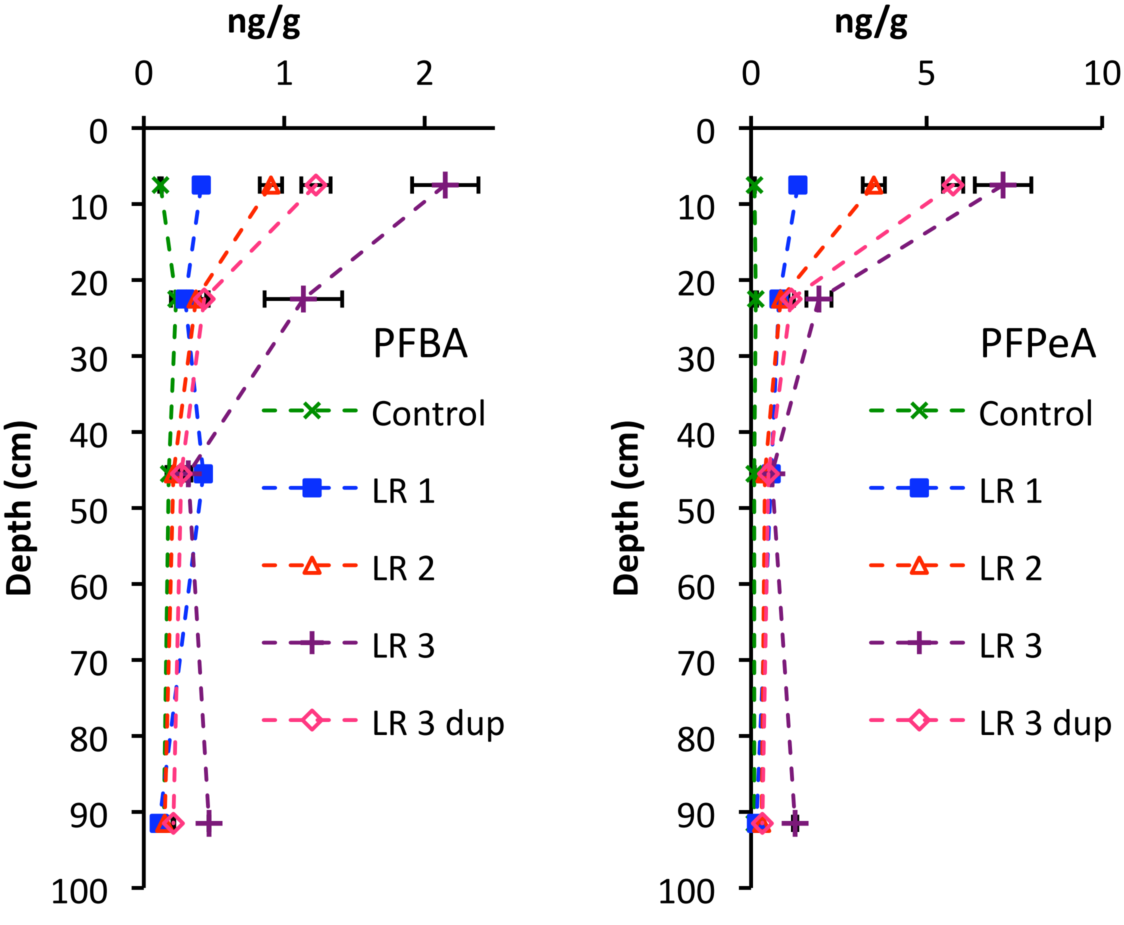
A value of N/A indicates that concentrations in the aqueous and/or solid phases were below detection and therefore recovery could not be calculated.

Table A.6: Individual and average K_{oc} results for Soils W, K, and General Fields

Analyte	Soil Type	Log K_{oc}	STDEV
PFHxA	Soil W	1.63	0.52
	Soil K	2.35	0.55
	Gen Fields	1.74	0.37
	Average	**1.91**	**0.39**
PFHpA	Soil W	2.22	0.12
	Soil K	2.82	0.11
	Gen Fields	1.52	0.73
	Average	**2.19**	**0.65**
PFOA	Soil W	2.42	0.24
	Soil K	2.59	0.21
	Gen Fields	1.92	0.31
	Average	**2.31**	**0.35**
PFNA	Soil W	2.42	0.05
	Soil K	2.59	0.12
	Gen Fields	1.99	0.24
	Average	**2.33**	**0.31**
PFDA	Soil W	3.14	0.07
	Soil K	3.32	0.05
	Gen Fields	3.05	0.07
	Average	**3.17**	**0.14**
PFHxS	Soil W	2.81	0.10
	Soil K	3.02	0.20
	Gen Fields	2.28	0.30
	Average	**2.70**	**0.38**
PFOS	Soil W	3.31	0.06
	Soil K	3.62	0.03
	Gen Fields	3.08	0.05
	Average	**3.34**	**0.27**

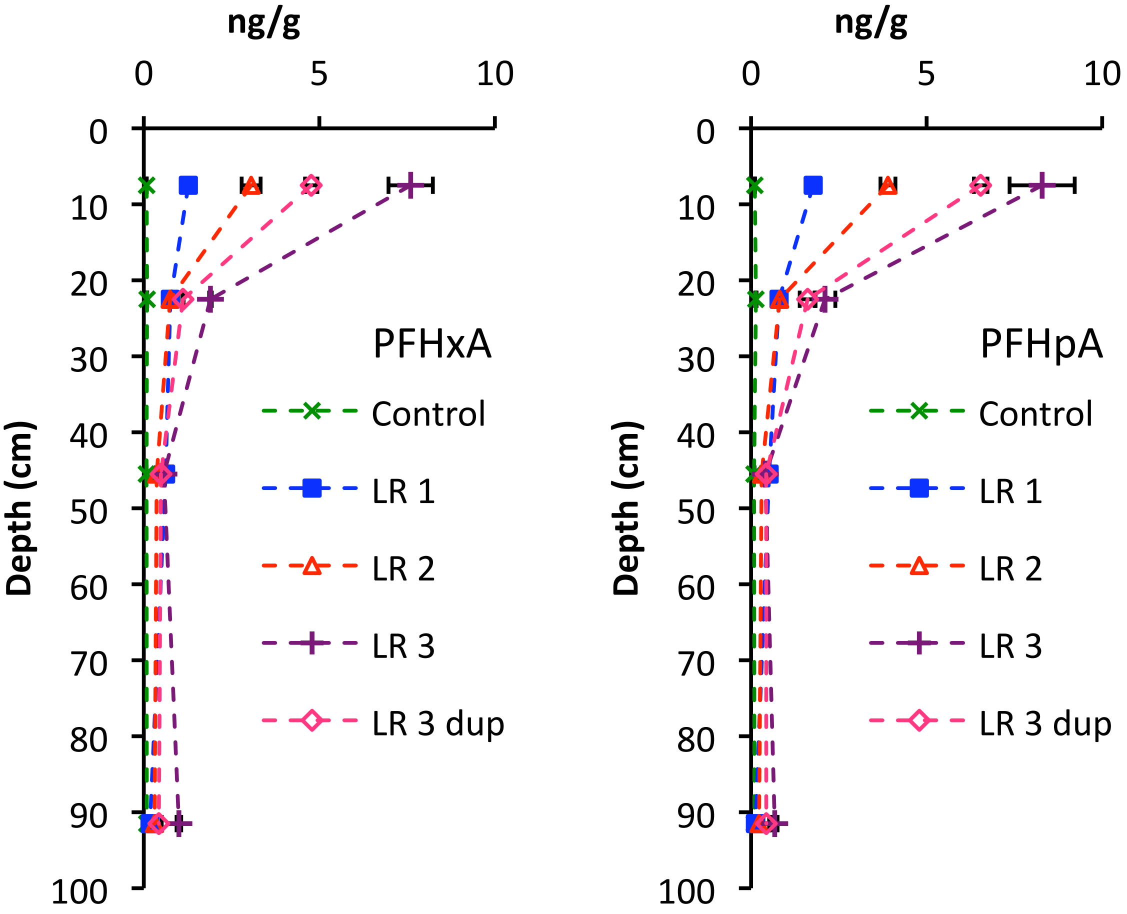
A.2.5 Soil Cores

Analysis of PFCs in soil cores from the long-term plots was completed to a depth of 120 cm (Figure A.4, Figure A.4, Figure A.4, Figure A.4, Figure A.4, Figure A.4, Figure A.4, Figure A.4)



(a) (b)

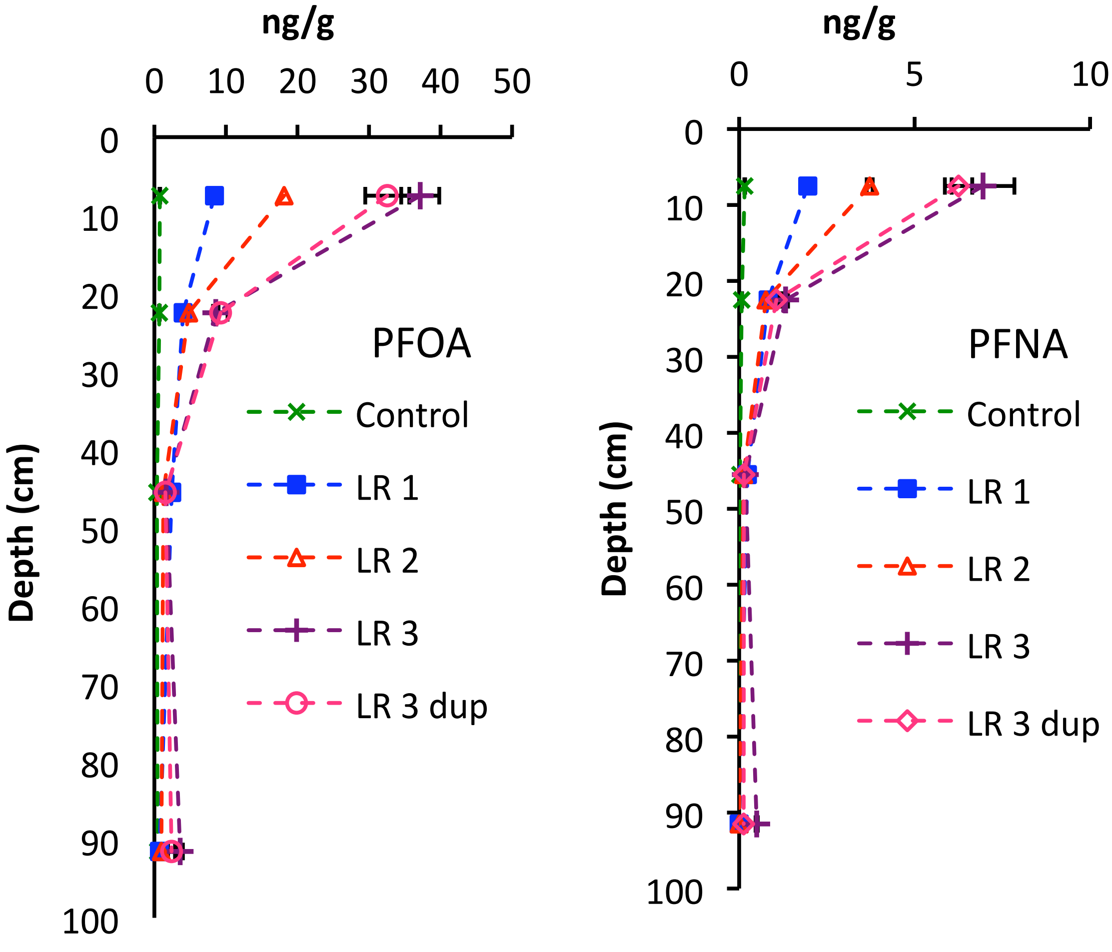
Figure A.4


ng/g
0
5
10
0
10
20
30
40
50
60
70
80
90
100
Depth (cm)
PFHxA
Control
LR 1
LR 2
LR 3
LR 3 dup
ng/g
0
5
10
0
10
20
30
40
50
60
70
80
90
100
Depth (cm)
PFHpA
Control
LR 1
LR 2
LR 3
LR 3 dup

(c)

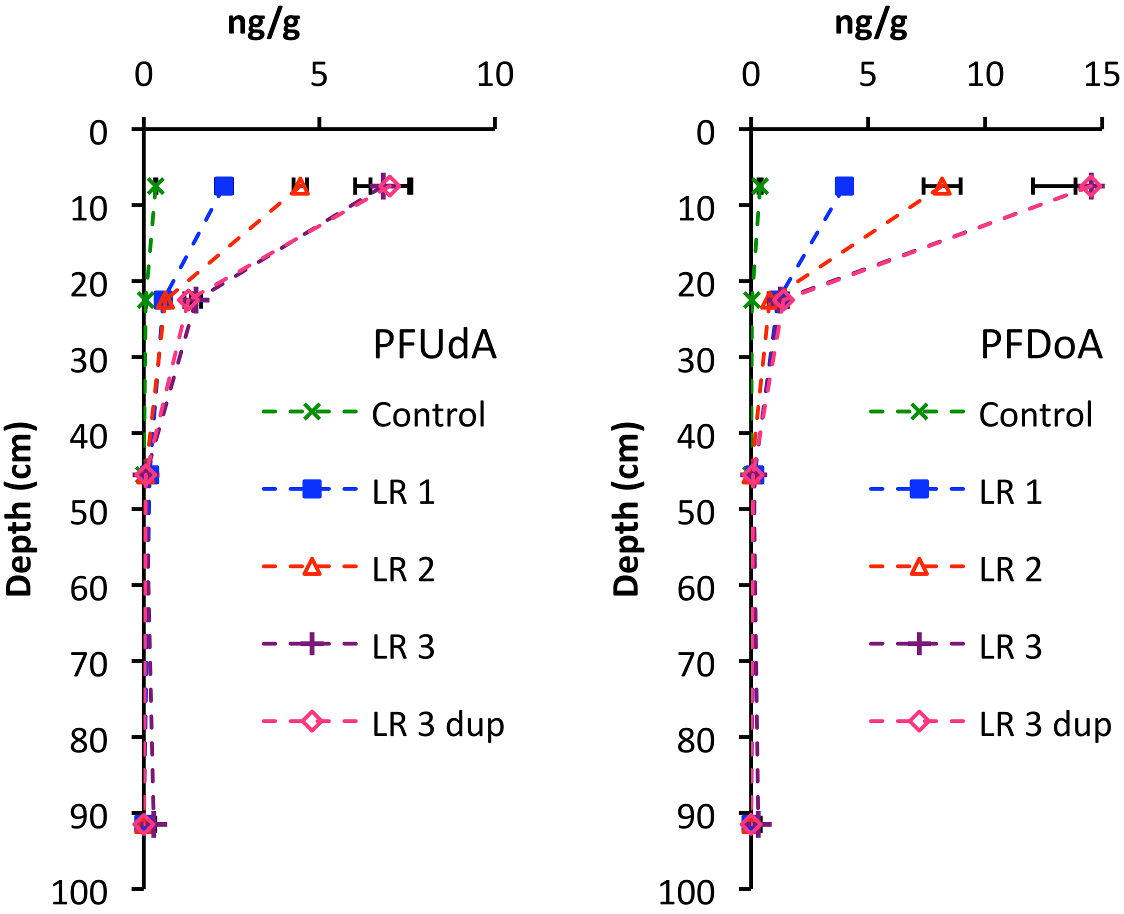
(d)

Figure A.4


ng/g
0
10
20
30
40
50
0
10
20
30
40
50
60
70
80
90
100
Depth (cm)
PFOA
Control
LR 1
LR 2
LR 3
LR 3 dup
ng/g
0
5
10
0
10
20
30
40
50
60
70
80
90
100
Depth (cm)
PFNA
Control
LR 1
LR 2
LR 3
LR 3 dup

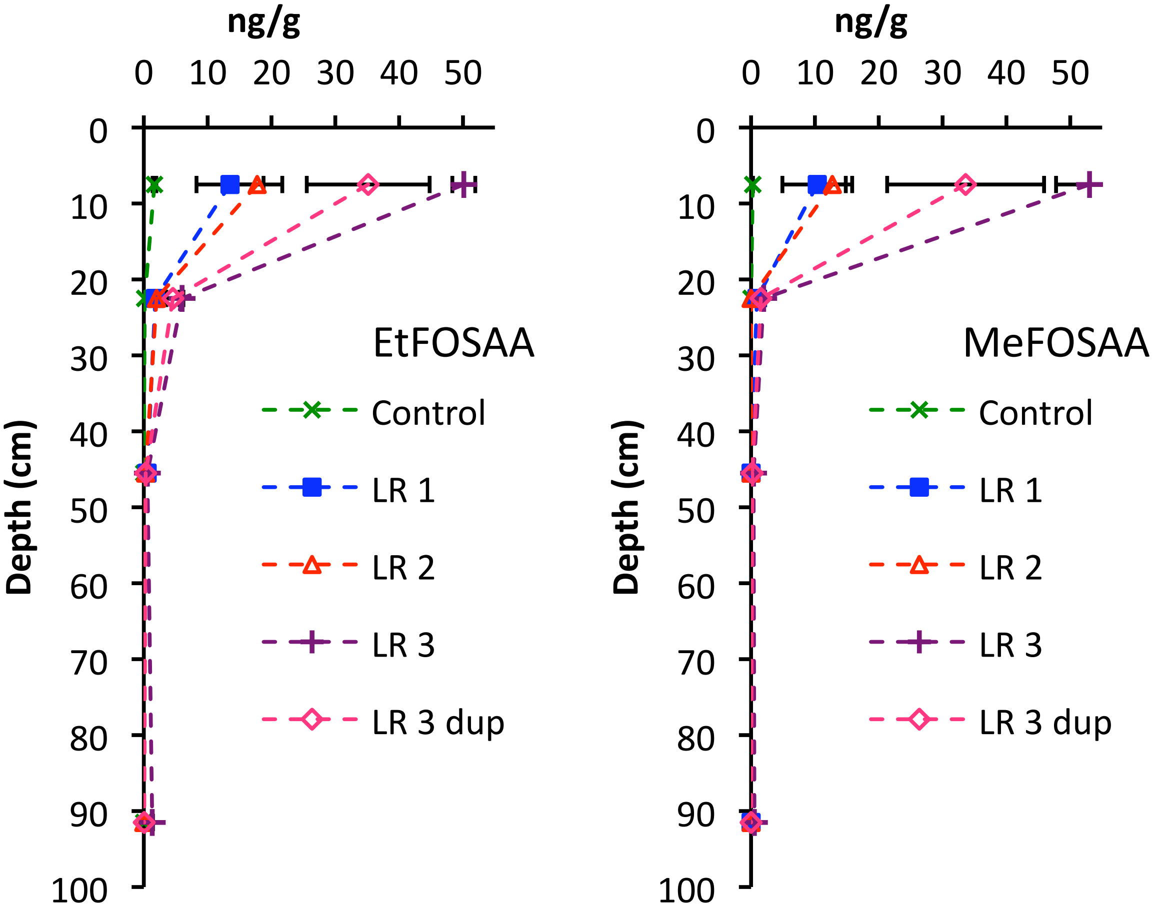
(e) (f)

Figure A.4


ng/g
0
5
10
0
10
20
30
40
50
60
70
80
90
100
Depth (cm)
PFUdA
Control
LR 1
LR 2
LR 3
LR 3 dup
ng/g
0
5
10
15
0
10
20
30
40
50
60
70
80
90
100
Depth (cm)
PFDoA
Control
LR 1
LR 2
LR 3
LR 3 dup

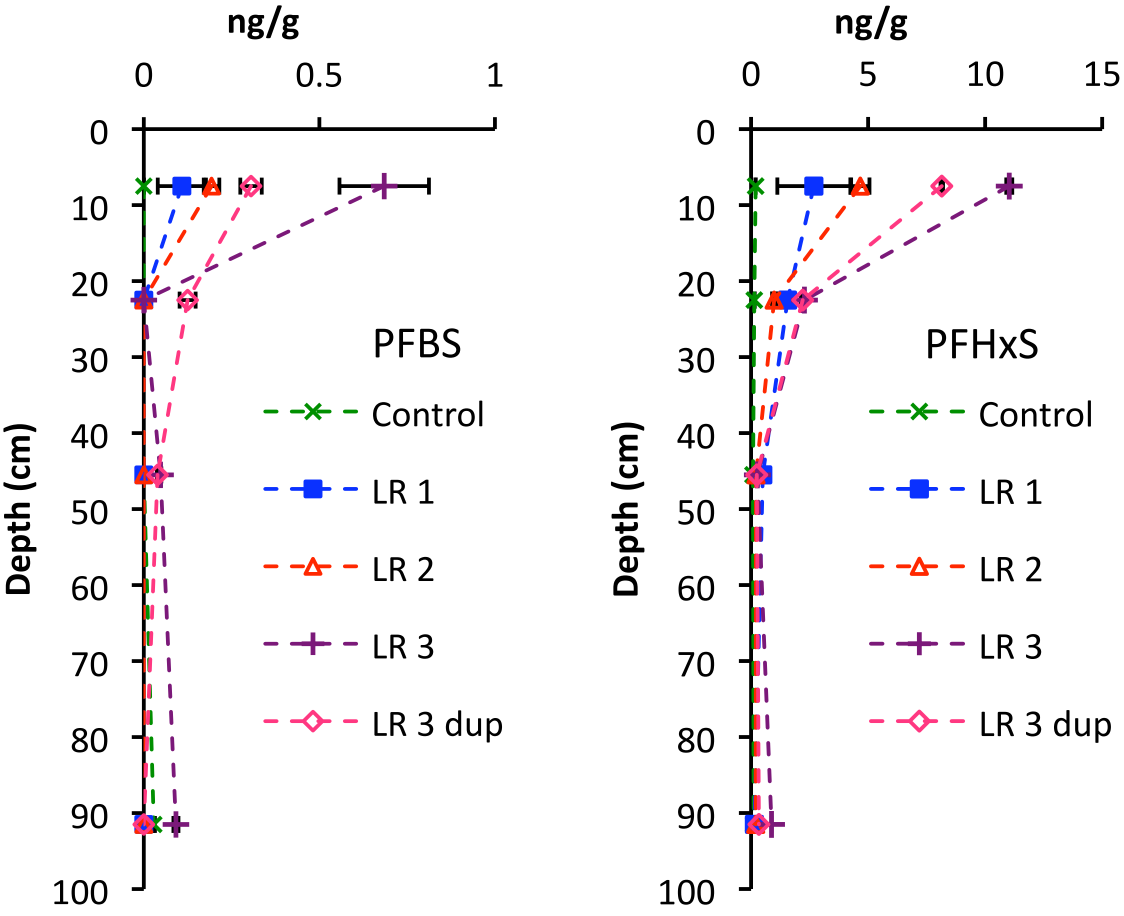
(g) (h)

Figure A.4


ng/g
0
10
20
30
40
50
Depth (cm)
0
10
20
30
40
50
60
70
80
90
100
EtFOSAA
Control
LR 1
LR 2
LR 3
LR 3 dup
ng/g
0
10
20
30
40
50
Depth (cm)
0
10
20
30
40
50
60
70
80
90
100
MeFOSAA
Control
LR 1
LR 2
LR 3
LR 3 dup

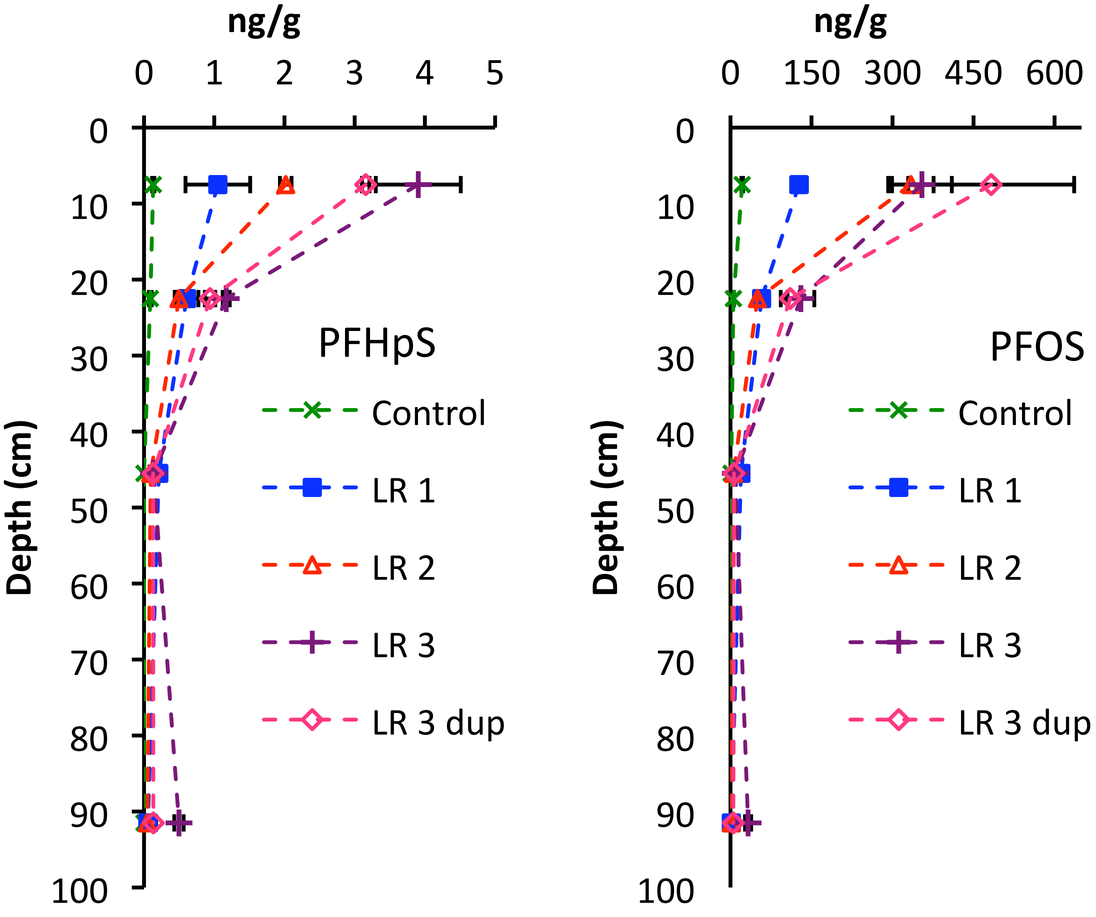
(i) (j)

Figure A.4


ng/g
0
0.5
1
Depth (cm)
0
10
20
30
40
50
60
70
80
90
100
PFBS
Control
LR 1
LR 2
LR 3
LR 3 dup
ng/g
0
5
10
15
Depth (cm)
0
10
20
30
40
50
60
70
80
90
100
PFHxS
Control
LR 1
LR 2
LR 3
LR 3 dup

(k) (l)

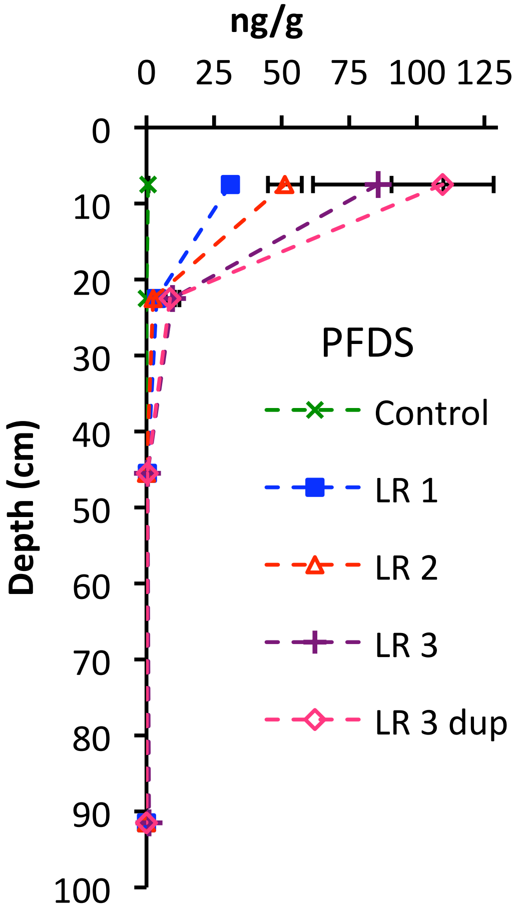
Figure A.4


ng/g
0
1
2
3
4
5
Depth (cm)
0
10
20
30
40
50
60
70
80
90
100
PFHpS
Control
LR 1
LR 2
LR 3
LR 3 dup
ng/g
0
150
300
450
600
Depth (cm)
0
10
20
30
40
50
60
70
80
90
100
PFOS
Control
LR 1
LR 2
LR 3
LR 3 dup

(m)

(n)

Figure A.4



(o)

Figure A.4: Concentrations of PFCs with depth in the long-term plots at various cumulative loading rates. Control = 0 Mg/ha, LR 1 = 553 Mg/ha, LR 2 = 1109 Mg/ha, and LR 3 and LR 3 dup = 2218 Mg/ha (on dry weight basis). In some instances, small increases in PFCs were measured between the 30-61 cm and 61-122 cm depth intervals, which could be simply due to preferential flow paths created as an artifact of excessive soil sampling because these plots have been sampled annually since 1973.

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APPENDIX B - SUPPORTING INFORMATION FOR SUBSURFACE TRANSPORT POTENTIAL OF PERFLUOROALKYL ACIDS AT AQUEOUS FILM-FORMING FOAM (AFFF)-IMPACTED SITES

B.1 Materials and Methods

This section contains the following tables: Table B.1Table B.2Table B.3

Table B.1: PFAAs and surrogate standards used in this study

Analyte	Surrogate Standard
PFBA	$[^{13}C_4]$PFBA
PFPeA	$[^{13}C_3]$PFPeA
PFHxA	$[^{13}C_2]$PFHxA
PFHpA	$[^{13}C_4]$PFHpA
PFOA	$[^{13}C_4]$PFOA
PFNA	$[^{13}C_5]$PFNA
PFDA	$[^{13}C_2]$PFDA
PFUnA	$[^{13}C_2]$PFUnA
PFBS	$[^{18}O_2]$PFHxS
PFHxS	$[^{18}O_2]$PFHxS
PFOS	$[^{13}C_4]$PFOS
6:2 FtS	$[^{13}C_4]$PFOS
8:2 FtS	$[^{13}C_4]$PFOS

Table B.2: Solid phase characteristics

Solid Phase	f_{oc}^1%	Sand %	Silt %	Clay%	ρ_b (g/cm^3)	pH	K (mg/kg)	Ca (mg/kg)	Mg (mg/kg)	Na (mg/kg)	H (mg/kg)	Fe^2 (g/kg)	Al^2 (g/kg)
Loamy Sand	1.7	81	1	9	1.14	6.1	319	1084	171	11	33	2.21	0.93
Loam	4.5	33	42	25	0.92	7.8	888	4418	607	14	21	6.14	1.67
Sandy Clay Loam	0.8	47	20	33	1.11	5.2	73	272	76	20	NM	24.17	3.99

1. Walkley-Black. 2. Citrate-bicarbonate-dithionite (CBD) extractable NM = not measured

Table B.3: Composition of artificial groundwater

Component	Concentration (mg/L)	Concentration (mM)
$MnSO_4 \cdot H_2O$	1	0.01
Na_2SO_4	180	1.27
$NaCl$	113	1.93
$NaHCO_3$	40	0.48
HCl	pH to 6.5	N/A

B.1.1 Batch Sorption Experiments

All sorption isotherms were measured as 5-point isotherms with initial aqueous concentrations of 0.5, 5, 50, 500, and 1000 µg/L. Triplicate reactors were prepared for each soil type and concentration point by transferring soil and artificial groundwater (Table B.3) with 1 g/L of sodium azide to a 50 mL polypropylene tube to achieve a soil-water ratio (rsw) of 0.375 g/mL. Preliminary calculations were done with previously measured K_{OC} values [6] to try and ensure that the soil to water ratios would yield aqueous concentrations of the strongest sorbing compounds that would be detectable over the majority of the isotherm. Reactors were then spiked with 20 µL of an appropriate concentration of PFAA mix spiking solution prepared in 70/30 such that methanol comprised only ~0.04% of the aqueous phase. Reactors were vortexed and placed on a shaker table (VWR 5000 STD 120V, West Chester, PA) for a period of 10 days based on previous work [6, 16]. Prior to sampling, the reactors were centrifuged (Eppendorf 5810, Hamburg, Germany) at 2,700 rpm (1467 RCF), for 20 min. At the completion of the 10-day sorption experiments, the aqueous phase was sampled and removed and the solid phase from all reactors was extracted to determine residual fraction of PFAAs in the solid phase and to enable the completion of mass balance calculations (Table B.7). Batch sorption isotherms with PFAA mix were measured in soils A, B, and C.

A series of sorption experiments was also conducted to study competitive effects, the impacts of NAPL, and the impacts of other AFFF hydrocarbon surfactants on PFAA sorption. To determine if there were any competitive effects amongst PFAAs, batch sorption isotherms with PFOA or PFOS only were measured in soils A and B. These reactors were prepared as described above but were spiked with 20 µL of a spiking solution in 70/30 that contained either PFOS or PFOA only. To determine the impacts of NAPL on PFAA sorption, isotherms were repeated for soils A and B; however the solid phase of these reactors was modified with 1 mL of TCE and stirred vigorously prior to the addition of aqueous phase or PFAA mix. Finally, sorption experiments in the presence of other AFFF surfactants were completed in soils A, B, and C. Reactors for these experiments were prepared as described above but were consecutively spiked with 20 µL of a spiking solution in 70/30 containing either sodium decyl sulfate (SDS) or n,n-dimethyldodecylamine n-oxide (AO). Reactors were spiked with 100 mg/L of either SDS or AO.

Prior to completing the isotherms with SDS and AO, preliminary single-point Kd measurements of PFAA sorption were completed in reactors with soils A and B spiked with 500 µg/L of PFAAs and either 0.5, 10, 50, 100 mg/L of either SDS or AO. PFAA results from these experiments are not utilized in this work; however reactors from these experiments were retained and analyzed for SDS or AO as appropriate to serve as a 4-point isotherm for these surfactants to serve as a semi-quantitative analysis of SDS or AO sorption relative to PFAAs. Unfortunately, matrix interference prevented use of analytical results of AO concentrations and those results were removed from further consideration. Because SDS analysis did not employ a stable-isotope surrogate standard, quantitative use of these results should be treated with caution. Additionally, the solid phase of these reactors was not extracted for SDS, so all sorption results are based on the aqueous loss method as described in previous work [6].

Finally, to understand the impacts of NAPL on PFAA sorption the partitioning of PFAAs in NAPL-water only systems was studied. Two model NAPLs, TCE and dodecane (DD), were selected. Though DD was not used in batch isotherms, PFAA-DD partitioning was studied to determine how NAPL type my impact PFAA sorptive behavior in the presence of NAPL. NAPL-water partitioning experiments were conducted in 50 mL glass centrifuge tubes with an actual capacity of 63 mL and were prepared with 12.5 mL of NAPL and 50 mL of artificial groundwater, yielding a NAPL-water ratio of 0.25 mL/mL. Glass tubes were utilized in NAPL experiments because TCE is incompatible with polypropylene. Experiments in glass tubes were designed to minimize the air space in the glass centrifuge tubes as PFAA loss to glass reactors appears to be controlled by the amount of surface area available for a meniscus to form (unpublished data). All NAPL-water experiments were spiked to an initial aqueous concentration of 500 µg/L and allowed to equilibrate on a shaker table for 3-days based on previous work [17]. At the end of the 3-day period, reactors were allowed to sit for 30 minutes prior to sampling the aqueous phase. Because DD is a liqht non-aqueous phase liquid (LNAPL), DD was siphoned from the top of batch reactors using a Pasteur pipet prior to sampling the aqueous phase. Residual DD remained after this process was complete; however, aqueous phase samples were taken from the center of the water column using a pipet extended through the residual DD phase.

B.1.2 Aqueous Sample Preparation

This section contains the following table: Table B.4.

To ensure that aqueous sample concentrations fell within the linear range of the calibration curve during analysis, each point in the batch isotherm was prepared with a specific dilution scheme (Table B.4). In general, an aliquot of aqueous phase from each batch reactor was diluted in a 2-mL microcentrifuge tube to create a 1500 µL interim sample. These interim samples were vortexed for 30 seconds and centrifuged (Fisher Scientific, accuSpin Micro 17) at 17,000 RCF for 30 minutes. Assuming spherical particles and an average particle density of 2.65 g/cm^3, the time, speed, and centrifuge properties (i.e. radius) can be used with Stokes Law to estimate the particle diameter removed during centrifugation. The maximum particle diameter that would stay in suspension during this process is approximately 0.04 µm. Clays, which are the smallest size classification and which comprise only a fraction of any soil in this study, are generally considered to be anything smaller than 2-4 µm indicating the potential for a significant amount of suspended soil particles is minimal. An aliquot of the interim sample was then used to prepare a 1500 µL final sample for analysis in an autosampler vial. Autosampler vials were vortexed 30 seconds prior to direct injection liquid chromatography tandem mass spectrometry (LC-MS/MS) analysis. Sample dilutions were designed assuming that none of the PFAA mass partitioned to the solid phase, thereby including a worst-case scenario to ensure final sample concentrations were within calibration range. Interim dilutions were 91% aqueous phase and 9% isopropanol. Final samples for analysis were 82% aqueous phase, 8% isopropanol and 10% 70/30 containing 0.3 ng surrogate standard.

Samples for SDS analysis were prepared from interim samples that were initially prepared for PFAA analysis using the 500 µg/L preparation scheme (Table B.4). Final samples for SDS analysis were prepared from these interim samples with dilution factors of 0.36, 0.05, 0.01, and 0.005 for reactors with initial aqueous concentration of SDS of 0.5, 10, 50, and 100 mg/L respectively. Final samples were prepared in autosampler vials with 9% isopropanol and 91% aqueous phase. Results were intended for semi-quantitative use only; therefore, no stable-isotope internal standard was used during these analyses.

Table B.4: Aqueous sample preparation scheme for batch sorption experiments.

	0.5 µg/L[a]	**5 µg/L**	**50 µg/L**	**500 µg/L**	**1000 µg/L**
Interim Sample Preparation:					
H_2O from batch reactor (µL)	NA	1215	900	150	25
Milli Q water (µL)	NA	150	465	1215	1340
Isopropanol (µL)	NA	135	135	135	135
Final Sample Preparation:					
H_2O from interim sample (µL)	NA	550	137	150	450
Diluent (MilliQ+9% isopropanol) (µL)	NA	800	1215	1200	900
Surrogate solution in 70/30 (µL)	NA	150	150	150	150

[a] Interim sample preparation was not required for this sample to be in calibration range and final sample was prepared directly from batch reactor as follows: 1215 µL of batch reactor aqueous phase, 135 µL of isopropanol, and 150 µL of surrogate solution.

B.1.3 Soil Extraction

This section contains the following table: Table B.5.

Moisture content of each sample was separately measured by drying overnight in an oven at 105^0C to enable reporting of the results on an oven-dry dry weight basis. After being sampled, the aqueous phase of batch sorption reactors was poured off and the remaining solid phase extracted in the 50 mL polypropylene conical tubes. A solvent mixture of 99:1 (v/v) methanol and ammonium hydroxide was employed for each extraction. Ten mL of the solvent mixture was added to each tube prior to vortexing and placement of each tube in a heated (30^0C) sonication bath (Fisher Scientific FS110H, Pittsburg, PA) for one hour. Each tube was subsequently removed and placed on a shaker table for two hours. The samples were then centrifuged at 2,700 rpm for 20 minutes (1467 RCF), and the extract was decanted into a clean, glass 20-mL scintillation vial. This procedure was repeated twice for a total of three extraction cycles. After each round of extraction, the extract was evaporated to dryness under nitrogen (Organomation Associates Inc. N-EVAP 112, Berlin, MA) and after the final extraction was reconstituted with 700 µL of 99:1 (v/v) methanol and acetic acid (acidic methanol). The reconstituted extract was transferred to a microcentrifuge tube containing 20-40 mg of ENVI-Carb (Supelco Inc., Bellefante, PA), vortexed by hand for thirty seconds, and centrifuged at 17,000 RCF for 30 minutes. . To ensure that soil extract concentrations fell within the linear range of the calibration curve during analysis, each point in the batch isotherm was prepared with a specific dilution scheme (Table B.5). In general, an aliquot of cleaned extract was transferred and diluted in a 2-mL microcentrifuge tube to create a 1800 µL interim sample. These interim samples were vortexed, and an aliquot of the interim sample was then used to prepare a 1500 µL final sample for analysis in an autosampler vial. Autosampler vials were vortexed 30 seconds prior to direct injection LC-MS/MS analysis. All interim dilutions were 70% acidic methanol and 30% dilution water (0.01% ammonium hydroxide in Milli-Q water). All final samples were 8.6% of a solution of 70/30 made with acidic methanol and dilution water, 1.4% of 70/30 containing 0.3 ng of surrogate solution, and 90% Milli-Q.

Table B.5: Solid extract preparation scheme for batch sorption experiments.

	0.5 µg/L[a]	**5 µg/L**	**50 µg/L**	**500 µg/L**	**1000 µg/L**
Interim Sample Preparation:					
Solid extract (µL)	NA	120	20	20	20
Acidic methanol (µL)	NA	1140	1240	1240	1240
Dilution water (µL)	NA	540	540	540	540
Final Sample Preparation:					
Interim Sample (µL)	NA	118	130	23	20
70% acidic MeOH 30% Dilution H_2O (µL)	NA	12	0	107	110
Milli-Q (µL)	NA	1350	1350	1350	1350
Surrogate solution in 70/30 (µL)	NA	20	20	20	20

[a] Interim sample preparation was not required for this sample to be in calibration range and final sample was prepared directly from soil extract as follows: 39 µL of soil extract, 91 µL of 70% acidic methanol/30% dilution water solution, 20 µL of surrogate solution, and 1350 of Milli-Q.

B.1.4 LC-MS/MS Analysis

Chromatography was performed using an aqueous ammonium acetate (10 mM) and methanol (10mM) gradient delivered at a flow rate of 800 µL/min by a Shimadzu LC system (Shimadzu LC-20AD) pump controlled by Shimadzu controller (Shimadzu CBB-20A). Samples and standards were injected (1 mL) by a CTC Analytics LEAP Technologies autosampler onto a 50 mm x 4.6 mm Gemini C18 column (3-micron particle size, Phenomenex, Torrance, CA) equipped with a C18 Guard Column and Guard Cartridge (Higgins Analytical). For analysis of soil extracts, initial eluent conditions were 50% methanol and 50% water. The percent methanol was ramped to 95% over 4 min, held at 95% over 4 min, ramped down over 1.5 min, and held at 50% for 2.5 min. For analysis of aqueous samples, initial eluent conditions were 5% methanol and 95% water. The percent methanol was ramped to 60% over 0.75 min, ramped to 100% over 4 min, held at 100% over 3 min, ramped down to 5% over 0.5 min, and held at 5% for 1.75 min. A MDS Sciex Applied Biosystems 3200 mass spectrometer (MDS Sciex, Ontario) operating in negative electrospray ionization scheduled multiple reaction monitoring (MRM) mode was employed for sample analysis. Two MRM transitions were acquired for all analytes. The monitored transitions were analyte dependent and are the same or similar to those used previously for PFAAs. For PFSAs, these transitions correspond to decarboxylation transitions, while the monitored PFAA transitions were the formation of the FSO_3^- ion (m/z = 99). Monitored SDS transitions were the formation of the HSO_4^- (m/z = 97) ion. Quantitation was performed using Analyst®, with calibration curves generally having r^2 values greater than 0.98 and the accuracy of each calibration point within 30% of its expected value.

Optimal instrumental source parameters were determined and are as follows: ionspray voltage -4,000 V, curtain gas flow 35 arbitrary units (au), nebulizer gas flow 50 au, turbo gas flow 50 au, medium collision gas flow, and source temperature 650 °C. Zero air provided by a Parker-Balston Source 5000 Zero Air Generator (Haverhill, MA) was used for the nebulizer and drier gas, and nitrogen was used as the curtain and collision gas.

B.1.5 Quality Assurance/Quality Control Measures

This section contains the following tables: Table B.6Table B.7

To account for variations in the samples, batch sorption reactors were prepared in triplicate and the aqueous phase and solid extracts analyzed from all reactors. In all cases, analytical results are reported as the average of the three values. If one of the three values was below detection then the average value was reported as below detection.

To determine the effectiveness of the soil extraction method when soils were amended with NAPL, soil/NAPL mixtures were spiked with a known amount of PFAA Mix. The extraction method recovered 64% (PFHxA) to 103% (PFBS) of PFAAs (Table B.6). Similarly, spike recovery experiments were conducted with aqueous phase samples to determine any potential loss of PFAAs during sample preparation. Artificial groundwater spiked with a known amount of PFAA stock standard solution and PFAA internal standard solution was placed in 50 mL polypropylene tubes and carried through the aqueous sample preparation process to test for losses during sample preparation. Recoveries for all analytes were 78% (PFOS) to 122% (PFDA) for all analytes except PFUnA (51%).

Table B.6: Spike recovery results for soils amended with NAPL

Analyte	**% Recovery**	±
PFBA	99.9%	5.53%
PFPeA	77.9%	9.13%
PFHxA	64.3%	10.08%
PFHpA	89.6%	16.82%
PFOA	96.3%	13.48%
PFNA	100.6%	15.74%
PFDA	99.5%	20.50%
PFUnA	91.6%	7.82%
PFBS	103.0%	14.07%
PFHxS	87.2%	13.74%
PFOS	102.2%	6.16%

Control isotherms were prepared for sorption experiments by control reactors as described above for batch sorption isotherms but with no solid phase. These reactors were placed on the shaker table and sampled on the final day. If losses for an analyte were greater than 10%, then these results were used to calculate the mass of PFAA lost to the reactor so that this could be accounted for in mass balance calculations of PFAAs recovered in the solid phase, aqueous phase, and reactor. Mass lost to the reactor was calculated similar to previous work (Higgins and Luthy [6]) as follows:

$$f_w = \frac{M_w}{M_t} = \frac{M_w}{M_w + M_v} = \frac{C_w V_w}{C_w V_w + \sigma_v A_v}$$

where M_w is the mass of analyte in water, M_T is the total mass, M_v is the mass lost to the reactor (i.e. vial), C_w is the measured aqueous concentration of the analyte, V_w is the volume of water in the control reactor, σ_{av} is the surface area normalized concentration of analyte on the vial, and A_v is the surface area of the vial. If we divide this equation by $C_w V_w$:

$$f_w = \frac{1}{1 + \frac{\sigma_v A_v}{C_w V_w}} = \frac{1}{1 + K_v r_{av}}$$

where K_v is the vial-water distribution coefficient, and r_{av} is the ratio of vial surface area to aqueous phase (A_v/V_w). In control vials, f_w is measured because a known amount of PFAA is spiked into the vial and the analyte mass recovered in the aqueous phase is measured during aqueous phase analysis. Since f_w is known, the equation can be rearranged to solve for $K_v r_{av}$. Because r_{av} is constant for all reactors, the $K_v r_{av}$ term from control reactors can be used to solve for PFAA mass lost to the vial in batch sorption isotherms:

$$K_v r_{av} = \frac{\sigma_{av} A_v}{C_w V_w} = \frac{M_v}{M_w}$$

The $K_v r_{av}$ term is determined in control reactors and M_w in isotherm batch reactors with solid phase is measured by aqueous phase analysis. Therefore, this equation can be rearranged to solve for M_v, which can be incorporated into mass balance equations.

Control reactors were also prepared in glass centrifuge vials to account for losses to this type of vial in NAPL-water partitioning experiments. Vials were prepared as described above for NAPL-water batch experiments except with no NAPL phase. Mass lost to the vial was calculated as described above.

Finally, in this study, all solid and aqueous phase concentrations were measured enabling completion of mass balance calculations for recovery of PFAAs between the solid phase, aqueous phase, and vial (Table S8). If the average recovery for any single concentration point in an isotherm was above 130%, that point was removed from consideration in the isotherm and subsequent regressions. All mass balance results below are the average recovery for all PFAA concentrations and solid phases of points that were included in the isotherms for each set of experiments. For instance, PFAA only mass balances are the average of each PFAA that was recovered in the A, B, and C soils in experiments that contained no co-contaminants. AO mass balance results were anomalous and are discussed in more detail below. It should be noted that low recovery of longer chain-length PFAAs is thought to be the result of underestimation of the PFAA mass lost to the vial. Because all solid and aqueous phase concentrations were measured (as opposed to estimating solid phase via aqueous loss), these analytes were still considered in this study. As a result of consistent over-recovery, 6:2 FTSA and 8:2 FTSA were removed from further consideration in this study.

As mentioned, AO mass balance data showed anomalous over recovery of PFAAs. Exceptionally high K_v values were obtained from the control isotherms containing 100 mg/L AO and these lead to high estimates of M_v for the mass balances, resulting in the over recovery reflected. Isotherms containing AO were conducted simultaneously with isotherms containing no co-contaminant and all were spiked simultaneously. No anomalous recovery issues were reflected in data from isotherms with no co-contaminant, suggesting experimental errors with the PFAA spiking solution were unlikely. Additonally, analytical data met all data quality criteria, indicating that this is likely not an analytical artifact. It is possible that the presence of the AO in the control reactors led to additional losses of PFAAs to the vial through the formation of hemimicelles on the vial wall. One would expect this effect to be lessened in vials containing soil, as some of the AO would partition to the solid phase. Therefore, AO mass balances were repeated using K_v values from control vials containing no co-contaminant. The resulting corrected mass balances showed recovery more typical of other mass balances and AO results were still considered in this study. It should be noted that the value used for K_v affects only the mass balance results and not the results of soil-water partitioning coefficients. This is because both solid and aqueous phase PFAA concentrations were measured and so estimates of M_v were not needed to calculate partitioning coefficients.

Table B.7: Mass balance results for batch isotherms

Analyte	PFAA Only Mass Balance	n	±	PFAA+ NAPL Mass Balance	n	PFAA+ SDS Mass Balance	n	±	PFAA+ AO Mass Balance	n	±	PFAA+ AO Corrected	n	±
PFPeA	109%	3	9%	105%	2	101%	3	1%	111%	3	10%	107%	3	8%
PFHxA	110%	3	7%	113%	2	111%	3	5%	129%	3	7%	122%	3	8%
PFHpA	117%	3	9%	118%	2	118%	3	18%	131%	3	20%	116%	3	17%
PFOA	102%	3	5%	108%	2	124%	3	20%	175%	3	47%	110%	3	21%
PFNA	84%	3	6%	75%	2	87%	3	16%	245%	3	136%	76%	3	20%
PFDA	66%	3	7%	53%	2	67%	3	13%	626%	3	207%	60%	3	16%
PFUnA	53%	1		35%	1	47%	1		NM			NM		
PFBS	116%	3	16%	132%	2	113%	3	14%	152%	3	25%	137%	3	19%
PFHxS	111%	3	6%	105%	2	100%	3	15%	214%	3	70%	107%	3	16%
PFOS	76%	3	15%	80%	2	77%	3	17%	621%	3	572%	77%	3	13%
NM=not measured														

B.2 Results and Discussion

This section contains the following figure and tables: Figure B.1, Table B.8, Table B.8, Table B.8, Table B.8, Table B.8, Table B.8, Table B.8, Table B.8 and Table B.9

Table B.8: Soil isotherm parameters and interpolated K_d values

Table B8. Soil isotherm parameters and interpolated K_d values

Loamy Sand PFC Isotherms

Analyte Name	Aqueous Min (µg/L)	Aqueous Max (µg/L)	Solid Min (µg/kg)	Solid Max (µg/kg)	Obs.	Log K_f (mg/kg) $(mg/L)^{-n}$	±	n	±	R^2
PFBA	8.72	1097.33	4.861	100.16	12	-1.00	0.1	0.74	0.06	0.98
PFPeA	18.26	906.0	3.05	74.7	12	-1.08	0.04	0.84	0.04	1.00
PFHxA	15.86	1302.0	1.96	149.08	12	-0.86	0.09	0.95	0.08	0.99
PFHpA	14.87	1176.0	5.15	272.03	12	-0.57	0.05	0.92	0.04	1.00
PFOA- Mix	2.72	920.67	1.29	271.40	15	-0.44	0.12	0.88	0.08	0.98
PFOA-Only	2.81	738.0	1.35	368.47	15	-0.25	0.08	0.98	0.05	0.99
PFNA	1.66	712.67	5.79	433.23	15	-0.19	0.13	0.81	0.08	0.97
PFDA	2.69	449.33	24.50	745.57	12	0.12	0.04	0.68	0.03	1.00
PFUnA	0.39	75.93	33.89	842.68	12	0.56	0.08	0.61	0.03	0.99
PFBS	2.61	1071.33	1.61	227.92	15	-0.64	0.07	0.81	0.04	0.99
PFHxS	2.56	1092.00	1.62	280.61	15	-0.52	0.13	0.80	0.09	0.97
PFOS-Mix	0.66	425.33	3.46	638.53	15	0.13	0.11	0.77	0.05	0.99
PFOS-Only	0.54	286.00	2.65	751.44	15	0.36	0.05	0.88	0.02	1.00

Loamy Sand Interpolated K_d

C_w (nM)	C_w (mg/L)	C_s (mg/kg)	Interp K_d (L/kg)	Log K_d @ 5nm	C_w (mg/L)	C_s (mg/kg)	Interp K_d (L/kg)	Log K_d @ 350 µg/L
5	0.0011	0.00064	0.61	-0.22	0.35	0.05	0.13	-0.88
5	0.0013	0.00031	0.24	-0.63	0.35	0.03	0.10	-1.01
5	0.0016	0.00029	0.19	-0.73	0.35	0.05	0.15	-0.84
5	0.0018	0.0008	0.44	-0.35	0.35	0.10	0.29	-0.54
5	0.0021	0.00153	0.74	-0.13	0.35	0.14	0.41	-0.39
5	0.0021	0.00131	0.63	-0.20	0.35	0.20	0.57	-0.24
5	0.0023	0.00475	2.05	0.31	0.35	0.27	0.79	-0.10
5	0.0026	0.0223	8.69	0.94	0.35	0.64	1.82	0.26
5	0.0028	0.1025	36.41	1.56	0.35	1.92	5.48	0.74
5	0.0015	0.00119	0.80	-0.10	0.35	0.10	0.28	-0.55
5	0.002	0.00208	1.04	0.02	0.35	0.13	0.37	-0.43
5	0.0025	0.01306	5.23	0.72	0.35	0.60	1.71	0.23
5	0.0025	0.01161	4.65	0.67	0.35	0.92	2.62	0.42

Loam (B) PFAA Isotherms

Analyte Name	Aqueous Min (µg/L)	Aqueous Max (µg/L)	Solid Min (µg/kg)	Solid Max (µg/kg)	Obs.	Log K_f (mg/kg) $(mg/L)^{-n}$	±	n	±	R^2
PFBA	8.72	982.0	13.65	328.03	12	-0.53	0.05	0.65	0.04	0.99
PFPeA	20.54	918.0	5.73	289.52	12	-0.51	0.09	0.98	0.09	0.98
PFHxA	13.80	1234.67	4.01	172.91	12	-0.85	0.05	0.81	0.05	0.99
PFHpA	13.87	1058.67	2.52	542.64	12	-0.28	0.03	0.85	0.02	1.00
PFOA- Mix	1.58	618.0	4.35	1174.01	15	0.26	0.09	0.89	0.05	0.99
PFOA-Only	1.44	500.67	4.39	987.62	15	0.25	0.07	0.89	0.04	0.99
PFNA	0.59	358.00	5.79	1784.97	15	0.70	0.10	0.87	0.05	0.99
PFDA	0.30	107.73	32.00	2510.18	12	0.97	0.14	0.69	0.06	0.98
PFUnA	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
PFBS	1.88	938.0	3.69	701.22	15	-0.13	0.05	0.82	0.03	1.00
PFHxS	0.97	770.67	6.36	1306.82	15	0.21	0.05	0.78	0.03	1.00
PFOS-Mix	0.15	107.73	6.55	1970.90	15	1.15	0.08	0.85	0.03	1.00
PFOS-Only	0.09	72.73	5.30	1558.55	15	1.11	0.05	0.83	0.02	1.00

NM = Sorption could not be measured because aqueous concentrations were below detection.

B Interpolated K_d

C_w (nM)	C_w (mg/L)	C_s (mg/kg)	Interp K_d (L/kg)	Log K_d @ 5nm	C_w (mg/L)	C_s (mg/kg)	Interp K_d (L/kg)	Log K_d @ 350 µg/L
5	0.0011	0.00339	3.18	0.50	0.35	0.15	0.42	-0.37
5	0.0013	0.00048	0.36	-0.44	0.35	0.11	0.32	-0.50
5	0.0016	0.00076	0.49	-0.31	0.35	0.06	0.17	-0.76
5	0.0018	0.00243	1.34	0.13	0.35	0.21	0.61	-0.22
5	0.0021	0.00719	3.48	0.54	0.35	0.71	2.02	0.31
5	0.0021	0.00723	3.50	0.54	0.35	0.70	1.99	0.30
5	0.0023	0.0256	11.06	1.04	0.35	2.00	5.72	0.76
5	0.0026	0.151	58.91	1.77	0.35	4.50	12.86	1.11
5	0.0028	NM	NM	NM	0.35	NM	NM	NM
5	0.0015	0.00351	2.35	0.37	0.35	0.31	0.90	-0.05
5	0.002	0.0125	6.27	0.80	0.35	0.71	2.03	0.31
5	0.0025	0.0861	34.49	1.54	0.35	5.76	16.46	1.22
5	0.0025	0.0914	36.63	1.56	0.35	5.46	15.61	1.19

Table B.8

Sandy Clay Loam (C) PFAA Isotherms

Analyte Name	Aqueous Min (μg/L)	Aqueous Max (μg/L)	Solid Min (μg/kg)	Solid Max (μg/kg)	Obs.	Log K_f (mg/kg)(mg/L)$^{-n}$	±	n	±	R^2
PFBA	0.15	431.33	0.17	340.84	15	-0.18	0.09	0.97	0.04	0.99
PFPeA	0.21	599.33	0.14	335.79	15	-0.31	0.06	0.99	0.03	1.00
PFHxA	0.21	391.33	0.07	178.54	15	-0.34	0.04	1.05	0.02	1.00
PFHpA	0.42	857.33	0.23	433.41	15	-0.33	0.04	1.00	0.02	1.00
PFOA	0.37	661.33	0.28	733.56	15	0.02	0.09	1.08	0.04	0.99
PFNA	0.14	367.33	0.31	746.18	15	0.26	0.06	0.99	0.03	1.00
PFDA	0.04	173.20	0.25	883.25	15	0.68	0.02	0.98	0.01	1.00
PFUnA	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
PFBS	0.56	1000.67	0.27	685.04	15	-0.19	0.03	1.05	0.01	1.00
PFHxS	0.37	847.33	0.28	758.85	15	-0.06	0.01	1.01	0.01	1.00
PFOS	0.13	311.33	0.76	1201.49	15	0.55	0.03	0.94	0.01	1.00

NM = Sorption could not be measured because aqueous concentrations were below detection.

C Interpolated K_d

C_w (nM)	C_w (mg/L)	C_s (mg/kg)	Interp K_d (L/kg)	Log K_d @ 5nm	C_w (mg/L)	C_s (mg/kg)	Interp K_d (L/kg)	Log K_d @ 350 μg/L
5	0.0011	0.00084	0.79	-0.10	0.35	0.24	0.68	-0.17
5	0.0013	0.00069	0.53	-0.28	0.35	0.17	0.49	-0.31
5	0.0016	0.00051	0.33	-0.49	0.35	0.15	0.43	-0.36
5	0.0018	0.00086	0.47	-0.33	0.35	0.16	0.47	-0.33
5	0.0021	0.00133	0.64	-0.19	0.35	0.34	0.96	-0.02
5	0.0023	0.00439	1.89	0.28	0.35	0.64	1.83	0.26
5	0.0026	0.0138	5.36	0.73	0.35	1.70	4.85	0.69
5	0.0026	NM	NM	NM	0.35	NM	NM	NM
5	0.0015	0.00068	0.46	-0.34	0.35	0.21	0.61	-0.22
5	0.002	0.0016	0.80	-0.10	0.35	0.30	0.86	-0.07
5	0.0025	0.0128	5.11	0.71	0.35	1.32	3.78	0.58

Loamy Sand (A)+1.46 g TCE PFAA Isotherms

Analyte Name	Aqueous Min (μg/L)	Aqueous Max (μg/L)	Solid Min (μg/kg)	Solid Max (μg/kg)	Obs.	Log K_f (mg/kg)(mg/L)$^{-n}$	±	n	±	R^2
PFBA	0.49	427.33	0.81	351.11	15	-0.18	0.11	0.92	0.05	0.99
PFPeA	0.19	556.0	0.24	197.51	15	-0.27	0.18	0.89	0.08	0.97
PFHxA	2.55	426.67	0.65	168.78	12	-0.39	0.02	1.08	0.01	1.00
PFHpA	5.67	983.33	1.86	440.43	12	-0.38	0.04	1.06	0.03	1.00
PFOA	3.15	696.0	2.37	547.98	12	-0.24	0.13	0.89	0.06	0.99
PFNA	0.21	424.0	0.71	554.14	15	-0.03	0.13	0.89	0.06	0.99
PFDA	0.06	785.57	0.78	785.57	15	0.46	0.13	0.88	0.05	0.99
PFUnA	0.12	63.40	2.09	616.58	12	0.90	0.13	0.90	0.05	0.99
PFBS	4.47	1168.0	3.0	606.96	12	-0.29	0.04	0.97	0.03	1.00
PFHxS	0.43	974.67	0.32	643.45	15	-0.21	0.02	0.98	0.01	1.00
PFOS	0.19	293.33	0.61	969.97	15	0.52	0.03	1.01	0.01	1.00

A + TCE Interpolated K_d

C_w (nM)	C_w (mg/L)	C_s (mg/kg)	Interp K_d (L/kg)	Log K_d @ 5nm	C_w (mg/L)	C_s (mg/kg)	Interp K_d (L/kg)	Log K_d @ 350 μg/L
5	0.0011	0.00119	1.12	0.05	0.35	0.25	0.72	-0.14
5	0.0013	0.00144	1.10	0.04	0.35	0.21	0.60	-0.22
5	0.0016	0.00038	0.24	-0.61	0.35	0.13	0.37	-0.43
5	0.0018	0.00052	0.29	-0.54	0.35	0.14	0.39	-0.41
5	0.0021	0.00231	1.12	0.05	0.35	0.23	0.65	-0.19
5	0.0023	0.0042	1.82	0.26	0.35	0.37	1.05	0.02
5	0.0026	0.015	5.86	0.77	0.35	1.14	3.25	0.51
5	0.0028	0.0406	14.426	1.16	0.35	3.08	8.79	0.94
5	0.0015	0.00097	0.65	-0.19	0.35	0.19	0.53	-0.27
5	0.002	0.0014	0.70	-0.15	0.35	0.22	0.63	-0.20
5	0.0025	0.0079	3.17	0.50	0.35	1.15	3.29	0.52

Table B.8

Loam (B) + 1.46 g TCE PFAA Isotherms										
Analyte Name	Aqueous Min (µg/L)	Aqueous Max (µg/L)	Solid Min (µg/kg)	Solid Max (µg/kg)	Obs.	Log K_f (mg/kg) (mg/L)$^{-n}$	±	n	±	R^2
PFBA	0.26	598.0	0.41	413.81	15	-0.14	0.28	1.07	0.18	0.94
PFPeA	3.01	550.67	1.86	364.97	12	-0.27	0.21	1.04	0.14	0.97
PFHxA	0.14	336.0	0.15	216.38	15	-0.34	0.18	0.93	0.08	0.98
PFHpA	4.29	774.67	3.25	585.37	12	-0.19	0.17	1.03	0.12	0.97
PFOA	0.32	642.67	0.80	881.67	15	0.001	0.14	0.91	0.07	0.98
PFNA	0.04	280.67	0.65	1106.82	15	0.42	0.14	0.83	0.05	0.99
PFDA	1.81	54.13	24.58	1111.52	9	1.54	0.16	1.14	0.08	1.00
PFUnA	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
PFBS	0.60	1270.67	0.60	726.15	15	-0.36	0.15	0.92	0.08	0.98
PFHxS	0.18	988.00	0.60	996.55	15	-0.11	0.15	0.86	0.07	0.98
PFOS	0.04	140.80	1.08	2016.87	15	1.01	0.15	0.90	0.05	0.99

NM = Sorption could not be measured because aqueous concentrations were below detection.

B + TCE Interpolated K_d								
C_w (nM)	C_w (mg/L)	C_s (mg/kg)	Interp K_d (L/kg)	Log K_d @ 5nm	C_w (mg/L)	C_s (mg/kg)	Interp K_d (L/kg)	Log K_d @ 350 µg/L
5	0.0011	0.00049	0.46	-0.34	0.35	0.24	0.68	-0.17
5	0.0013	0.00055	0.42	-0.38	0.35	0.18	0.51	-0.29
5	0.0016	0.00116	0.74	-0.13	0.35	0.17	0.50	-0.30
5	0.0018	0.00099	0.54	-0.26	0.35	0.22	0.63	-0.20
5	0.0021	0.00361	1.75	0.24	0.35	0.39	1.10	0.04
5	0.0023	0.0172	7.41	0.87	0.35	1.10	3.15	0.50
5	0.0026	0.0384	14.95	1.17	0.35	10.41	29.75	1.47
5	0.0023	NM	NM	NM	0.35	NM	NM	NM
5	0.0015	0.0011	0.73	-0.13	0.35	0.17	0.48	-0.32
5	0.002	0.00374	1.87	0.27	0.35	0.32	0.90	-0.05
5	0.0025	0.0464	18.58	1.27	0.35	3.98	11.37	1.06

Loamy Sand (A) PFAA Isotherms + 100 mg/L SDS										
Analyte Name	Aqueous Min (µg/L)	Aqueous Max (µg/L)	Solid Min (µg/kg)	Solid Max (µg/kg)	Obs.	Log K_f (mg/kg) (mg/L)$^{-n}$	±	n	±	R^2
PFBA	0.17	472.00	0.10	1.90	15	-0.21	0.05	0.99	0.02	1.00
PFPeA	2.07	596.00	1.85	365.57	12	-0.23	0.01	0.93	0.01	1.00
PFHxA	2.16	487.33	1.76	241.56	12	-0.33	0.03	0.92	0.02	1.00
PFHpA	0.46	966.00	0.29	535.14	15	-0.26	0.02	0.98	0.01	1.00
PFOA	0.37	851.33	0.27	520.95	15	-0.19	0.07	0.96	0.03	1.00
PFNA	0.25	620.67	0.31	518.81	15	-0.08	0.03	0.94	0.01	1.00
PFDA	0.09	343.33	0.40	750.04	15	0.33	0.03	0.91	0.01	1.00
PFUnA	0.27	95.87	3.16	780.10	12	0.79	0.17	0.90	0.07	0.99
PFBS	0.55	1298.67	0.55	598.75	15	-0.32	0.02	0.91	0.01	1.00
PFHxS	0.39	1014.67	0.41	635.07	15	-0.19	0.02	0.93	0.01	1.00
PFOS	0.12	376.00	0.41	637.22	15	0.21	0.03	0.91	0.01	1.00

A + SDS Interpolated K_d								
C_w (nM)	C_w (mg/L)	C_s (mg/kg)	Interp K_d (L/kg)	Log K_d @ 5nm	C_w (mg/L)	C_s (mg/kg)	Interp K_d (L/kg)	Log K_d @ 350 µg/L
5	0.0011	0.00069	0.64	-0.19	0.35	0.22	0.63	-0.20
5	0.0013	0.00123	0.93	-0.03	0.35	0.22	0.64	-0.20
5	0.0016	0.00126	0.80	-0.10	0.35	0.18	0.51	-0.29
5	0.0018	0.00111	0.61	-0.21	0.35	0.19	0.56	-0.26
5	0.0021	0.00174	0.84	-0.07	0.35	0.24	0.67	-0.17
5	0.0023	0.00276	1.19	0.08	0.35	0.31	0.88	-0.06
5	0.0026	0.00921	3.59	0.56	0.35	0.82	2.33	0.37
5	0.0026	0.0289	11.27	1.05	0.35	2.42	6.90	0.84
5	0.0015	0.00131	0.87	-0.06	0.35	0.18	0.52	-0.28
5	0.002	0.00194	0.97	-0.01	0.35	0.24	0.69	-0.16
5	0.0025	0.00685	2.74	0.44	0.35	0.62	1.76	0.25

Table B.8

Loam (B) PFAA Isotherms + 100 mg/L SDS										
Analyte Name	Aqueous Min (μg/L)	Aqueous Max (μg/L)	Solid Min (μg/kg)	Solid Max (μg/kg)	Obs.	Log K_f (mg/kg) $(mg/L)^{-n}$	±	n	±	R^2
PFBA	0.21	408.00	0.14	343.59	15	-0.03	0.03	1.03	0.01	1.00
PFPeA	1.94	568.00	2.42	461.23	12	-0.08	0.03	0.94	0.02	1.00
PFHxA	2.14	428.00	2.17	345.69	12	-0.12	0.02	0.96	0.01	1.00
PFHpA	0.30	808.00	0.56	734.26	15	-0.03	0.04	0.93	0.02	1.00
PFOA	0.13	587.00	0.60	930.64	15	0.13	0.08	0.84	0.03	1.00
PFNA	0.10	256.00	0.71	1126.98	15	0.60	0.02	0.94	0.01	1.00
PFDA	0.03	121.07	0.68	1292.35	15	0.97	0.03	0.90	0.01	1.00
PFUnA	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
PFBS	0.44	893.00	0.94	793.18	15	-0.05	0.04	0.93	0.03	1.00
PFHxS	0.05	616.00	1.04	1210.85	15	0.17	0.10	0.77	0.04	0.99
PFOS	0.05	80.33	1.09	1362.76	15	1.17	0.02	0.95	0.01	1.00

NM = Sorption could not be measured because aqueous concentrations were below detection.

B + SDS Interpolated K_d								
C_w (nM)	C_w (mg/L)	C_s (mg/kg)	Interp K_d (L/kg)	Log K_d @ 5nm	C_w (mg/L)	C_s (mg/kg)	Interp K_d (L/kg)	Log K_d @ 350 μg/L
5	0.0011	0.0008	0.75	-0.13	0.35	0.31	0.89	-0.05
5	0.0013	0.00165	1.26	0.10	0.35	0.31	0.89	-0.05
5	0.0016	0.00157	1.00	0.00	0.35	0.28	0.80	-0.10
5	0.0018	0.00272	1.50	0.18	0.35	0.35	1.01	0.01
5	0.0021	0.00748	3.62	0.56	0.35	0.56	1.60	0.20
5	0.0023	0.0134	5.78	0.76	0.35	1.48	4.24	0.63
5	0.0026	0.0436	16.99	1.23	0.35	3.62	10.36	1.02
5	0.0026	NM	NM	NM	0.35	NM	NM	NM
5	0.0015	0.002	1.36	0.13	0.35	0.33	0.95	-0.02
5	0.002	0.0125	6.28	0.80	0.35	0.66	1.89	0.28
5	0.0025	0.0502	20.11	1.30	0.35	5.48	15.65	1.19

Sandy Clay Loam (C) PFAA Isotherms + 100 mg/L SDS										
Analyte Name	Aqueous Min (μg/L)	Aqueous Max (μg/L)	Solid Min (μg/kg)	Solid Max (μg/kg)	Obs.	Log K_f (mg/kg) $(mg/L)^{-n}$	±	n	±	R^2
PFBA	0.14	460.67	0.15	304.36	15	1.17	0.14	0.94	0.06	0.99
PFPeA	0.18	519.33	0.14	369.10	15	-0.32	0.12	0.97	0.05	0.99
PFHxA	0.24	446.00	0.25	272.41	15	-0.42	0.14	0.92	0.06	0.99
PFHpA	0.47	842.67	0.31	805.60	15	-0.21	0.11	1.01	0.06	0.99
PFOA	0.38	583.33	0.26	1416.73	15	0.18	0.14	1.13	0.07	0.99
PFNA	0.19	395.33	0.38	1200.30	15	0.33	0.11	1.03	0.05	0.99
PFDA	0.06	200.47	0.30	2041.57	15	1.02	0.04	1.08	0.01	1.00
PFUnA	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
PFBS	0.54	787.33	0.32	854.50	15	-0.11	0.09	1.05	0.05	0.99
PFHxS	0.34	726.67	0.31	1282.43	15	0.01	0.14	1.03	0.07	0.99
PFOS	0.16	259.33	0.76	1858.27	15	0.73	0.10	1.03	0.04	1.00

NM = Sorption could not be measured because aqueous concentrations were below detection.

C + SDS Interpolated K_d								
C_w (nM)	C_w (mg/L)	C_s (mg/kg)	Interp K_d (L/kg)	Log K_d @ 5nm	C_w (mg/L)	C_s (mg/kg)	Interp K_d (L/kg)	Log K_d @ 350 μg/L
5	0.0011	0.0233	21.83	1.34	0.35	5.51	15.74	1.20
5	0.0013	0.00075	0.57	-0.24	0.35	0.17	0.49	-0.31
5	0.0016	0.00102	0.65	-0.19	0.35	0.15	0.42	-0.38
5	0.0018	0.00103	0.57	-0.25	0.35	0.21	0.61	-0.21
5	0.0021	0.00143	0.69	-0.16	0.35	0.46	1.32	0.12
5	0.0023	0.00423	1.83	0.26	0.35	0.73	2.09	0.32
5	0.0026	0.0162	6.33	0.80	0.35	3.33	9.50	0.98
5	0.0026	NM	NM	NM	0.35	NM	NM	NM
5	0.0015	0.00083	0.56	-0.25	0.35	0.26	0.74	-0.13
5	0.002	0.00175	0.88	-0.06	0.35	0.35	1.01	0.00
5	0.0025	0.0112	4.50	0.65	0.35	1.84	5.24	0.72

Table B.8

Loamy Sand (A) PFAA Isotherms + 100 mg/L AO

Analyte Name	Aqueous Min (µg/L)	Aqueous Max (µg/L)	Solid Min (µg/kg)	Solid Max (µg/kg)	Obs.	Log K_f (mg/kg) (mg/L)$^{-n}$	±	n	±	R^2
PFBA	0.13	458.67	0.09	442.30	15	0.03	0.04	1.04	0.02	1.00
PFPeA	0.24	548.00	0.05	433.38	15	0.02	0.10	1.17	0.05	1.00
PFHxA	0.27	403.33	0.03	218.43	15	-0.13	0.09	1.20	0.04	1.00
PFHpA	0.52	884.00	0.08	562.78	15	-0.17	0.07	1.17	0.04	1.00
PFOA	0.45	724.67	0.07	833.55	15	0.17	0.11	1.25	0.06	0.99
PFNA	0.21	393.33	0.12	670.86	15	0.34	0.10	1.13	0.04	1.00
PFDA	0.05	196.67	0.13	1079.78	15	0.83	0.08	1.10	0.03	1.00
PFUnA	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
PFBS	0.58	984.67	0.20	888.16	15	0.02	0.13	1.09	0.07	0.99
PFHxS	0.34	806.00	0.14	875.01	15	0.10	0.10	1.10	0.05	0.99
PFOS	0.09	353.33	0.32	1250.33	15	0.54	0.07	0.98	0.03	1.00

NM = Sorption could not be measured because aqueous concentrations were below detection.

A + AO Interpolated K_d

C_w (nM)	C_w (mg/L)	C_s (mg/kg)	Interp K_d (L/kg)	Log K_d @ 5nm	C_w (mg/L)	C_s (mg/kg)	Interp K_d (L/kg)	Log K_d @ 350 µg/L
5	0.0011	0.00085	0.80	-0.10	0.35	0.36	1.03	0.01
5	0.0013	0.00045	0.34	-0.46	0.35	0.31	0.88	-0.06
5	0.0016	0.00033	0.21	-0.68	0.35	0.21	0.61	-0.22
5	0.0018	0.00043	0.23	-0.63	0.35	0.20	0.56	-0.25
5	0.0021	0.00067	0.32	-0.49	0.35	0.40	1.15	0.06
5	0.0023	0.00228	0.99	-0.01	0.35	0.66	1.90	0.28
5	0.0026	0.0095	3.70	0.57	0.35	2.13	6.09	0.78
5	0.0023	NM	NM	NM	0.35	NM	NM	NM
5	0.0015	0.00088	0.59	-0.23	0.35	0.34	0.96	-0.02
5	0.002	0.00137	0.69	-0.16	0.35	0.40	1.14	0.06
5	0.0025	0.01	4.02	0.60	0.35	1.25	3.56	0.55

Loam (B) PFAA Isotherms + 100 mg/L AO

Analyte Name	Aqueous Min (µg/L)	Aqueous Max (µg/L)	Solid Min (µg/kg)	Solid Max (µg/kg)	Obs.	Log K_f (mg/kg) (mg/L)$^{-n}$	±	n	±	R^2
PFBA	0.16	453.33	0.40	161.79	15	-0.23	0.19	0.85	0.09	0.97
PFPeA	0.27	627.33	0.26	175.33	15	-0.32	0.16	0.91	0.08	0.98
PFHxA	0.26	459.33	0.18	89.37	15	-0.50	0.17	0.91	0.08	0.98
PFHpA	0.36	978.00	0.44	260.34	15	-0.33	0.14	0.88	0.07	0.98
PFOA	0.22	618.00	0.72	582.87	15	0.15	0.14	0.91	0.06	0.99
PFNA	0.06	225.07	0.58	558.82	15	0.56	0.17	0.89	0.06	0.98
PFDA	0.13	63.73	4.53	726.77	12	1.08	0.24	0.86	0.10	0.98
PFUnA	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
PFBS	0.66	794.00	2.31	367.93	15	-0.11	0.17	0.81	0.09	0.96
PFHxS	0.06	580.67	0.98	506.61	15	0.09	0.17	0.76	0.97	0.97
PFOS	0.20	85.87	1.37	791.88	12	0.98	0.26	0.81	0.11	0.97

NM = Sorption could not be measured because aqueous concentrations were below detection.

B + AO Interpolated K_d

C_w (nM)	C_w (mg/L)	C_s (mg/kg)	Interp K_d (L/kg)	Log K_d @ 5nm	C_w (mg/L)	C_s (mg/kg)	Interp K_d (L/kg)	Log K_d @ 350 µg/L
5	0.0011	0.00177	1.67	0.22	0.35	0.24	0.68	-0.16
5	0.0013	0.00112	0.85	-0.07	0.35	0.18	0.53	-0.28
5	0.0016	0.00089	0.57	-0.24	0.35	0.12	0.35	-0.46
5	0.0018	0.0018	0.99	0.00	0.35	0.18	0.53	-0.28
5	0.0021	0.00495	2.40	0.38	0.35	0.54	1.53	0.19
5	0.0023	0.0161	6.95	0.84	0.35	1.43	4.08	0.61
5	0.0026	0.0706	27.50	1.44	0.35	4.88	13.94	1.14
5	0.0023	NM	NM	NM	0.35	NM	NM	NM
5	0.0015	0.00392	2.62	0.42	0.35	0.33	0.95	-0.02
5	0.002	0.0113	5.66	0.75	0.35	0.56	1.60	0.20
5	0.0025	0.0751	30.10	1.48	0.35	4.06	11.60	1.06

Table B.8

Sandy Clay Loam (C) PFAA Isotherms + 100 mg/L AO

Analyte Name	Aqueous Min (µg/L)	Aqueous Max (µg/L)	Solid Min (µg/kg)	Solid Max (µg/kg)	Obs.	Log K_f (mg/kg) $(mg/L)^{-n}$	±	n	±	R^2
PFBA	0.14	444.67	0.46	461.15	15	-0.24	0.18	0.86	0.08	0.97
PFPeA	0.19	537.33	0.16	476.96	15	-0.20	0.09	0.98	0.04	0.99
PFHxA	0.23	392.00	0.10	258.91	15	-0.28	0.08	1.04	0.04	1.00
PFHpA	0.35	674.00	0.41	819.49	15	0.05	0.03	1.01	0.02	1.00
PFOA	0.21	239.27	0.59	1978.06	15	0.98	0.03	1.15	0.01	1.00
PFNA	0.06	139.00	0.46	1788.75	15	1.28	0.10	1.08	0.04	1.00
PFDA	0.13	126.13	4.33	1784.11	12	1.20	0.27	0.87	0.10	0.97
PFUnA	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
PFBS	0.42	710.00	0.47	1339.82	15	0.24	0.03	1.05	0.02	1.00
PFHxS	0.18	235.33	0.85	2420.37	15	1.07	0.02	1.10	0.01	1.00
PFOS	0.04	89.60	1.19	2212.01	15	1.53	0.20	0.97	0.07	0.99

NM = Sorption could not be measured because aqueous concentrations were below detection.

C+AO Interpolated K_d

C_w (nM)	C_w (mg/L)	C_s (mg/kg)	Interp K_d (L/kg)	Log K_d @ 5nm	C_w (mg/L)	C_s (mg/kg)	Interp K_d (L/kg)	Log K_d @ 350 µg/L
5	0.0011	0.00157	1.47	0.17	0.35	0.23	0.67	-0.17
5	0.0013	0.00093	0.71	-0.15	0.35	0.22	0.64	-0.19
5	0.0016	0.00065	0.42	-0.38	0.35	0.18	0.50	-0.30
5	0.0018	0.00196	1.08	0.03	0.35	0.39	1.12	0.05
5	0.0021	0.00779	3.77	0.58	0.35	2.84	8.11	0.91
5	0.0023	0.0276	11.90	1.08	0.35	6.13	17.52	1.24
5	0.0026	0.0864	33.68	1.53	0.35	6.34	18.12	1.26
5	0.0023	NM	NM	NM	0.35	NM	NM	NM
5	0.0015	0.00182	1.22	0.09	0.35	0.57	1.63	0.21
5	0.002	0.0123	6.17	0.79	0.35	3.67	10.50	1.02
5	0.0025	0.1025	41.07	1.61	0.35	12.31	35.16	1.55

Table B.9: Summary of Freundlich n-values measured in PFAA and PFAA + co-contaminant isotherms

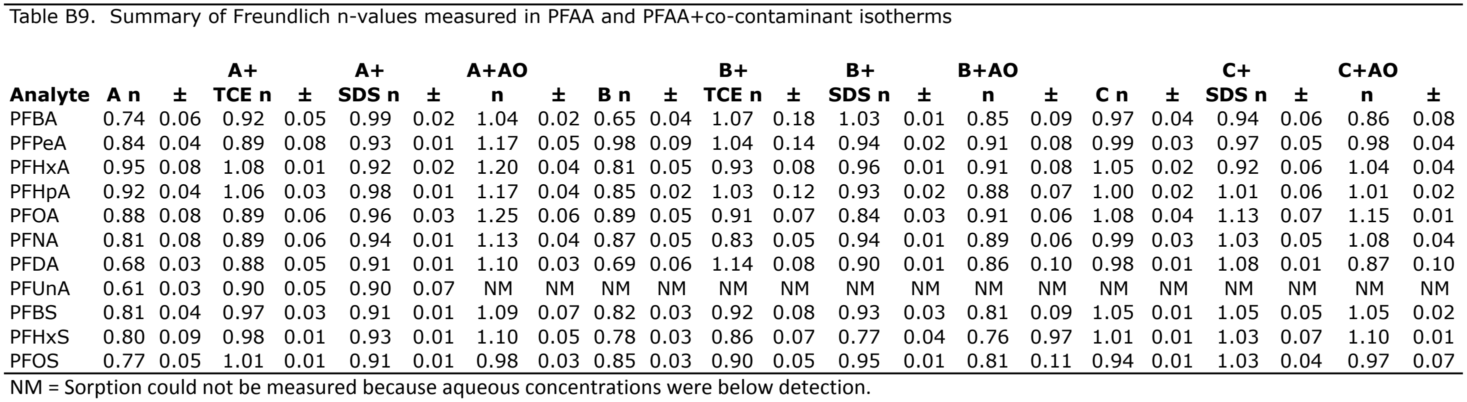
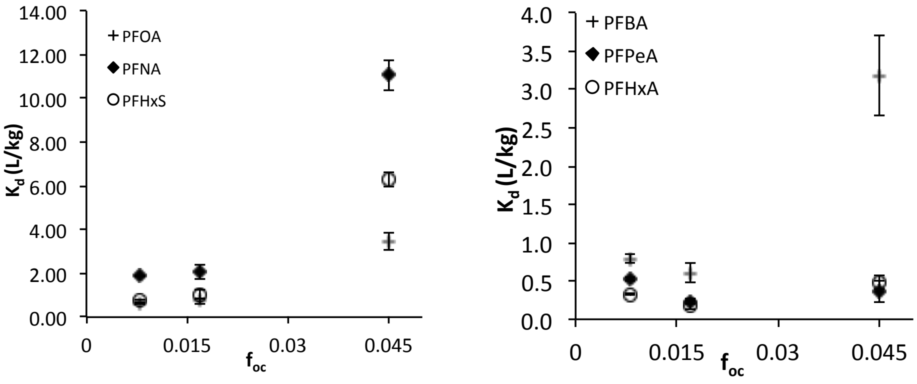


Table B9. Summary of Freundlich n-values measured in PFAA and PFAA+co-contaminant isotherms

Analyte	**A n**	**±**	**A+ TCE n**	**±**	**A+ SDS n**	**±**	**A+AO n**	**±**	**B n**	**±**	**B+ TCE n**	**±**	**B+ SDS n**	**±**	**B+AO n**	**±**	**C n**	**±**	**C+ SDS n**	**±**	**C+AO n**	**±**
PFBA	0.74	0.06	0.92	0.05	0.99	0.02	1.04	0.02	0.65	0.04	1.07	0.18	1.03	0.01	0.85	0.09	0.97	0.04	0.94	0.06	0.86	0.08
PFPeA	0.84	0.04	0.89	0.08	0.93	0.01	1.17	0.05	0.98	0.09	1.04	0.14	0.94	0.02	0.91	0.08	0.99	0.03	0.97	0.05	0.98	0.04
PFHxA	0.95	0.08	1.08	0.01	0.92	0.02	1.20	0.04	0.81	0.05	0.93	0.08	0.96	0.01	0.91	0.08	1.05	0.02	0.92	0.06	1.04	0.04
PFHpA	0.92	0.04	1.06	0.03	0.98	0.01	1.17	0.04	0.85	0.02	1.03	0.12	0.93	0.02	0.88	0.07	1.00	0.02	1.01	0.06	1.01	0.02
PFOA	0.88	0.08	0.89	0.06	0.96	0.03	1.25	0.06	0.89	0.05	0.91	0.07	0.84	0.03	0.91	0.06	1.08	0.04	1.13	0.07	1.15	0.01
PFNA	0.81	0.08	0.89	0.06	0.94	0.01	1.13	0.04	0.87	0.05	0.83	0.05	0.94	0.01	0.89	0.06	0.99	0.03	1.03	0.05	1.08	0.04
PFDA	0.68	0.03	0.88	0.05	0.91	0.01	1.10	0.03	0.69	0.06	1.14	0.08	0.90	0.01	0.86	0.10	0.98	0.01	1.08	0.01	0.87	0.10
PFUnA	0.61	0.03	0.90	0.05	0.90	0.07	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
PFBS	0.81	0.04	0.97	0.03	0.91	0.01	1.09	0.07	0.82	0.03	0.92	0.08	0.93	0.03	0.81	0.09	1.05	0.01	1.05	0.05	1.05	0.02
PFHxS	0.80	0.09	0.98	0.01	0.93	0.01	1.10	0.05	0.78	0.03	0.86	0.07	0.77	0.04	0.76	0.97	1.01	0.01	1.03	0.07	1.10	0.01
PFOS	0.77	0.05	1.01	0.01	0.91	0.01	0.98	0.03	0.85	0.03	0.90	0.05	0.95	0.01	0.81	0.11	0.94	0.01	1.03	0.04	0.97	0.07

NM = Sorption could not be measured because aqueous concentrations were below detection.



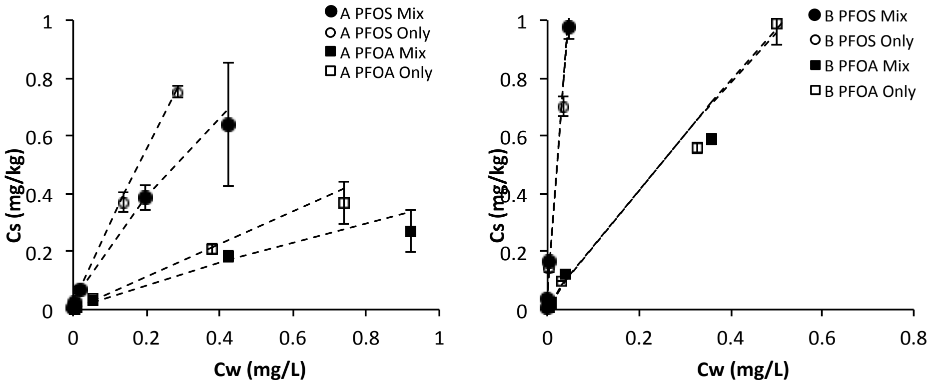
(a) (b)

Figure B.1: Trends of select PFAAs with soil f_{oc}. K_d values are concentration specific values calculated from Freundlich K_f and n values obtained from fitting sorption isotherms. Error bars represent the range of K_d values possible based on the standard deviations of fitted K_f and n values.

B.2.1 Competitive PFAA Sorption

This section contains the following figure: Figure B.2

Previous work found no competitive effects for PFOS when sorption occurred in a PFAA-mix vs. a PFOS only system,1 but the systems studied used fewer PFAAs and a lower concentration range than included herein. Single-solute isotherms for PFOA and PFOS were compared to PFOA/PFOS isotherms measured in a mixed-PFAA system (Figure B.2). In soil B, there was no statistical difference between sorption of either PFOA or PFOS in single vs. mixed-PFAA systems (Figure B.2). Minor competitive effects were evident in both PFOA and PFOS in soil A (Figure B.2). Because f_{oc} of the loamy sand is much lower than that of the loam (Figure B.2), competitive effects in the loamy sand may arise due to a more limited number of sites available for sorption. This indicates that competitive effects amongst PFAAs may be a factor in low foc environments; however overall effects observed in this study were considered to be minor and remaining experiments were conducted with a mix of the 13 PFAAs considered.



(a) (b)

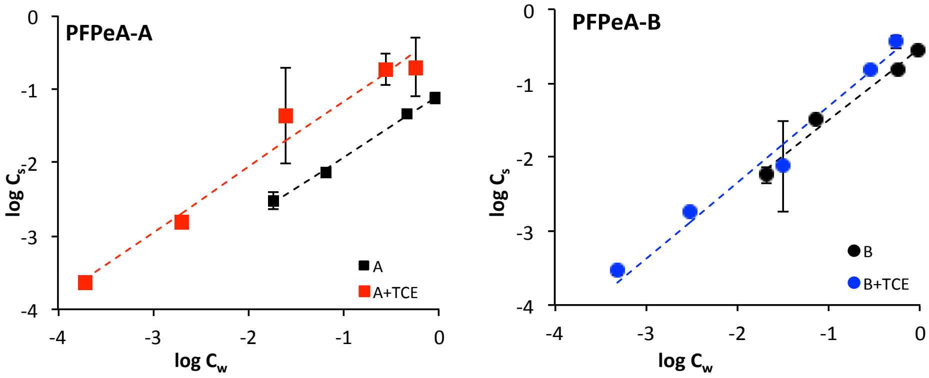
Figure B.2: Sorption of PFOA and PFOS to soils A and B in both mixed-PFAA (closed symbols) and single solute (open symbols) systems. Dashed lines are fitted Freundlich isotherms.

B.2.2 PFAA Log K_{oc}

This section contains the following tables: Table B.10, Table B.11

B.2.3 Impacts of NAPL

This section contains the following figures and table: Figure B.3, Figure B.3, Figure B.4, and Figure B.5.



(a) (b)

Figure B.3

Table B.10: Log K_{oc} values calculated in this work and compared to previous studies

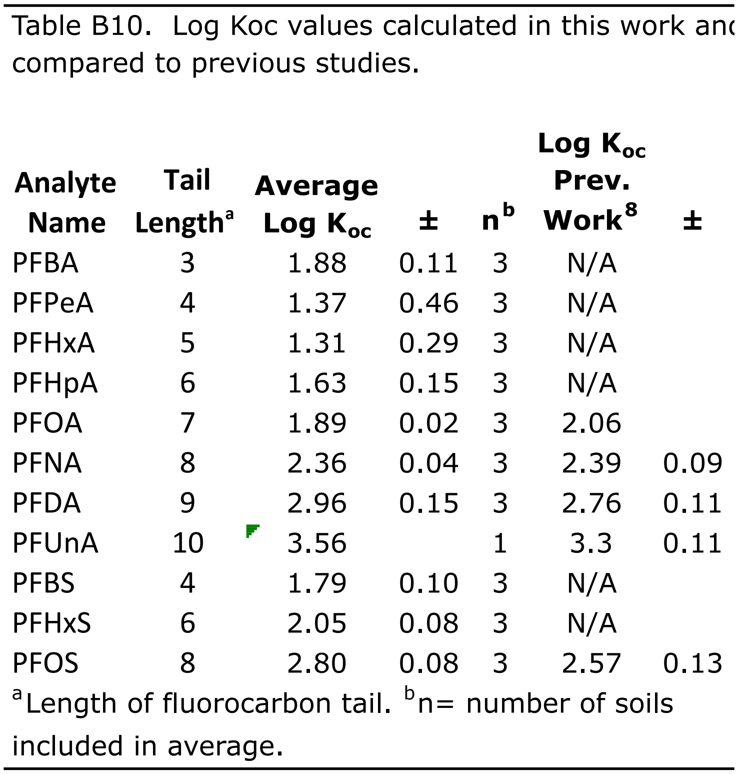


Table B10. Log Koc values calculated in this work an
compared to previous studies.

Analyte Name	Tail Length[a]	Average Log K_{oc}	±	n[b]	Log K_{oc} Prev. Work[8]	±
PFBA	3	1.88	0.11	3	N/A	
PFPeA	4	1.37	0.46	3	N/A	
PFHxA	5	1.31	0.29	3	N/A	
PFHpA	6	1.63	0.15	3	N/A	
PFOA	7	1.89	0.02	3	2.06	
PFNA	8	2.36	0.04	3	2.39	0.09
PFDA	9	2.96	0.15	3	2.76	0.11
PFUnA	10	3.56		1	3.3	0.11
PFBS	4	1.79	0.10	3	N/A	
PFHxS	6	2.05	0.08	3	N/A	
PFOS	8	2.80	0.08	3	2.57	0.13

[a] Length of fluorocarbon tail. [b] n= number of soils included in average.

Table B.11: K_{NAPL} values measured for DD and TCE

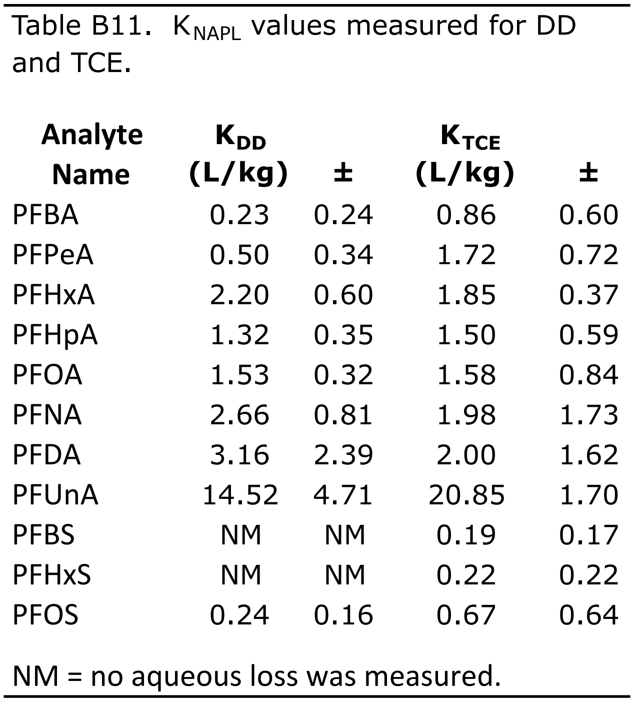
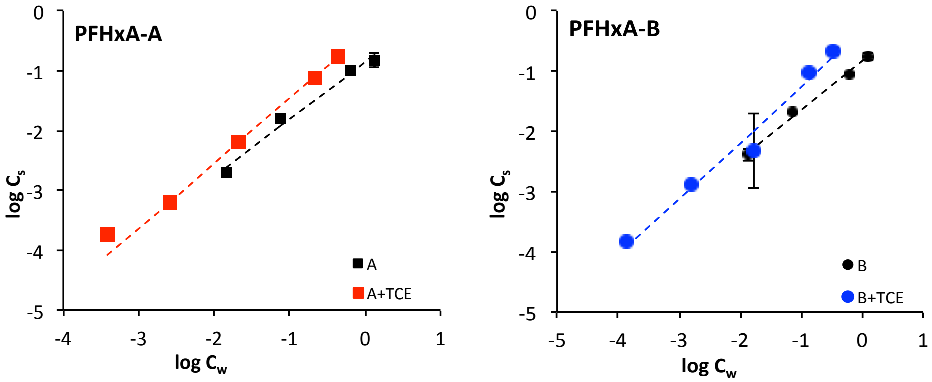


Table B11. K_{NAPL} values measured for DD and TCE.

Analyte Name	K_{DD} (L/kg)	±	K_{TCE} (L/kg)	±
PFBA	0.23	0.24	0.86	0.60
PFPeA	0.50	0.34	1.72	0.72
PFHxA	2.20	0.60	1.85	0.37
PFHpA	1.32	0.35	1.50	0.59
PFOA	1.53	0.32	1.58	0.84
PFNA	2.66	0.81	1.98	1.73
PFDA	3.16	2.39	2.00	1.62
PFUnA	14.52	4.71	20.85	1.70
PFBS	NM	NM	0.19	0.17
PFHxS	NM	NM	0.22	0.22
PFOS	0.24	0.16	0.67	0.64

NM = no aqueous loss was measured.



(c) (d)

Figure B.3: Sorption of PFPeA, and PFHxA to A (squares) and B (circles) soils in the absence (black) and presence (red) of TCE. Dashed lines are fitted Freundlich isotherms. Error bars represent relative error in triplicate measurements of C_s.

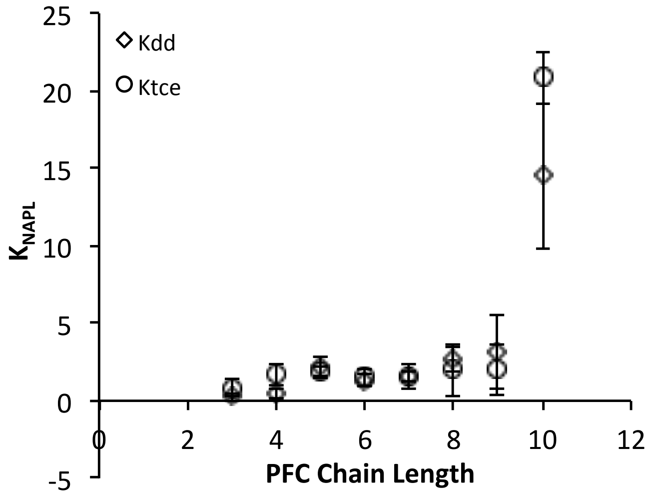


Figure B.4: Measured values for K_{NAPL} with PFAA chain length for PFCAs. Diamonds are values measured for DD (K_{DD}) and circles are values measured for TCE (K_{TCE}).

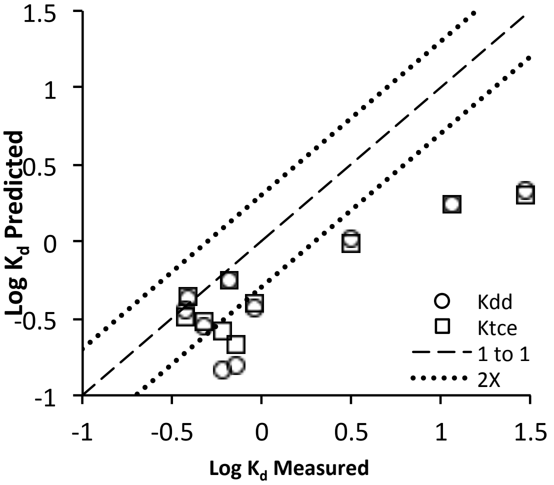


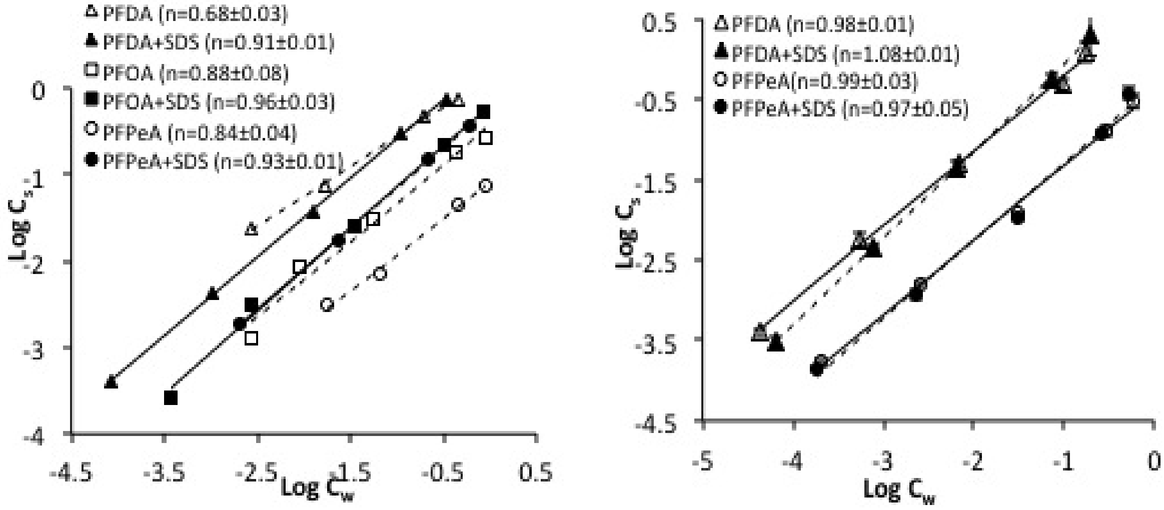
Figure B.5: Modeled vs. measured Log K_d values of PFAA sorption in the presence of TCE. Circles represent values modeled with K_{DD} and squares represent values modeled with K_{TCE}.

B.2.4 Impacts of SDS

This section contains the following tables and figures: Figure B.6 Figure B.8 Figure B.8 Figure B.8 Figure B.8 Figure B.8 Figure B.8 Figure B.8

This study utilized preliminary measurements of PFAA sorption in the presence of varying amounts of SDS to aid in determining the concentration of SDS to be used in final SDS+PFAA isotherms. Data from these experiments were not utilized, but they yielded sets of control (aqueous phase only) reactors with 0.5 mg/L of PFAAs and varying concentrations of SDS (Figure B.10). The change in aqueous PFAA concentrations with varying amounts of SDS in these control reactors may be taken as a proxy for changes to PFAA aqueous concentrations in the presence of SDS. Changes to PFAA aqueous concentrations varied. PFBA, PFOA, PFDA, PFUnA, and PFOS exhibited no statistically significant change in concentration with varying amounts of SDS. PFPeA, PFBS, and PFHxS showed increases in aqueous concentrations with SDS; however, these increases did not correspond to a decrease in sorption in the presence of SDS. Rather these compounds exhibited no change (PFHxS) or increases (PFPeA and PFBS) in sorption when SDS was present. PFHxA, PFHpA, and PFNA exhibited decreases in aqueous concentrations when SDS was present. PFHxA and

PFHpA showed increases in sorption when SDS was present; however PFNA sorption decreased despite decreased aqueous concentrations. If these changes in aqueous concentrations are assumed to be indicative of trends in PFAA solubility when SDS is present then collectively, this suggests that while solubility changes occur in some cases, it is not the most important factor determining changes to PFAA sorption when SDS is present.



(a) (b)

Figure B.6: Sorption of PFPeA (circles) and PFDA (triangles) in the presence (closed symbols) and absence (open symbols) of SDS to soils A and C. Solid lines are fitted Freundlich isotherms for open symbols and dashed lines are fitted Freundlich isotherms for closed symbols. Error bars represent relative error in triplicate measurements of C_s.

B.2.5 Impacts of AO

This section contains the following figures: Figure B.9 Figure B.10 Figure B.10 Figure B.10 Figure B.10 Figure B.10 Figure B.10 Figure B.10 Figure B.10

Similar to SDS, this study utilized preliminary measurements of PFAA sorption in the presence of varying amounts of AO to aid in determining the concentration of AO to be used in final AO+PFAA isotherms. As with SDS these experiments yielded sets of control reactors with 0.5 mg/L of PFAAs and varying concentrations of AO (Figure B.10). There was no statistically significant change in aqueous concentrations of PFBA, PFPeA, PFHxA,

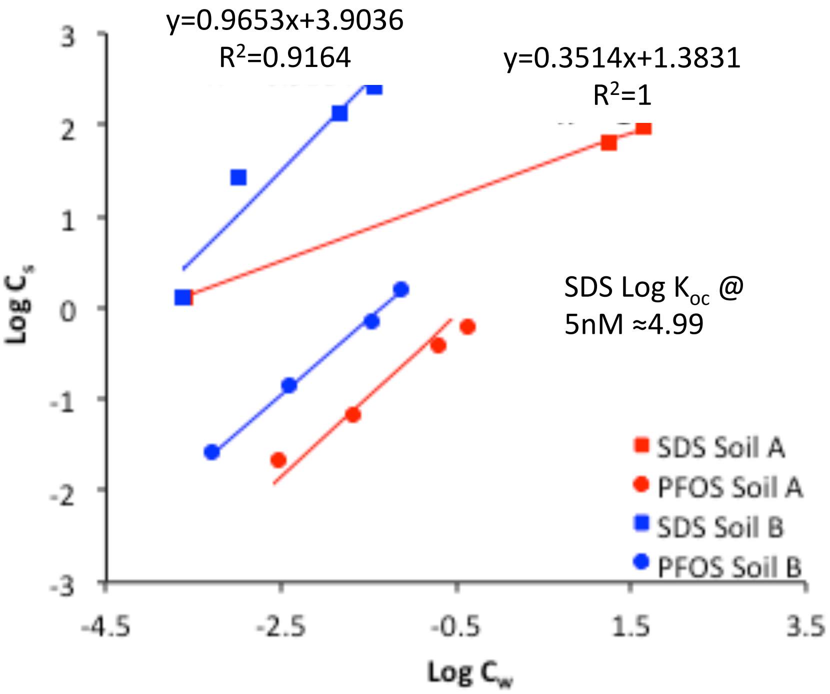
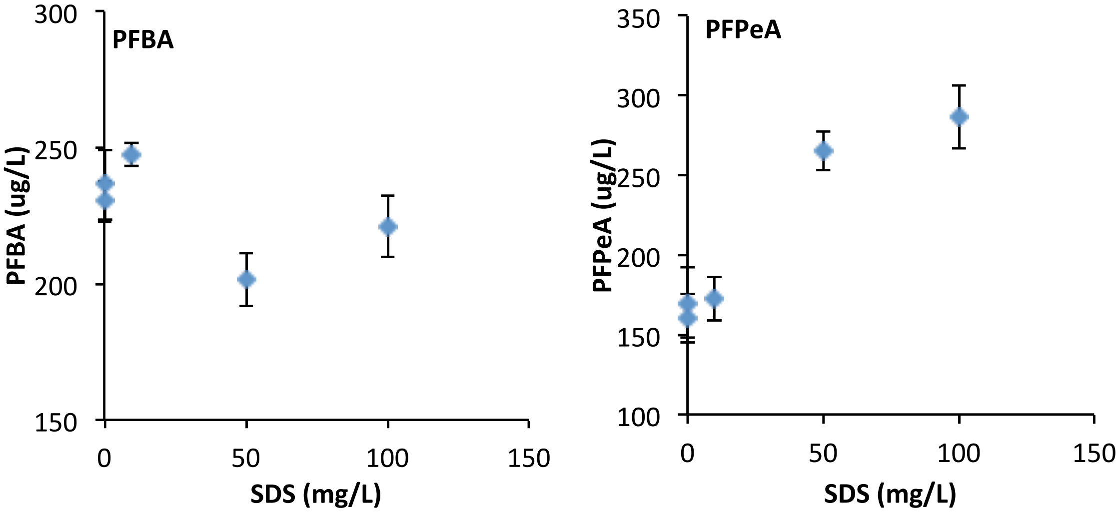
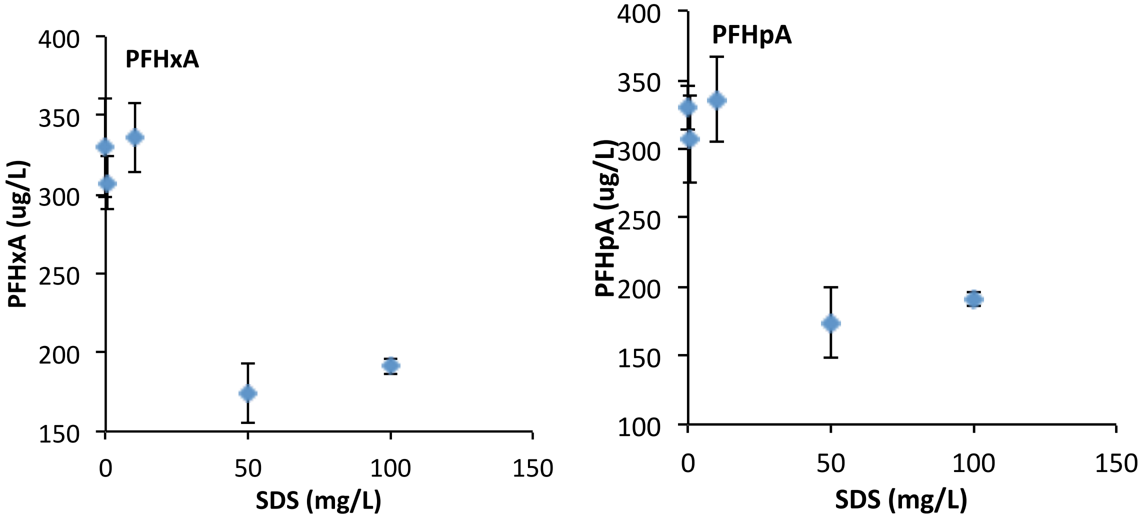


Figure B.7: SDS sorption isotherms for SDS (squares) and PFOS (circles) in soils A (red) and B (blue). Lines are are fitted Freundlich isotherms. Isotherm parameters and r2 values for SDS are shown on figure and are available for PFOS in Table B.8. Average Log K_{oc} for SDS at 5 nM is approximately 4.99 L/kg_{oc}.



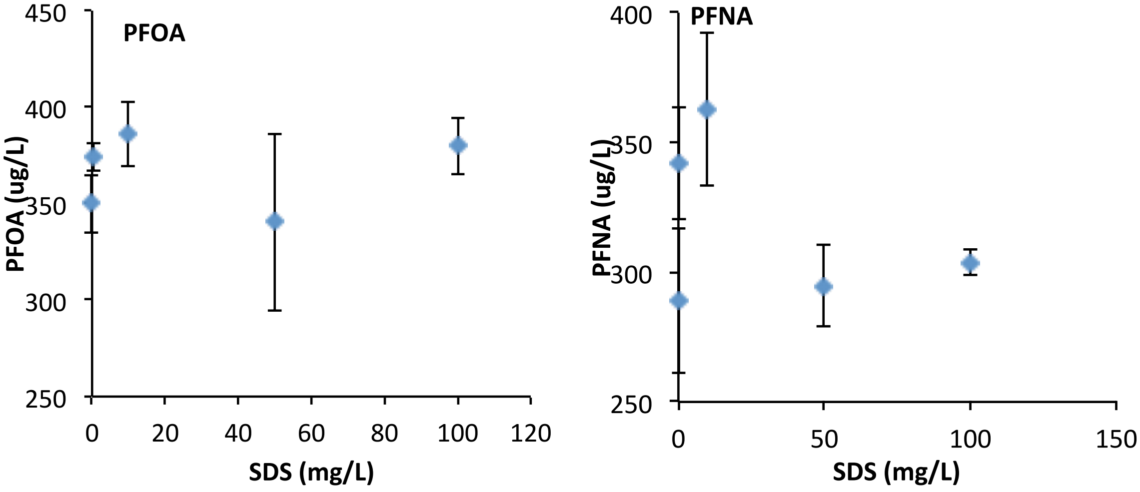
(a) (b)

Figure B.8



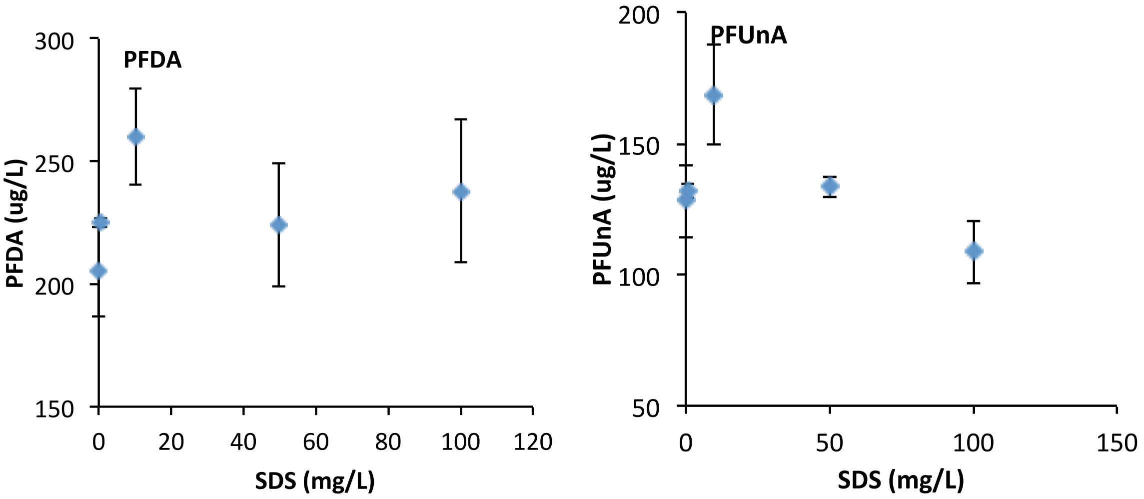
(c) (d)

Figure B.8



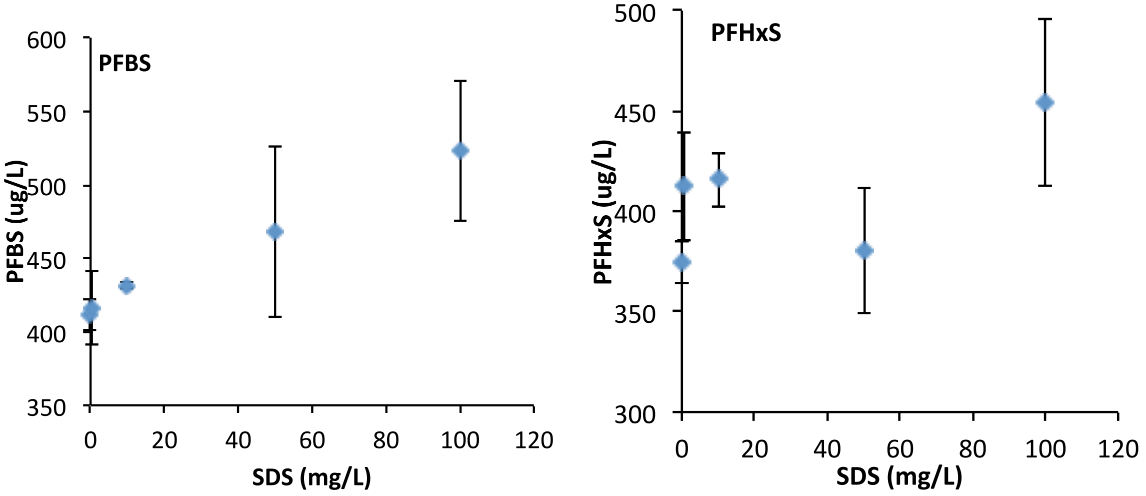
(e) (f)

Figure B.8



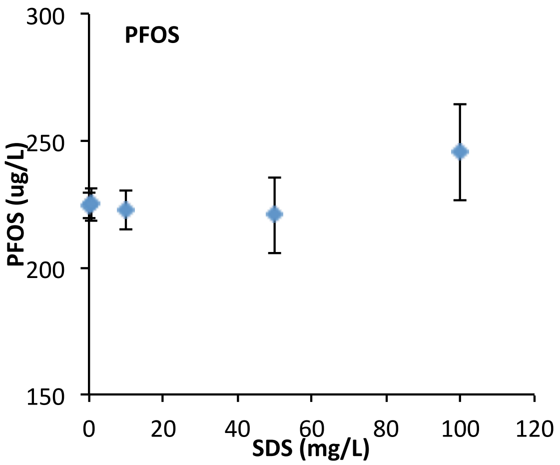
(g) (h)

Figure B.8



(i) (j)

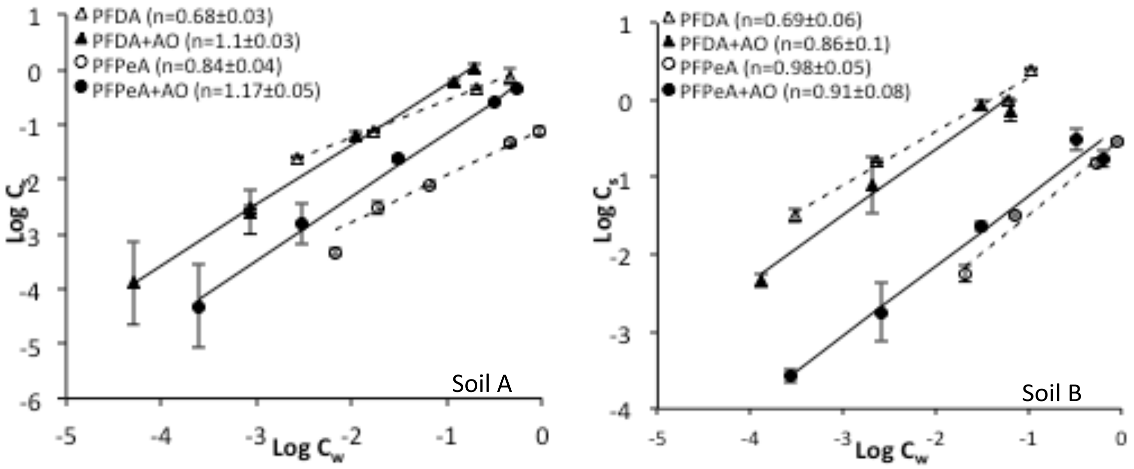
Figure B.8



(k)

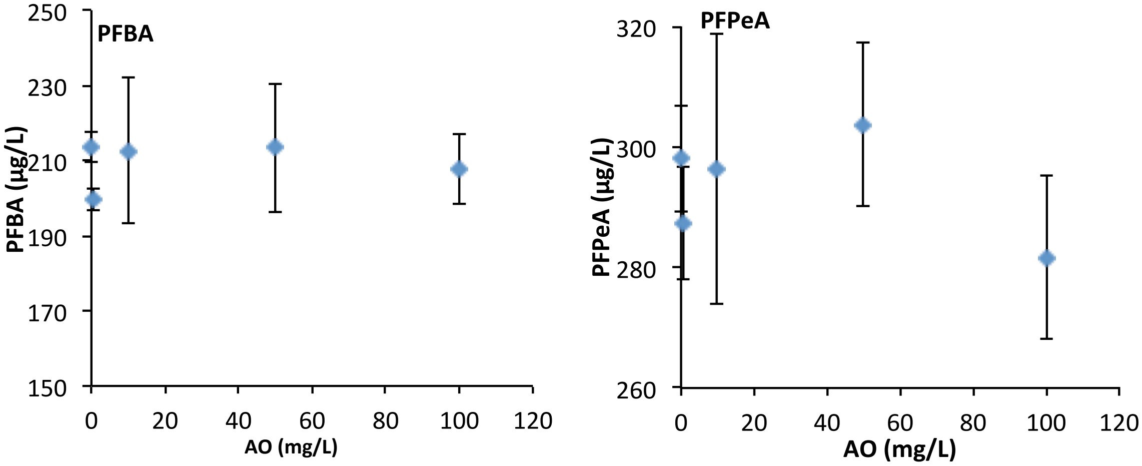
Figure B.8: Aqueous PFAA concentrations measured in the presence of varying concentrations of SDS. Reactors were prepared with 0.5 mg/L PFAAs and 0, 0.5, 10, 50, and 100 mg/L SDS. Note that Y-axis scales were varied based on aqueous PFAA concentrations measured.

PFHpA, or PFOA with varying amounts of AO; however, aqueous concentrations of PFNA and PFDA decreased. Similarly there was no change in the aqueous concentration of PFBS while the aqueous concentration of PFHxS and PFOS decreased. If these trends are assumed to be a proxy for aqueous PFAA trends when AO is present, then this implies a chain-length dependant trend in solubility wherein AO leads to an increase in affinity for the solid phase for the longer-chain length PFAAs. If this mechanism were a primary factor influencing changes to PFAA sorption in the presence of AO, then sorption would be expected to increase as aqueous concentrations decreased due to increased partitioning of long-chain PFAAs. This trend was observed in soil C indicating that this mechanism may be a primary factor causing changes to PFAA sorption with the addition of AO to this system. However, there was no corresponding trend in soils B or A. For instance, sorption of PFDA in soil B decreased despite a corresponding decrease in aqueous PFAA concentrations. Collectively, this suggests that solubility changes may be the predominant mechanism influencing changes to PFAA sorption with AO in positively charged soils, but that other mechanisms play a relatively more important role in negatively charged solid phases.



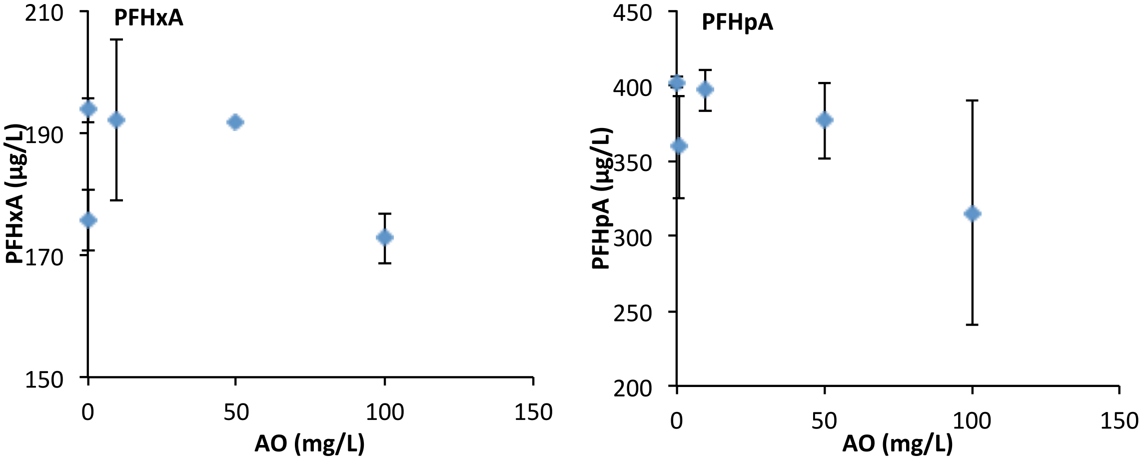
(a) (b)

Figure B.9: Sorption of PFPeA (circles) and PFDA (triangles) in the presence (closed symbols) and absence (open symbols) of AO to soils A and B. Solid lines are fitted Freundlich isotherms for closed symbols and dashed lines are fitted Freundlich isotherms for open symbols. Error bars represent relative error in triplicate measurements of C_s.



(a) (b)

Figure B.10



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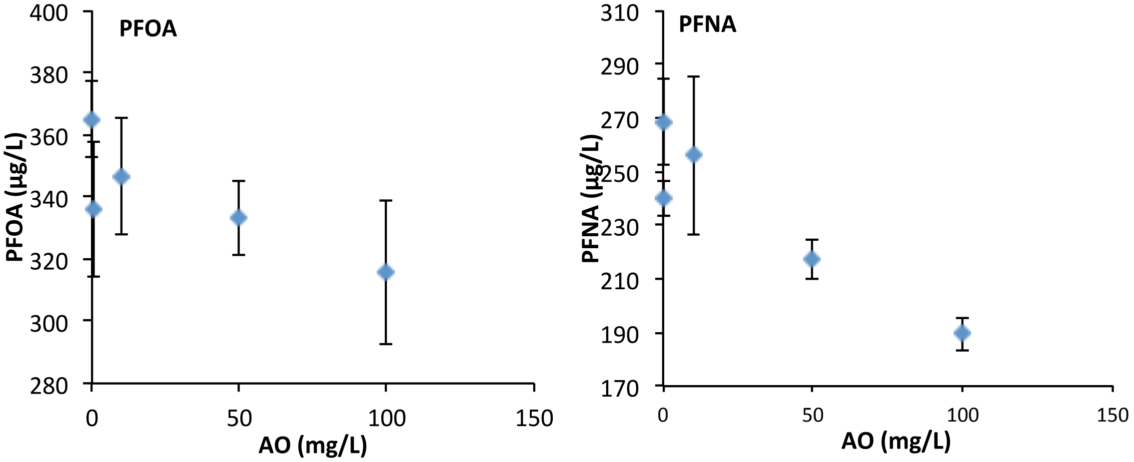

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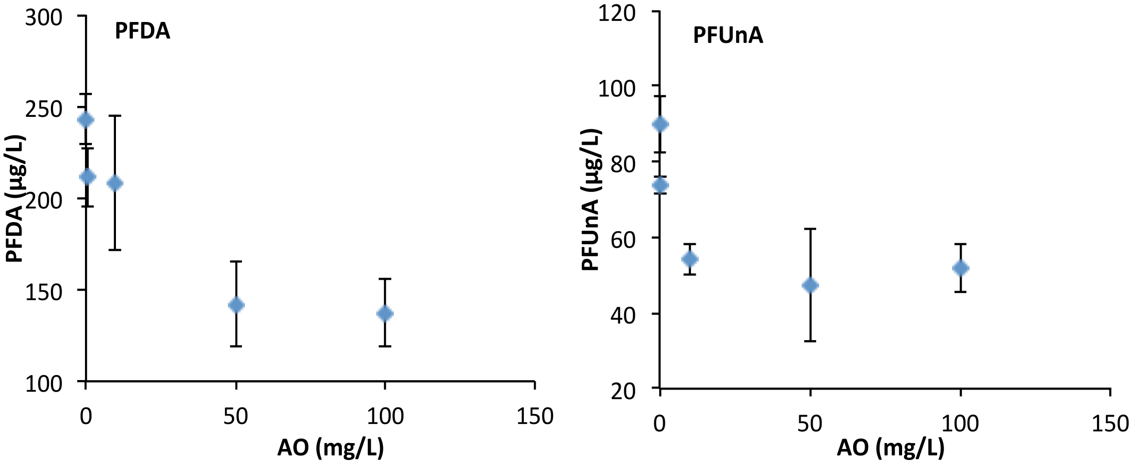
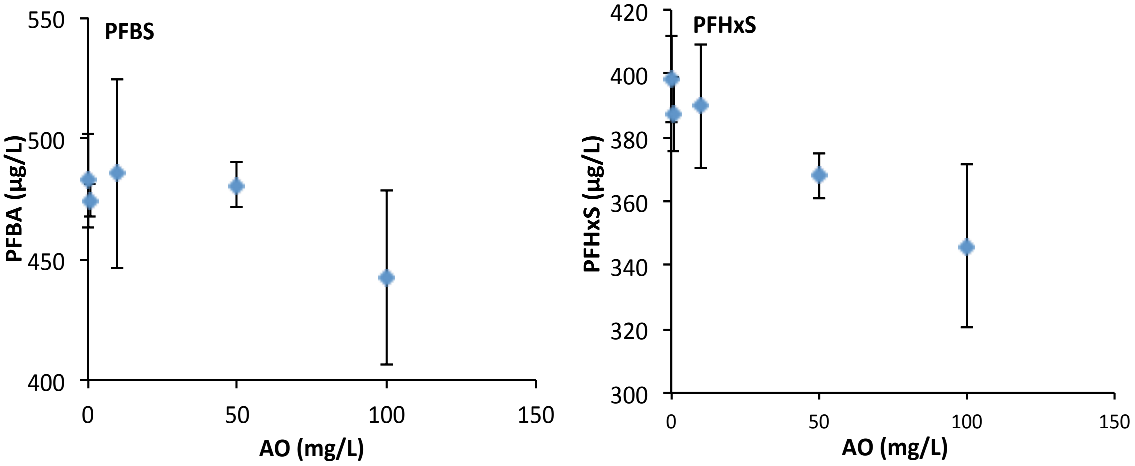


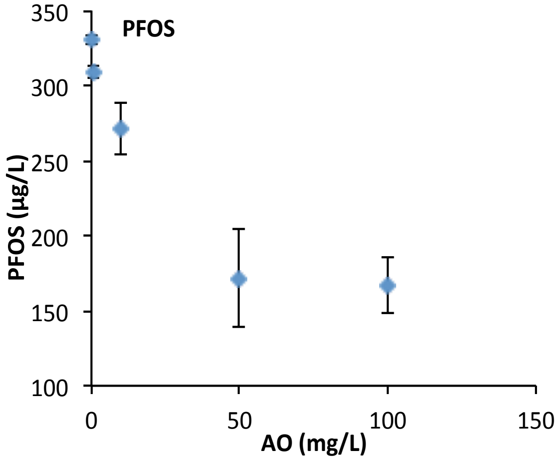
(g) (h)

Figure B.10



(i) (j)

Figure B.10



(k)

Figure B.10: Aqueous PFAA concentrations measured in the presence of varying concentrations of AO. Reactors were prepared with 0.5 mg/L PFAAs and 0, 0.5, 10, 50, and 100 mg/L AO. Note that Y-axis scales were varied based on aqueous PFAA concentrations measured.

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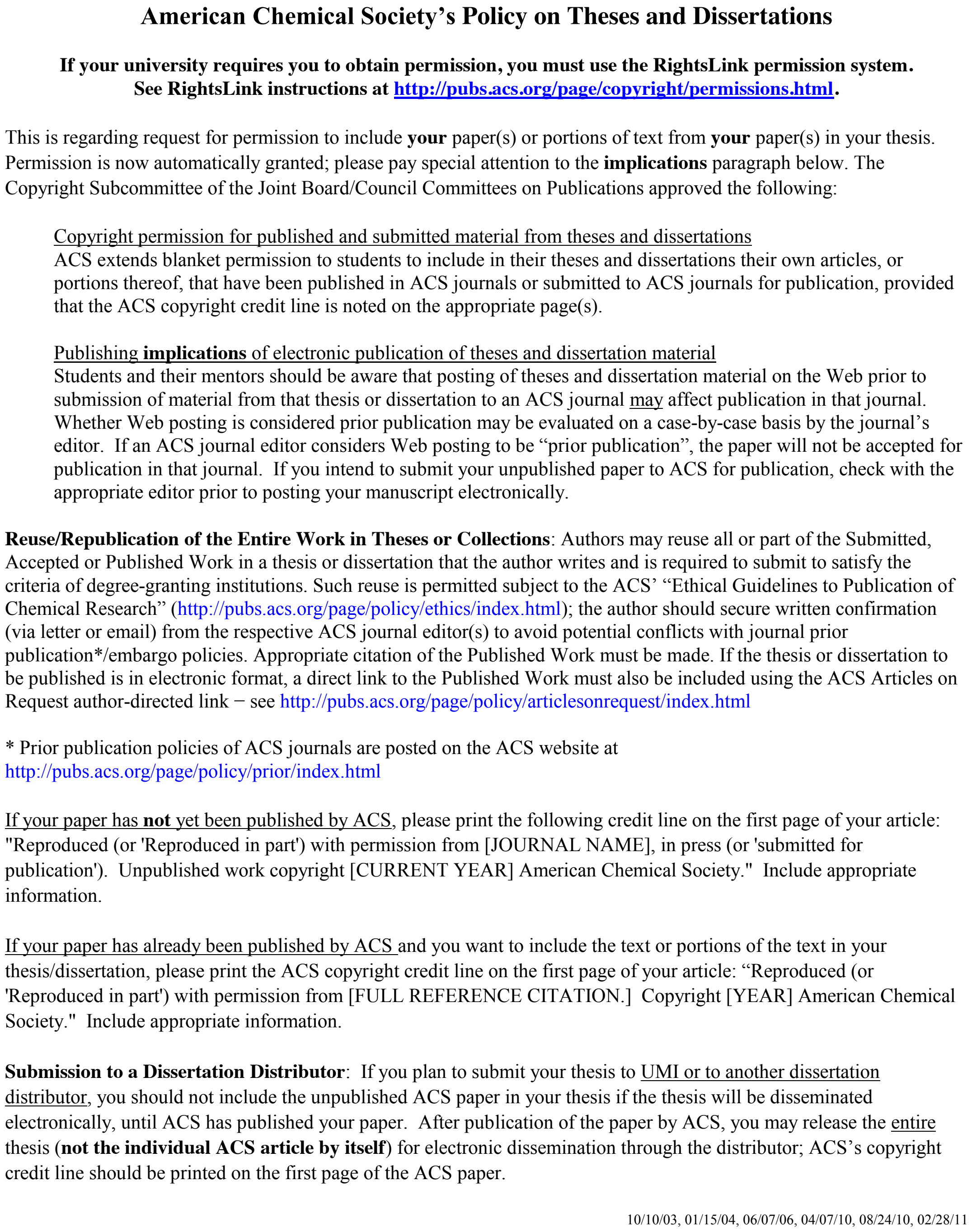

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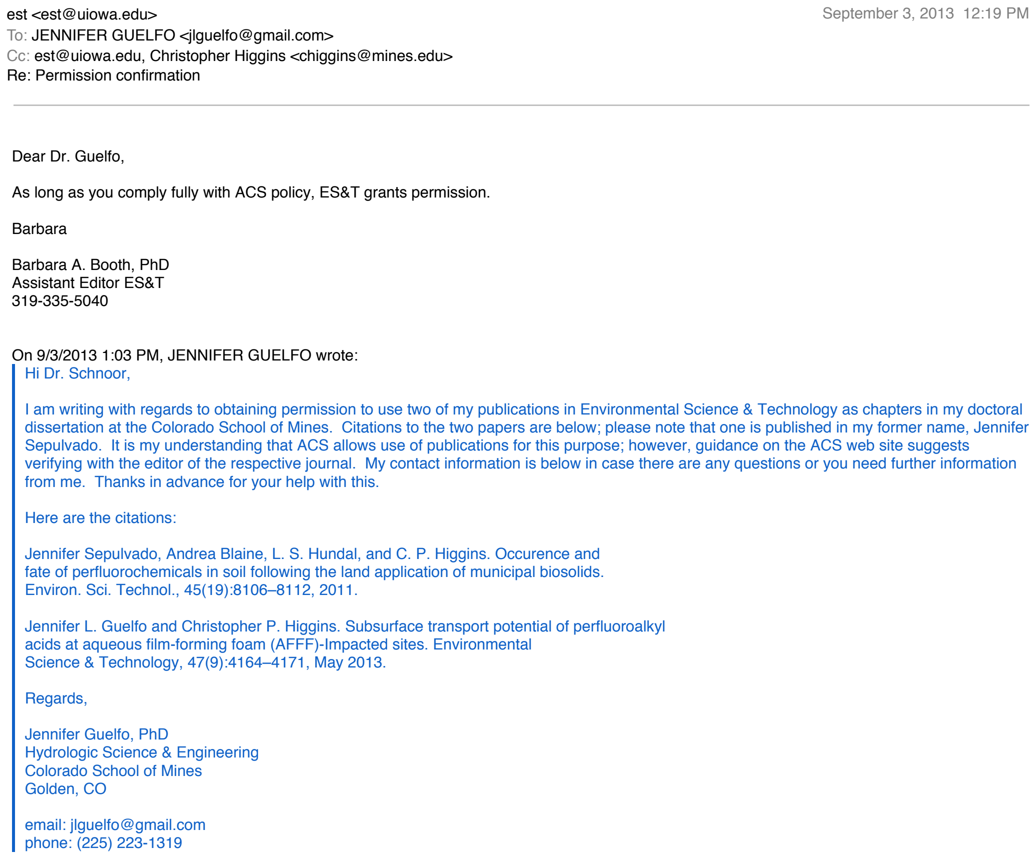

est <est@uiowa.edu>
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Cc: est@uiowa.edu, Christopher Higgins <chiggins@mines.edu>
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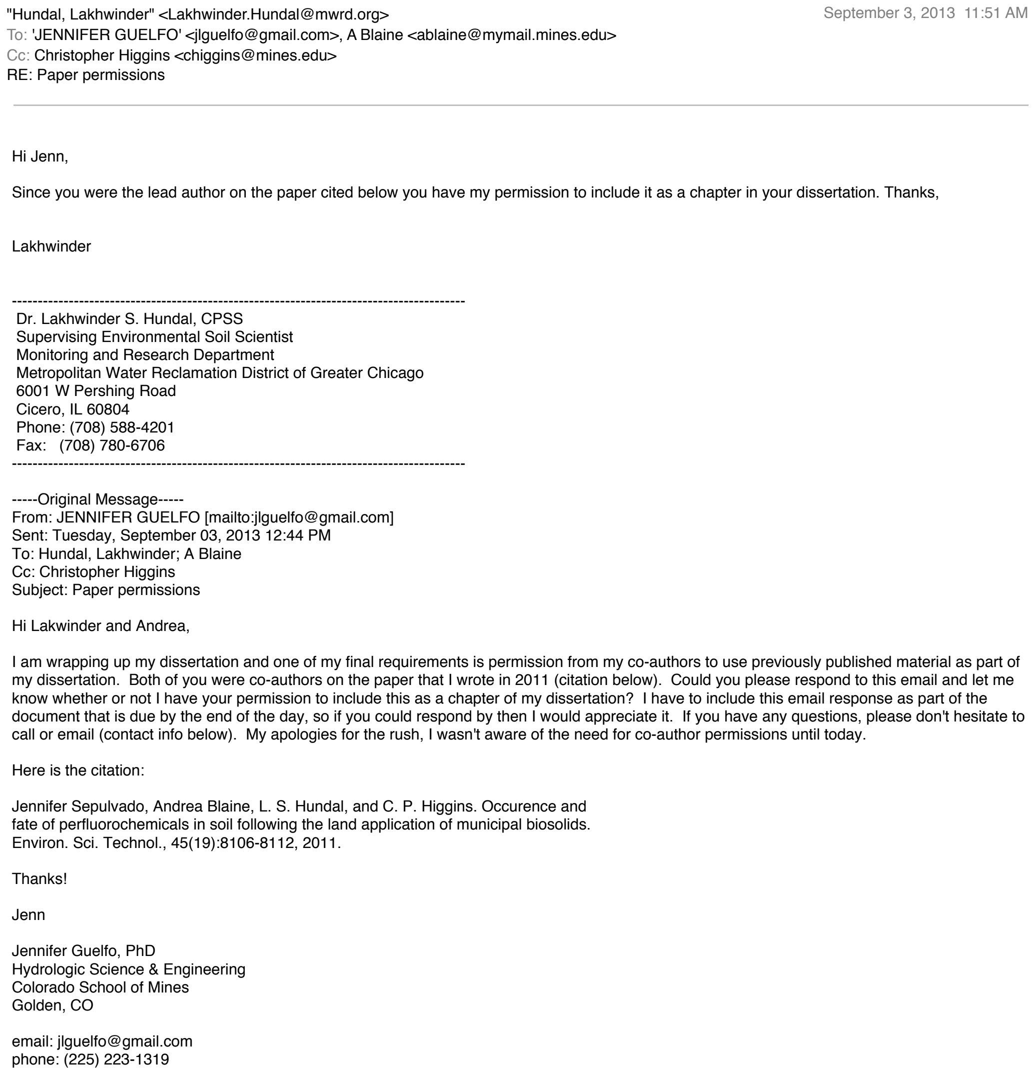

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Metropolitan Water Reclamation District of Greater Chicago
6001 W Pershing Road
Cicero, IL 60804
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Thanks!

Jenn

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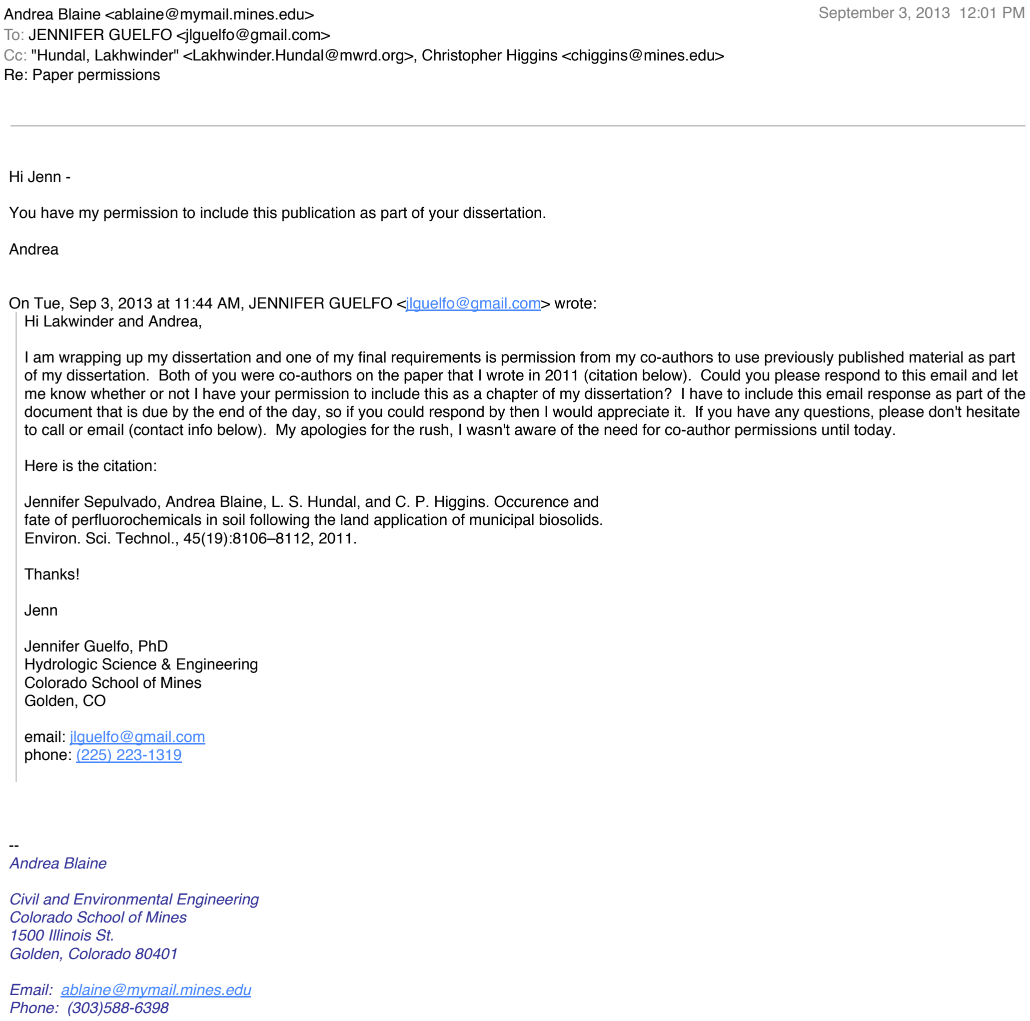

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Cc: "Hundal, Lakhwinder" <Lakhwinder.Hundal@mwrd.org>, Christopher Higgins <chiggins@mines.edu>
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> Environ. Sci. Technol., 45(19):8106–8112, 2011.
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> Thanks!
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> Jenn
>
> Jennifer Guelfo, PhD
> Hydrologic Science & Engineering
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> Golden, CO
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> email: jlguelfo@gmail.com
> phone: (225) 223-1319

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Andrea Blaine

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