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Occurrence of select perfluoroalkyl substances at U.S. Air Force aqueous film-forming foam release sites other than fire-training areas: Field-validation of critical fate and transport properties

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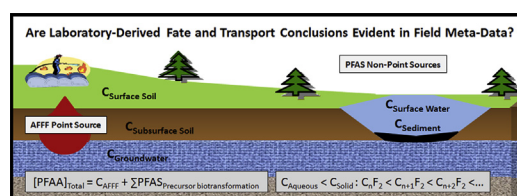
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HIGHLIGHTS

- Differences in detection frequencies and observed concentrations due to AFFF release volume are demonstrated.
- Background sources of PFOA are evident.
- Non-linear carbon chain-length dependence on relative sorption potential is empirically demonstrated.
- In situ PFOS and PFHxS formation (40% and 36%, respectively), presumably due to precursor biotransformation, is empirically demonstrated.

GRAPHICAL ABSTRACT



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ABSTRACT

The use of aqueous film-forming foam (AFFF) to extinguish hydrocarbon-based fires is recognized as a significant source of environmental poly- and perfluoroalkyl substances (PFASs). Although the occurrence of select PFASs in soil and groundwater at former fire-training areas (FTAs) at military installations operable since 1970 has been consistently confirmed, studies reporting the occurrence of PFASs at other AFFF-impacted sites (e.g. emergency response locations, AFFF lagoons, hangar-related AFFF storage tanks and pipelines, and fire station testing and maintenance areas) are largely missing from the literature. Further, studies have mostly focused on a single site (i.e., FTAs at military installations) and, thus, lack a comparison of sites with diverse AFFF release history. Therefore, the purpose of this investigation was to evaluate select PFAS occurrence at non-FTA sites on active U.S. Air Force installations with historic AFFF use of varying magnitude. Concentrations of fifteen perfluoroalkyl acids (PFAAs) and perfluorooctane sulfonamide (PFOSA), an important PFOS precursor, were measured from several hundred samples among multiple media (i.e., surface soil, subsurface soil, sediment, surface water, and groundwater) collected from forty AFFF-impacted sites across ten installations between March and September 2014, representing one of the most comprehensive datasets on environmental PFAS occurrence to date. Differences in detection frequencies and observed concentrations due to AFFF release volume are presented along with rigorous data analyses that quantitatively demonstrate phase-dependent (i.e., solid-phase vs aqueous-phase) differences in the chemical signature as a function of carbon chain-length and in situ PFOS (and to a slightly lesser extent PFHxS) formation, presumably due to precursor biotransformation.

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1. Introduction

Poly- and perfluoroalkyl substances (PFASs) are a class of synthetic fluorinated hydrocarbons used in many industrial and consumer products since the 1950s. In the early 1970s, municipalities, the hydrocarbon-processing industry, and the U.S. military began using PFAS-based aqueous film-forming foam (AFFF) to efficiently extinguish hydrocarbon-based fires (Moody and Field, 2000). During fire training, equipment maintenance, and emergency response, AFFF was released directly to the environment and it is suggested that decades of AFFF use is a significant source of environmental PFASs (Moody and Field, 1999; Moody et al., 2003). PFASs, in particular long-chain perfluoroalkyl acids (PFAAs), are under increased scrutiny from the regulatory community because they are environmentally persistent, globally distributed, bioaccumulate, and have demonstrated some toxicity in laboratory animals resulting in concerns about human and ecological exposure (USEPA, 2009; OECD, 2013). The science surrounding PFAS-mediated health and environmental effects is still evolving.

AFFF was developed in the late 1960s by 3M and the U.S. Navy specifically to efficiently extinguish hydrocarbon-based fires. Specific U.S. Department of Defense (DoD) Military Specification Regulation requires AFFF that conforms to specific performance and quality control standards, such as extinguishing time, re-ignition potential, and surface tension as well as acute LC₅₀ and biological and chemical oxygen demand criteria (MILSPEC, 1992). PFASs are the critical active component of AFFF; see Buck et al. (2011) for a comprehensive overview of PFAS chemistry and nomenclature. The use of fluorinated surfactant components within AFFF is a requirement for the U.S. DoD and the U.S. Federal Aviation Administration (FAA). To date, alternative foams that do not contain PFASs have been developed, but performance relative to AFFF is questionable.

Since the initial military specification requirements for AFFF, there have been numerous companies that have manufactured and supplied AFFF to the U.S. DoD (Place and Field, 2012). The exact composition of each AFFF formulation is proprietary, but are all known to be a complex mixture of fluorinated surfactants. The PFASs within AFFF can be synthesized by either electrochemical fluorination or telomerization processes (Kissa, 1994; Buck et al., 2011). AFFF originally sold by 3M contained PFASs synthesized by electrochemical fluorination and, therefore, contained fully fluorinated perfluoroalkyl sulfonic acids (PFSAs), such as perfluorooctane sulfonate (PFOS) and other CF₂ homologues, as well as various perfluoroalkyl sulfonamides and their derivatives (Buck et al., 2011; Backe et al., 2013). AFFF formulations synthesized via telomerization (all other manufacturers), however, contain structurally distinct PFASs; the carbon chains are not fully fluorinated, and instead have homologues of varying C₂F₄ units and are known to contain a highly diverse suite of fluorotelomers (Buck et al., 2011; Backe et al., 2013). The fluorotelomers have been shown to exclusively degrade to perfluorooctanoic acid (PFOA) and other perfluoroalkyl carboxylic acids (PFCAs) in microcosm and computational studies (Wallington et al., 2006; Wang et al., 2011; Weiner et al., 2013; Jackson et al., 2013). Conversely, perfluoroalkyl sulfonamides and their derivatives can degrade to PFOS and other PFSAs (Houtz et al., 2013; Avendaño and Liu 2015). Importantly, these “precursor” compounds ultimately result in the formation of specific PFAAs (either PFCAs or PFSAs) in situ depending on the applicable source of PFASs released to the environment; note traditionally “precursors” have been defined as any PFAS that results in the production of a PFCA or PFSA with ≥7 or ≥6 perfluoroalkyl carbons, respectively (OECD, 2013). Efforts to reverse engineer the chemical composition of AFFF stocks and elucidate all degradation pathways, as well as to account for the entire mass

balance of PFASs in environmental samples, are on-going (e.g., Barzen-Hanson and Field, 2015; Houtz et al., 2013).

In addition to uncertainty about the original product formulations and degradation pathways, studies reporting the occurrence and distribution of PFASs in environmental samples from AFFF-impacted sites are still somewhat scarce. Further, most studies (to date) have mostly focused on a single site and, thus, lack a comparison of sites with diverse release history and environmental conditions (Awad et al., 2011; D'Agostino and Mabury, 2013; Filipovic et al., 2014). Specifically, the occurrence of select PFASs in groundwater as a result of historic AFFF use was first identified at several fire-training areas (FTAs) at U.S. DoD facilities (Levine et al., 1997; Moody and Field, 1999; Schultz et al., 2004), highlighting the occurrence of PFASs in groundwater decades after release. Consequently, the U.S. Air Force (USAF) Civil Engineer Center's Emerging Issues and Emerging Contaminants Program has since performed sampling at numerous FTAs and confirmed that at all FTAs operable since 1970 that used AFFF for training purposes, select PFASs in soil and groundwater can still be identified (data not published). Detections of PFASs at FTAs coincides with 1) the operational time-frame of PFAS-based AFFF use at U.S. DoD facilities and 2) the fact that older FTAs were often not lined and were not constructed to prevent infiltration or runoff of AFFF and combustion products. However, FTAs represent only one type of AFFF release location within the U.S. DoD. A significant data gap exists regarding the magnitude of PFASs associated with other AFFF release sites (e.g. emergency response locations, AFFF lagoons, hangar-related AFFF storage tanks and pipelines, and fire station testing and maintenance areas).

Therefore, the purpose of this investigation was to evaluate select PFAS occurrence at a diverse group of non-FTA sites on active USAF installations with historic AFFF use of varying magnitude. Concentrations of fifteen PFAAs and perfluorooctane sulfonamide (PFOSA), an important PFOS precursor (as suggested by Gebbink et al., 2009 and Tomy et al., 2004), were measured for several hundred samples among multiple media (i.e., surface soil, subsurface soil, sediment, surface water, and groundwater) collected from forty AFFF-impacted sites across ten installations between March and September 2014, representing one of the most comprehensive datasets on environmental PFAS occurrence to date. Specific objectives addressed herein are to 1) report the detection frequency and environmentally-relevant concentrations for a suite of PFASs, 2) determine whether or not the various PFASs are statistically distinguishable among environmental media, and 3) critically evaluate empirical evidence of precursor biotransformation. Results are presented within the context of validating research efforts to date and inform future studies related to PFASs in environmental media.

2. Methods

2.1. Field work

A total of ten active USAF installations were selected for investigation throughout the continental United States, including Alaska. At each installation, potential investigation sites were considered candidate if there was known historic AFFF release. Candidate historic releases occurred after 1970 but before approximately 1990 (see Introduction) such that the observed PFAS profile at each site is recognized to reflect the net effect of several decades worth of all applicable environmental processes. Typically, AFFF is used in either a 3% or 6% aqueous solution by volume and is potentially released to the environment during training, emergency response, or maintenance and testing at those concentrations. There have also been releases of neat product (pre-mix concentrate) due to

equipment failures, vehicle (fire truck) accidents, and human error. Reported AFFF release volumes ranged from less than one gallon in a single event to hundreds of gallons over a period of decades. FTAs were specifically excluded from this evaluation in order to focus the investigation on other sites where relatively smaller volumes of AFFF were released. Candidate sites were ranked in terms of logistical criteria (e.g., access, availability of monitoring wells, etc.) and the top four sites at each installation were strategically selected for limited investigation. Although previous remedial activities for co-occurring contaminants were not specifically controlled for in the site selection process, active remedies had not been applied at any of the sites ultimately selected for evaluation. Thus, the effect of remediation-induced alterations to the observed PFAS composition observed by other researchers (McGuire et al., 2014; McKenzie et al., 2015) likely does not confound these results to a significant extent. Selected sites were categorized into three groups according to the assumed volume of AFFF release: low-volume (emergency response locations), usually a single AFFF release; medium-volume (hangars and buildings), one to five AFFF releases; and high-volume (testing and maintenance), multiple releases in the same location over a period of years. The “testing and maintenance” category refers to regular maintenance and equipment performance testing of emergency vehicles and performance testing of the AFFF solution. Approximately ten samples were collected from each site distributed among soil (surface and unsaturated subsurface), groundwater, sediment, and surface water. Groundwater samples were collected from a combination of existing monitoring wells and temporary monitoring wells installed with direct push technology (DPT). Direct push technology employs a small drill rig to “push” small diameter rods and tools into the subsurface for investigative purposes; applications include soil and groundwater sampling, geophysical sensing, and soil gas sampling. Samples from existing wells were collected at the top of the well screen. Groundwater samples from temporary wells were collected at the water table interface. Surface soil (0–1 ft below ground surface [bgs]) and sediment samples (0–1 ft below top of the sediment) were collected directly into sample containers. Surface water samples were co-located with each sediment sample. Sediment and surface water samples were collected at locations where the conceptual site model (CSM) indicated a hydraulic connection, either through surface water flow (overland sheet flow) or where groundwater discharged to surface waters. Sample locations included engineered storm water channels, engineered AFFF ponds, and natural streams. Approximately three subsurface soil samples were collected at intervals from each DPT boring between the top of the water table and the 0–1 ft bgs sample. At two installations subsurface geology prevented the use of DPT; only surface soils and groundwater samples from existing monitoring wells were collected. Each water sample consisted of a minimum of 250 mL collected into a 1 L high-density polyethylene (HDPE) container. Each soil/sediment sample consisted of a minimum of 10 g collected into a 250 mL HDPE container. Field duplicate samples and matrix spike/matrix spike duplicate samples were collected at a rate of one field duplicate per twenty samples in all media. One field blank and one equipment blank were collected per sampling event. All known or suspected PFAS-containing materials were avoided during sample collection, handling, and transport. Table 1 summarizes all samples collected.

2.2. Analytical analysis

All PFAS analytes selected for evaluation are reported in Supplemental Information Table S1 and include the standard, commercially-available suite of PFASs, including PFOSA, an important PFOS precursor. Other relevant precursors – the fluorotelomer

sulfonates (FTSs), such as 6:2 FTS and 8:2 FTS – were not analyzed nor were the fluorotelomers identified by Place and Field (2012). Further, the shorter chain-length (<C4) PFASs recently identified by Barzen-Hanson and Field (2015) were not targeted for analysis either. Therefore, the total PFAS profile for each sampled location was obviously not resolved and, thus, reported results likely underestimate the total mass of PFASs.

Analysis of all samples was conducted through a combination of matrix-specific preparatory methods employing solid-phase extraction for aqueous samples and liquid extraction of solid samples, followed by liquid chromatography and detection with tandem mass spectrometry following USEPA Method 537 for drinking water as modified by TestAmerica's proprietary standard operating procedures (SOPs DV-LC-0012 and DV-LC-0019), for aqueous and solid samples, respectively. For all compounds except PFOSA, water samples were prepared for analysis using solid phase extraction employing a reversed-phase, weak anion exchange mixed-mode sorbent. Compounds were eluted from the cartridge with an ammonium hydroxide-methanol solution. For PFOSA, a silica-based bonded phase was used as the sorbent and methanol as the elutant. For soils, all samples were mixed with sodium hydroxide, followed by the addition of methanol. The soil/solvent mixture was then sonicated, tumbled, and adjusted to pH < 2. The extracts were centrifuged, concentrated, solvent-exchanged, cleaned, and reduced to a final volume of 1 mL. Extract cleanup was accomplished using one of several techniques, including solid phase extraction, temperature-modified phase separation, or graphitized carbon. ¹³C- or ¹⁸O-labeled PFASs were used as isotope dilution standards. Target analytes without a corresponding labeled analog were quantified using the internal standard technique using the most similar internal standard in terms of carbon chain length. All data reported herein were validated against the quality control and quality assurance parameters reported in Supplemental Information Table S2. Median reporting limits (RLs) for each PFAS in each environmental matrix are presented in Supplemental Information Table S3.

2.3. Statistical analysis

Linear discriminant analysis was used to evaluate inter-media variability as a function of all 16 PFASs analyzed. For this purpose, surface soil and subsurface soil samples were evaluated indiscriminately. All units were standardized to reflect parts per billion (ppb) for the respective media and non-detects were substituted with ½ the RL (see Supplemental Information Table S3 for median RLs). All data were subsequently log₁₀ transformed to satisfy the normality assumption for error estimation. The standardized canonical structure (defined for each PFAS as the correlation coefficient between the predicted values of the linear discriminant function [i.e., the canonical scores] and the actual values) was used to determine the relative order of PFASs that defined differences in the chemical signature among environmental media. Canonical variables (abbreviated herein as “CAN”) are orthogonal (i.e., contain non-overlapping pieces of information) and were, thus, evaluated independently. In general, discriminant analysis is applicable when multiple quantitative response variables belong to two or more levels of a classification variable and some linear function is of interest in terms of quantitatively describing the inter-class variation. The resulting CAN variables must subsequently be interpreted within the context of the separation observed among the applicable variable space (CAN1, CAN2, etc.). In the current context, the quantitative response variables are the measured concentrations of the various PFASs and the classification variable is the environmental matrix (i.e., soil, sediment, surface water, and groundwater). Thus, the linear discriminant function quantifies inter-media

Table 1
Sample sizes (N_{Total}) of all environmental samples collected by site-classification.

Site classification	AFFF release	N_{Sites}	Matrix				
			Surface soil	Subsurface soil	Sediment	Surface water	Groundwater
Emergency response	Low	5	12	17	3	2	24
Hangars and buildings	Medium	27	56	64	35	32	100
Testing and maintenance	High	8	32	31	2	2	25

variability as a function of all 16 PFASs analyzed. Discriminant analysis was performed using Proc DISCRIM in 64-bit SAS[®] version 9.4 for Windows and considered significant at $p \leq 0.05$.

Categorical data analysis methods were used to evaluate differences between surface and subsurface soil samples, specifically to test the hypothesis that sorption is more likely to occur for longer-chain PFASs resulting in inverted depth profiles that reflect limited transport. All units were standardized and non-detects were substituted with $\frac{1}{2}$ the reporting limit. Only sites with both surface and subsurface soil samples were evaluated. Sites were dichotomized for each PFAS according to whether or not mean surface (0–1 ft bgs) concentrations exceeded mean subsurface concentrations (>1 ft bgs). All PFASs were also dichotomized according to carbon chain-length where C6 and less were considered “short-chain” PFASs and all C7 and above were considered “long-chain” PFASs consistent with the description by Buck et al. (2011). Logistic regression was applied to evaluate chain-length dependence on the probability of observing inverted depth profiles (reflecting limited transport), whereas a 2×2 cross-classification analysis (i.e., contingency table) was applied to evaluate the more general categorical association. Logistic regression and the cross-classification analyses were performed using Proc LOGISTIC and Proc FREQ, respectively, in 64-bit SAS[®] version 9.4 for Windows and considered significant at $p \leq 0.05$.

Two-way analysis of variance (ANOVA) was used to evaluate differences in mean PFAS concentrations among the various site classifications that reflect increasing volumes of AFFF release. The inherent assumption is made that, at higher-volume release sites, greater potential exists for precursor biotransformation and (if true) would result in relatively higher concentrations of select PFASs, primarily since the candidate AFFF release sites have all undergone many years of weathering. Therefore, a departure in parallelism (i.e., significant interaction between the site-classification variable and the PFAS variable) was specifically tested. However, because discriminant analysis resulted in significant differences in the PFAS signature among environmental media (as well as the fact that the absolute concentrations are inconsequential), ANOVA was performed on media-normalized concentrations to avoid confounding. Log₁₀ transformed data were normalized by subtracting the media-specific mean from each observation and dividing by the media-specific standard deviation (i.e., standard normal distributions were generated). Consistent with the discriminant analysis, surface soil and subsurface soil samples were evaluated indiscriminately, all units were standardized to reflect parts per billion (ppb) for the respective media, and non-detects were substituted with $\frac{1}{2}$ the reporting limit. ANOVA was performed with the site as a random variable using Proc Mixed in 64-bit SAS[®] version 9.4 for Windows and considered significant at $p \leq 0.05$.

3. Results and discussion

3.1. General summary

Summary statistics for all 16 PFASs are presented by site-

classification (i.e., estimated AFFF release volume) and matrix in Supplemental Information Table S4 and by matrix independently in Table 2. Across all sites and media, PFOS was the predominate PFAS detected, followed by PFHxS. While PFOA was frequently detected in all media, concentrations were generally much lower. This profile is consistent with previous investigations of AFFF-impacted groundwater at FTAs associated with U.S. military installations, wherein PFOS and PFHxS are the prominent PFASs detected, followed by PFOA (Barzen-Hanson and Field, 2015; Moody et al., 2003). Although additional accounts of such a wide suite of PFAS compounds at various AFFF release locations are lacking, detection frequencies and concentrations of PFASs herein are consistent with AFFF formulations and environmental release. Detection frequencies for most PFASs were similar at the high-volume (i.e., “testing and maintenance”) and medium-volume (i.e., “hangars and buildings”) sites but were considerably lower at the low-volume (i.e., “emergency response”) sites where only a one-time release of AFFF occurred. Interestingly, however, PFOA detection frequencies were similar among all three site-classifications, although concentrations varied with the estimated volume of AFFF release, suggesting a trace-level background source of PFOA, potentially atmospheric deposition (Kim and Kannan, 2007; Wallington et al., 2006). In general, the range in concentrations for PFOA and PFOS in groundwater is similar to concentrations previously reported at FTAs (Moody and Field, 1999, 2000; Moody et al., 2003; Schultz et al., 2004); however, this is the first study to assess a variety of AFFF-impacted sites to assess detection frequencies of these 16 PFASs. The high degree of variability in measured concentrations within site-classifications (Supplemental Information Table S4) simply reflects site-specific conditions and installation-specific operational practices.

Although not definitive as an independent line of evidence (due primarily because the FTs were not evaluated), predominance of PFOS and PFHxS (both PFASs) in all media from all site-classifications suggests that 3M AFFF is at least a significant contributing source of PFASs at these sites, if not the predominant source (discussed further below). However, while PFASs dominate the overall multivariate PFAS signature among the various matrices, at least some degree of telomer-based AFFF contamination may be evident given the sporadic occurrence of select PFCAs (i.e., PFNA) that are not present in past 3M AFFF formulations (Backe et al., 2013); the extent to which biotransformation of the various precursor compounds in 3M AFFF results in the accumulation of PFCAs remains uncertain. Nevertheless, multivariate PFAS chemical signatures may also be applicable to source apportionment studies given the seeming ubiquity of PFAS sources reported to date. For example, contrasting PFAS chemical signatures from different sources has been demonstrated (So et al., 2007). Further, PFCAs have been shown as the dominant PFAS signature in multiple studies where samples were collected in urban areas impacted by diffuse non-point PFAS sources (e.g., Loganathan et al., 2007; Nguyen et al., 2012). Quantitative multivariate comparisons of PFAS profiles along groundwater or surface water flow paths may prove useful for distinguishing some AFFF releases from other (i.e., non-AFFF) sources, such as landfill leachate, urban runoff, etc.

Table 2
Summary statistics^a for all 16 PFASs measured^b by matrix.

PFAS	Parameter	Matrix				
		Surface soil	Subsurface soil	Sediment	Surface water	Groundwater
PFBA	DF ^c	38.46%	29.81%	24.24%	84.00%	85.51%
	Median	1.00	0.960	1.70	0.076	0.180
	Maximum	31.0	14.0	140	110	64.0
PFBS	DF	35.16%	34.62%	39.39%	80.00%	78.26%
	Median	0.775	1.30	0.710	0.106	0.200
	Maximum	52.0	79.0	340	317	110
PFPA	DF	53.85%	45.19%	45.45%	92.00%	87.68%
	Median	1.20	0.960	1.70	0.230	0.530
	Maximum	30.0	50.0	210	133	66.0
PFHxA	DF	70.33%	65.38%	63.64%	96.00%	94.20%
	Median	1.75	1.04	1.70	0.320	0.820
	Maximum	51.0	140	710	292	120
PFHxS	DF	76.92%	59.62%	72.73%	88.00%	94.93%
	Median	5.70	4.40	9.10	0.710	0.870
	Maximum	1300	520	2700	815	290
PFHpA	DF	59.34%	45.19%	48.48%	84.00%	85.51%
	Median	0.705	0.660	1.07	0.099	0.235
	Maximum	11.4	17.0	130	57.0	75.0
PFOA	DF	79.12%	48.08%	66.67%	88.00%	89.86%
	Median	1.45	1.55	2.45	0.382	0.405
	Maximum	58.0	140	950	210	250
PFOSA	DF	64.84%	29.81%	75.76%	52.00%	48.55%
	Median	1.20	0.470	1.30	0.014	0.032
	Maximum	620	160	380	15.0	12.0
PFOS	DF	98.90%	78.85%	93.94%	96.00%	84.06%
	Median	52.5	11.5	31.0	2.17	4.22
	Maximum	9700	1700	190000	8970	4300
PFNA	DF	71.43%	14.42%	12.12%	36.00%	46.38%
	Median	1.30	1.50	1.10	0.096	0.105
	Maximum	23.0	6.49	59.0	10.0	3.00
PFDA	DF	67.03%	12.50%	48.48%	52.00%	34.78%
	Median	0.980	1.40	1.90	0.067	0.023
	Maximum	15.0	9.40	59.0	3.20	1.80
PFDS	DF	48.35%	11.54%	33.33%	8.00%	20.29%
	Median	3.70	3.55	2.00	17.8	0.125
	Maximum	265	56.0	2200	35.6	2.00
PFUnA	DF	45.05	9.62	24.24	20.00	8.70
	Median	0.798	1.15	1.60	0.021	0.025
	Maximum	10.0	2.00	14.0	0.210	0.086
PFDoA	DF	21.98%	6.73%	45.45%	20.00%	4.35%
	Median	1.95	2.40	2.80	0.058	0.022
	Maximum	18.0	5.10	84.0	0.071	0.062
PFTriA	DF	15.38%	13.46%	24.24%	0.00%	1.45%
	Median	0.665	1.90	1.65	na	0.019
	Maximum	6.40	4.70	29.0	na	0.019
PFTeA	DF	10.99%	6.73%	15.15%	0.00%	1.45%
	Median	1.10	3.40	1.66	na	0.021
	Maximum	4.70	5.40	4.16	na	0.027

^a Median values are reported using only detected concentrations.

^b All soil and sediment values reported in µg/kg and all water samples reported in µg/l.

^c Detection frequency.

3.2. Discriminant analysis

Linear discriminant analysis resulted in three significant canonical variables with an overall 28.2% classification error. However, the first canonical variable (CAN1) accounted for almost all of the pooled covariance (98.4%), whereas CAN2 and CAN3 accounted for 1.26% and 0.340%, respectively. Therefore, only CAN1 and CAN2 are reported. Fig. 1 illustrates the orthogonal canonical scores for CAN1 and CAN2. Readily apparent is the complete vertical separation (CAN1) between all solid-phase data (soil and sediment) and all aqueous-phase data (groundwater and surface water) and the partial horizontal (CAN2) separation between the soil and sediment data. Thus, although statistically-significant signatures are distinguishable between soil and sediment, the overwhelmingly predominant pattern evident in these data define phase-dependent (i.e., solid-phase vs aqueous-phase) differences in PFAS

concentration and composition.

The standardized canonical structure for CAN1 is presented in Fig. 2. All coefficients are positive values reflecting higher mean (log-transformed) soil and sediment concentrations (ppb equivalence) relative to surface water and groundwater (given the direction of the vertical separation observed in Fig. 1). And, the magnitude of the coefficients quantifies relative differences among the PFASs proportional to their difference. These results, however, are to some extent confounded by differences in the sensitivities among the analytical method for water samples relative to soil and sediment (see Supplemental Information Table S3) because non-detects were substituted with ½ the RL, but is considered trivial given that multiple PFASs were detected in almost every single sample regardless of media (see Table 2 and Supplemental Information Table S4 for detection frequencies). So, PFASs with higher coefficients are interpreted as empirical evidence of a

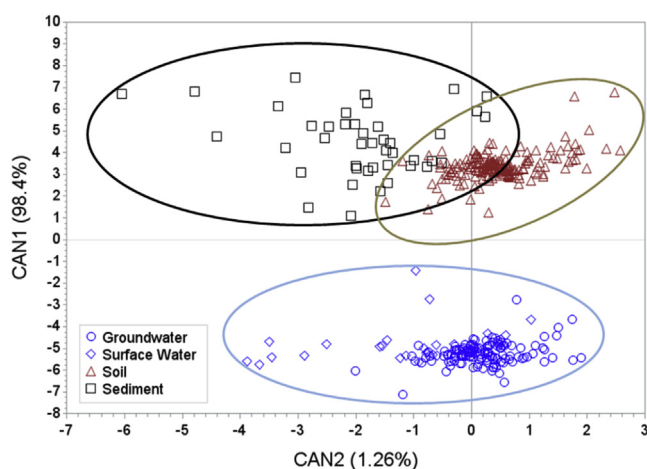


Fig. 1. Canonical scores from linear discriminant analysis. Includes all data presented in Table 2. Surface and subsurface soil results were evaluated collectively.

greater solid-phase affinity than PFASs with smaller coefficients. Although no obvious pattern is evident among the PFASs with different functional groups, almost complete concordance is observed between the coefficients and the total carbon chain-length (Fig. 2). Further, excluding PFDoA and PFTeA, the rank order of the coefficients is not significantly correlated with differences in mean RLs between the corresponding analytical methods (data not shown). Therefore, these results conclusively illustrate carbon chain-length dependence on PFAS transport. An alternative way of looking at these same results is to simply plot the CAN1 coefficients against carbon chain-length for both the PFCAs and PFSA and is presented in Supplemental Information Figure S1. Subtle differences in the observed sorption behavior between PFCAs and PFSA is apparent but only among the PFASs with smaller chain-lengths (<C8) where moderately greater sorption is observed among the PFSA. Also, among all of the PFASs there is an obvious inflection point between C8 and C10. Overall, these results suggest that the effect of carbon chain-length on PFAS sorption behavior is non-linear and functional group-mediated differences are secondary relative to the effect of total carbon chain-length. It should be noted that in the present context, the total carbon chain-length and the fully fluorinated chain-length differ proportionally

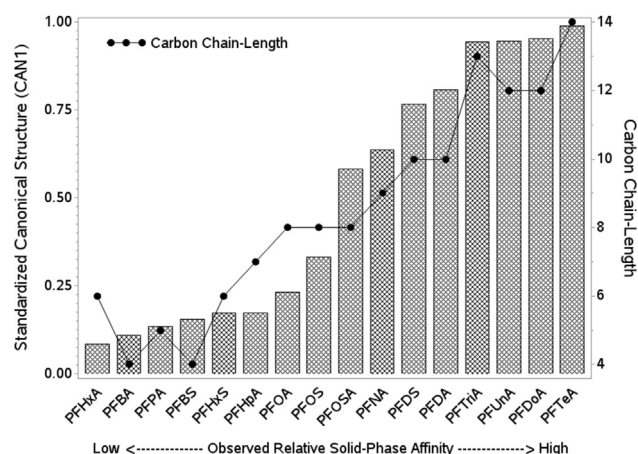


Fig. 2. Standardized canonical structure of the CAN1 variable presented in Fig. 1. The standardized canonical structure is defined for each PFAS as the correlation coefficient between the predicted values of the linear discriminant function (i.e., the canonical scores presented in Fig. 1) and the actual values.

(n-1) among all 16 compounds, and, thus, does not affect the results. To date, sorption-mediated differences due to PFAS chain-length have only been field-validated qualitatively in other (albeit relatively limited) reports of regional PFAS occurrence (Ahrens et al., 2009; Murakami et al., 2009; Gellrich et al., 2012).

The standardized canonical structure for CAN2 is presented in Fig. 3. All coefficients except PFNA are negative reflecting higher mean log-transformed sediment concentrations relative to soil (given the direction of the horizontal separation observed in Fig. 1). Although the maximum observed concentration occurred in sediment (Table 2), the median and mean of the log-transformed values for PFNA is higher in soil indicating inherent log-normality and reflect an upward shift in the low-to mid-range of observed concentrations relative to sediment (Table 2). This is particularly noteworthy because the mean RL for sediment was 2.76-fold higher than soil (see Supplemental Information Table S3). Thus, non-detects substituted as $\frac{1}{2}$ the RL would tend to bias results higher for sediment. Although CAN2 only accounted for 1.26% of the total covariance, these results are highly significant ($p < 0.0001$).

There are potentially many different explanations for the observed pattern in CAN2. Primarily, the observed statistically-significant discrimination is largely driven by the general differences in concentrations rather than composition; among the 15 PFASs observed with higher mean log-transformed sediment concentrations (see Fig. 3), no pattern is evident among the different functional groups or carbon chain-lengths. In general, the observed higher sediment concentrations reflect the greater sorption capacity of sediment (f_{oc}) because all samples were collected from known source areas and are consistent with other investigations (Yang et al., 2011; Ahrens and Bundschuh, 2014; Zareitalabad et al., 2013; Ahrens, 2011). Nevertheless, the anomalous pattern observed for PFNA is intriguing. Because sediments are oxygen limited relative to typical aerobic soil, reductive defluorination as discussed by Park et al. (2009) could be operative at relatively low concentrations but is purely speculative; indirect accounts of the redox sensitivity of PFNA from wastewater treatment plants with anaerobic digestion have not demonstrated the disappearance of PFNA (Loganathan et al., 2007; Shivakoti et al., 2010). An alternative explanation is simply a greater biotransformation rate (aerobic) of telomer-based PFNA precursors in soil relative to sediment that was not observed among the other PFCAs.

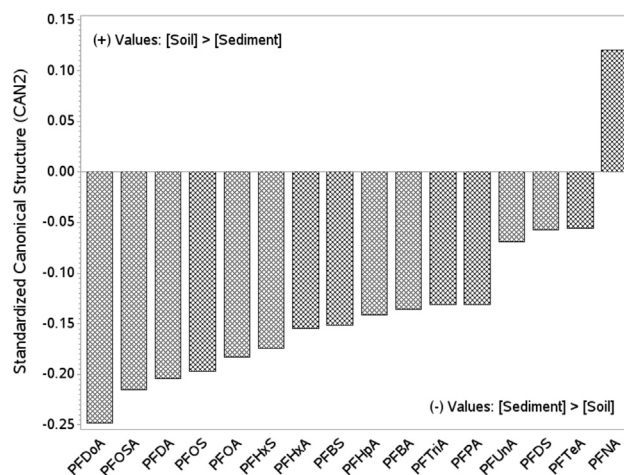


Fig. 3. Standardized canonical structure of the CAN2 variable presented in Fig. 1. The standardized canonical structure is defined for each PFAS as the correlation coefficient between the predicted values of the linear discriminant function (i.e., the canonical scores presented in Fig. 1) and the actual values.

3.3. Categorical analyses

Additional analyses were applied specifically to evaluate differences in PFAS concentrations between surface and subsurface soil samples as a function of carbon chain-length. Logistic regression did not yield any significant results and was not improved by also evaluating differences between functional groups. However, the categorical association between long-chain PFASs and cases where mean surface soil concentrations exceeded mean subsurface soil concentrations was significant ($p = 0.027$) with an odds ratio of 2.61 illustrating a strong association. So, while a categorical association was observed consistent with the results of the discriminant analysis (Fig. 2) and previous investigation of the PFAS depth profile in soil as a result of municipal biosolids application (Sepulvado et al., 2011), excess variability prevented a quantitative relationship. Obviously, carbon chain-length dependence reflects partitioning to the various sorption sites within the amorphous soil organic matter (SOM) matrix. Notwithstanding the synergistic effect of co-contaminants on PFAA sorption to soil (Guelfo and Higgins, 2013) and potential pH-dependent ionic interactions (Higgins and Luthy, 2006; Ahrens et al., 2009), solid-phase PFAS sorption (at least those evaluated, in particular the PFAAs) is, therefore, at least a function of both the carbon chain-length and the SOM content and composition (Gellrich et al. 2012; Guelfo and Higgins, 2013). Unfortunately, however, soil physiochemical properties were not analyzed as part of this field effort, nor were co-contaminants. A more comprehensive dataset including these parameters would most likely account in some capacity for observed inter-site heterogeneity in PFAS depth profiles that are not accounted for by chain-length alone.

3.4. Precursor biotransformation

ANOVA resulted in a significant ($p < 0.0001$) interaction between the site classification variable and the PFAS variable. The interaction plot is presented in Fig. 4. Increasing trends among mean concentrations from low-volume release sites (i.e., “emergency response”) to high-volume release sites (i.e., “testing and maintenance”) were expected due to increases in cumulative AFFF release volumes, but of particular interest is the relative trend among the various PFASs. The relative increase is notably greater for PFOS followed by PFHxS. PFOS concentrations increased by 1.06 standard normal units followed by PFHxS, which increased by 0.650 units. PFOA, however, only increased by 0.353 units, which was well within the range of the other PFASs. Because only PFASs were observed with anomalously higher trends (as well as relatively higher concentrations – discussed above), 3M AFFF is most likely the dominant source of PFASs at the sites evaluated; telomer-based AFFF neither contains nor results in the in situ formation of PFOS or PFHxS (Wang et al., 2011; Weiner et al., 2013). Predominance of telomer-based AFFF should eventually result in significant production of PFCAs in situ (Wang et al., 2011; Weiner et al., 2013). A fundamental uncertainty, however, is the biotransformation rates under ambient field conditions. So, an alternative conclusion may be that telomer-based precursors at the sites evaluated simply have yet to undergo biotransformation to PFCAs, although previous investigation of precursor prevalence from past AFFF releases has clearly shown evidence of biotransformation (Houtz et al., 2013). Based on the mean difference in the normalized concentrations among all PFASs except PFOS and PFHxS (assumed to reflect differences in the AFFF release volume), approximately 40% of the PFOS and 36% of the PFHxS observed at the high-volume release sites appears to have originated in situ. Collectively, these results reflect the dominance of PFSA precursor biotransformation relative to the carboxylic analogs at the sites evaluated, although future

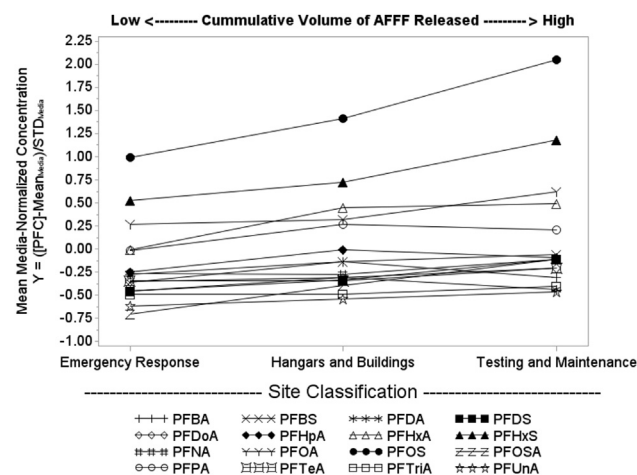


Fig. 4. Interaction plot illustrating a departure from parallelism (i.e., significant interaction between the site classification variable and the PFAS variable). All sites were classified according to the estimated volume of AFFF release, which consisted of “emergency response”, “hangars and buildings”, and “testing and maintenance” sites corresponding to low, medium, and high cumulative release volumes, respectively.

investigations should at least include evaluation of the FTSs for comparison to PFAAs. However, PFOSA was not observed with a decreasing trend and, thus, cannot be confirmed as a relevant precursor notwithstanding 1) stoichiometric degradation is rarely observed with field data and 2) relevant precursors and reaction pathways are still the subject of intensive research (Houtz et al., 2013). Overall, these results demonstrate that PFOS (and to a slightly lesser extent PFHxS) was formed in situ with a magnitude dependent on the cumulative volume of AFFF released.

4. Conclusions

In summary, multivariate data analyses suggests 3M AFFF is a significant contributing source of PFASs at the sites evaluated. Differences have been observed in detection frequencies and observed concentrations as a result of AFFF release volume. Furthermore, field-validation of two fundamental conclusions of laboratory-based research to date has been provided. Non-linear phase-dependent (i.e., solid-phase vs aqueous-phase) differences in the PFAS chemical signature as a function of carbon chain-length and in situ PFOS and PFHxS formation (40% and 36%, respectively), presumably due to precursor biotransformation, have been empirically demonstrated. Additional investigation, however, is needed to validate mechanistic assumptions of PFAS transport that account for site-specific physiochemical properties. Future investigations should at least also include an evaluation of the FTSs for comparison to PFAAs and quantification of the total oxidizable precursors (Houtz et al., 2013). In general, this investigation demonstrates the complexity of issues practitioners are faced with accurately characterizing the nature and extent of PFASs at AFFF-impacted sites.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.chemosphere.2016.01.014>.

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