AN ABSTRACT OF THE DISSERTATION OF

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Title: Per- and Polyfluoroalkyl Substances (PFAS) in Environmental Air-Water Matrices and Light Non-Aqueous Phase Liquids (LNAPL)

Abstract approved:

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The presence of per- and polyfluoroalkyl substances (PFAS), organic contaminants first synthesized in the 1940s, has been reported worldwide in a variety of environmental matrices and ultimately in biological systems including humans. Ongoing research into PFAS has included identifying novel PFAS, assessing their fate and transport in the environment, and identifying exposure routes. These topics ultimately allow risk assessments and remediation efforts to commence.

In Chapter 2, a method was developed to analyze for PFAS in naturally-occurring foams on a freshwater lake by liquid chromatography time-of-flight mass spectrometry (LC-QToF). Concentrations in the foam were compared to the underlying bulk water to generate enrichment factors. Select samples were analyzed by ^{1}H NMR to characterize the functional group composition in the foam and bulk water. Enrichment in the foam was correlated with the relative hydrophobicities of the individual PFAS, as well as increased enrichment for linear isomers when compared to branched isomers. The foam and bulk water were also characterized for dissolved organic carbon (DOC), of which the PFAS comprised <0.1% of the overall

DOC. This was the first published work quantifying PFAS in naturally-occurring foam and suggested the DOC as the overall driver of foam that provides an enrichment mechanism for foam.

In Chapter 3, existing methods for sampling the surface microlayer (SML) were deployed on a PFAS-impacted lake to determine the optimal approach for sampling of the microlayer with respect to PFAS. The accuracy, precision, and limits of quantification were used to support a recommendation of the sampling techniques. The PFAS enrichment in the microlayer was compared to PFAS enrichment in open ocean SMLs, foam, and sea-spray aerosols. The precision of the methods was then used to assess SML variability on the 1m scale and the sampling site (km) scale. Finally, for PFAS enriched in the SML, interfacial partitioning coefficients were generated for the first time using field data.

In Chapter 4, a novel method was developed for quantifying PFAS in light non-aqueous phase liquids (LNAPL). A micro liquid-liquid extraction prepared samples to be analyzed by LC-QToF for 50 targets and up to 800 suspect PFAS. A novel quantitation technique was used to estimate concentrations for suspect PFAS, which do not have analytical standards. This method was used to analyze 17 field LNAPL samples. The PFAS found in LNAPL samples indicates that LNAPL may serve as a long-term source of PFAS and sites with PFAS and LNAPL contamination may require further characterization.

Per- and Polyfluoroalkyl Substances (PFAS) in Environmental Air-Water Matrices and Light Non-Aqueous Phase Liquids (NAPL)

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I understand that my dissertation will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my dissertation to any reader upon request.

Trever Schwichtenberg, Author

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CONTRIBUTION OF AUTHORS

In Chapter 2, Dr. Dorin Bogdan provided the samples and site information and manuscript edits. Dr. Courtney Carignan provided the exposure estimates and manuscript edits. Dr. Patrick Reardon and Thomas Wanzek provided the NMR analysis and manuscript edits. Dr. Justin Rewerts provided statistical consultation, and Dr. Jennifer A. Field provided experimental design and manuscript edits.

In Chapter 3, Dr. Dorin Bogdan provided access to the sampling site, site information, and manuscript edits. Dr. Jennifer Field helped perform the sampling, guided the experimental design, and contributed manuscript edits.

In Chapter 4, Dr. Emerson Christie performed preliminary extraction experiments, Christopher Schmokel performed the final extractions. Dr. Konstantinos Kostarelos, William H. DiGuiseppi, and Dr. Jennifer Field helped with manuscript edits.

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CHAPTER 1 - INTRODUCTION

1.1 Per- and Polyfluoroalkyl Substances (PFAS)

Per- and polyfluorinated substances (PFAS) are a group of organic chemicals first synthesized industrially in the 1940s.[1] These chemicals are synthetic and not natural to the environment. Common features are a polar head group, which can be nonionic, anionic, cationic, or zwitterionic, and an aliphatic carbon tail where all (per-) or some (poly-) of the C-H bonds are replaced by C-F bonds.[2] There are >4,700 PFAS compounds that exist, including transformation products and terminal products. Once in these terminal states, there is very little degradation in the environment and these chemicals have earned the nickname 'forever chemicals'. These carbon-fluorine bonds give the molecules both water and oil-repelling properties which make them useful as nonstick coatings in papers, textiles, and cookware, and for creating fire-fighting foams (aqueous film-forming foams or AFFFs) that can extinguish hydrocarbon-based fuel fires.[3] Their extensive use has led to PFAS contamination in the environment[4] and in a random sample of 1,700 U.S. 12-80 year olds were quantified in the blood of 97% of participants.[5]

PFAS contamination is a global issue, with regulations lagging behind contamination. In the United States, the Environmental Protection Agency (EPA) has issued a Health Advisory Limit (HAL) of 70 ng/L in drinking for the combined concentrations of just two of the most common PFAS, PFOA and PFOS.[6] The HAL is a non-enforceable decree but stricter regulations are in progress.[7] Given the large quantity of PFAS, there is a growing movement to regulate PFAS as a class, as opposed to individual molecules. A benefit of this forward-thinking approach is the ability to regulate current PFAS as well as those discovered in the future, which could be transformation products in the environment.[8, 9]

1.2 PFAS as Surfactants

As surfactants, PFAS have specific behaviors that create challenges for sampling and modeling transport in the environment.[10, 11] PFAS are driven to interfaces due to their hydrophobic and oleophobic properties. Partitioning behavior varies between PFAS molecules and depends on the specific properties of the molecule including whether they are neutral, cationic, anionic, or zwitterionic, and their relative hydrophobicities. Interfaces of interest in the environment are air-water, soil-water, and nonaqueous phase liquid (NAPL)-water.[12-14]

1.3 PFAS and Air-Water Interfaces

Examples of air-water interfaces in the environment are the vadose zone of groundwater, sea-spray aerosols, foam, and in open surface waters a layer called the surface microlayer (SML).[12, 15-17] Enrichment in these layers from the underlying bulk water is driven by the Gibbs equation:

$$d\gamma = -\sum \Gamma_i \, d\mu_i$$

where $d\gamma$ is the change in surface tension, Γ_i is the surface excess, and $d\mu_i$ is the change in chemical potential of the component.[1] The surface excess is the difference in surfactant concentration in the surface region and the bulk phase. The hydrophobic interactions with water drive PFAS to the air-water interface, a more thermodynamically favorable position. Two understudied interfaces and how PFAS enrich in them are foam and the SML. Foam occurs when gas is dispersed within a liquid and surface-active substances (surfactants) stabilize it. [18-21]The magnitude of PFAS enrichment in foam and what PFAS properties affect that enrichment has not been studied, even as foam near PFAS-impacted sites has been reported.[22, 23] Enrichment of PFAS in the SML has been evaluated in the ocean, but for a limited number of analytes from only two PFAS classes, perfluorocarboxylates and perfluorsulfonates.[16, 24] In addition, these studies were not done locations near of direct PFAS contamination nor done with the explicit goal of evaluating techniques for SML sampling of PFAS.

1.4 PFAS and Non-aqueous Phase Liquids (NAPL)

Due to high PFAS concentrations (g/L)[25, 26] in AFFFs, U.S. military bases that used AFFFs for firefighter training have extensive PFAS contamination in the groundwater.[27] These military bases have also released NAPL through intentional waste dumping or spills and leaks. The release of NAPL and PFAS are often in the same location at these bases, thus the presence of PFAS in NAPL is of interest. Currently, no method is published for PFAS in NAPL and only one method has been published for a NAPL-like matrix, automotive lubricant.[28] The extraction was a lengthy process involving centrifuging, blowdowns, reconstitution in water, and a final clean up step of weak anion exchange solid phase extraction (WAX SPE). The water reconstitution step may lead to a loss of long chain PFAS and the SPE step us unable to extraction cations and may be inadequate at extracting zwitterionic compounds, which are prevalent in AFFF.[29]

1.5 PFAS and High Resolution Mass Spectrometry

Most analytical methods for PFAS rely on a triple-quadrupole detector mass spectrometer (TQD-MS) to perform quantitative analysis. Advances in mass spectrometry have produced higher resolution instruments and have allowed for suspect and nontarget screening to be performed on environmental samples.[30, 31] Common high-resolution instruments include a quadrupole time-of-flight (QToF) and ion-mobility mass spectrometer (IMS).[32, 33] Discovery and confirmation of compounds, and subsequent quantitation, still rely on certified analytical standards which significantly lag in production compared to the PFAS that exist on suspect lists.[34, 35] For estimating concentrations, labs have matched suspect and nontarget PFAS to those with analytical standards, assume an equal molar response, and borrowed the calibration curve to estimate the concentration. Various matching schemes exist, which are different across laboratories, and will change over time as more PFAS are discovered and more analytical standards are produced.[36, 37] A unified method for estimating concentrations of suspect and nontarget PFAS would improve data comparisons both across labs and across time.

1.6 Summary of Work Performed

In Chapter 2, a method for foam analysis by liquid chromatography time-of-flight mass spectrometry (LC-QToF) was developed for 50 targets and 140 suspect PFAS. Enrichment factors for PFAS and dissolved organic carbon (DOC) were calculated from values in the foam and underlying bulk water. Two foam and bulk water pairs and a background foam were analyzed by ^{1}H NMR to characterize the DOC functional groups. Finally, preliminary estimates of exposure and risk from swimming and incidental ingestion of foam and surface water were calculated.

In Chapter 3, three SML sampling techniques were deployed at 10 sites in an AFFF-impacted freshwater area. Bulk water was sampled at two different depths (3 and 30 cm) to calculate SML enrichment factors. To support a sampling technique recommendation, accuracy, precision, limits of detection and quantification were determined. Enrichment in the SML was compared to ocean SMLs and SSAs, and freshwater foam. The precision of the techniques was used to interpret SML variability at the 1m scale and field (km) scale.

In Chapter 4, a PFAS in LNAPL method was developed by combining a micro liquid-liquid extraction and LC-QToF to quantify 50 target and estimate up to 800 suspect PFAS by a novel quantitation technique. The method was then applied to 17 LNAPL samples collected from the field.

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CHAPTER 2 – PFAS AND DISSOLVED ORGANIC CARBON ENRICHMENT IN SURFACE WATER FOAMS ON A NORTHERN U.S. FRESHWATER LAKE

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2.1 Abstract

Information is needed on the concentration of per- and polyfluoroalkyl substances (PFAS) in foams on surface waters impacted by aqueous film forming foam (AFFF). Nine pairs of foam and underlying bulk water were collected from a single freshwater lake impacted by PFAS and analyzed for PFAS by liquid chromatography quadrupole time-of-flight mass spectrometry (LC-QToF) and for DOC. The DOC of two foam:bulk water pairs were characterized by ^{1}H NMR. Foams were comprised of 16 PFAS with concentrations as high as 97,000 ng/L (PFOS) along with longer-chain, more hydrophobic PFAS. Only five PFAS (PFOS and shorter chain lengths) were quantified in underlying bulk waters. Enrichment factors (foam: bulk water) ranged from 10 (PFHxA) up to 2,830 (PFOS). Foams impacted by AFFF gave the greatest concentrations and number of PFAS classes with PFOS concentrations exceeding the EPA health advisory level (70 ng/L). PFAS concentrations were significantly below published critical micelle concentrations and constituted <0.1% of overall DOC concentrations in foam, indicating that PFAS are a minor fraction of DOC and that DOC likely plays a central role in foam formation. Estimates indicate that foam ingestion is a potentially important route of exposure for children and adults when they are in surface waters where foam is present.

2.2 Introduction

PFAS are a group of synthetic organic molecules classified as emerging contaminants.[1] Thermal stability coupled with water and oil repelling properties make them useful in a variety of consumer products and aqueous film-forming foams (AFFFs), which are used for fighting fuel-based fires.[2, 3] However, increased monitoring data indicates that wastewater treatment plants, landfill leachates, industrial discharge, and AFFF-impacted groundwater are some of the sources that contribute to PFAS observed in surface waters.[4-10]

Recent media reports captured public concern over foam containing high (μg/L) concentrations of PFAS on surface waters in areas impacted by AFFF.[11, 12] Although reports indicate μg/L PFAS levels in foam, there is little information on the number and concentrations of individual PFAS in foam and associated bulk water.[13, 14] The state of Michigan issued a warning to avoid the foam based on a preliminary risk assessment.[15] However, that analysis included only four individual PFAS (PFOA, PFNA, PFHxS, and PFOS). Information on PFAS in foam has not yet been placed into the context of dissolved organic carbon concentrations (DOC), thus it is difficult to determine if PFAS are a major or minor component of foam.

Foam (dispersion of gas within a liquid) forms when air is introduced into water enriched with surface-active substances, or surfactants.[16-20] Naturally occurring foam is comprised of a mixture of naturally derived surfactants such as humic and fulvic acids, lipids, and proteins originating from decaying plants and other organic matter.[16] Thus, foam can occur in pristine and contaminated surface water.[16-18] Natural forming foam is hypothesized to originate from the surface microlayer.[16]
As anthropogenic substances, PFAS are considered 'super surfactants' due to their ability to lower the surface tension of water to a greater degree than hydrocarbon surfactants.[20-22] Laboratory studies indicate enrichment of PFAS in foams,[23]aerosols,[24] and gas bubbles associated with carbonaceous (remedial) sorbents.[25] Enrichment factors (EFs) for PFAS are reported for surface microlayers and aerosols under laboratory conditions and are computed from the PFAS concentration in an upper phase divided by that in underlying bulk water.[24, 26-28] In contrast, there are only two reports of EFs but only for PFOS and PFOA in natural seawater surface microlayers.[29, 30]

To date, the PFAS composition and concentration of foam and underlying bulk water have not been characterized in detail for target and suspect PFAS. In addition, PFAS concentrations in foam have not been framed in the context of DOC concentrations. Therefore, for this study, nine pairs of foam and underlying bulk water were collected from a single freshwater lake impacted by multiple sources of PFAS, including AFFF, landfill leachate, and potentially septic systems (Figure 1). A method for foam analysis by liquid chromatography quadrupole time-of-flight mass spectrometry (LC-QToF) was developed for up to 50 target and >1400 suspect PFAS.[31] Enrichment factors were calculated from the PFAS and DOC concentrations in foam and underlying bulk water. Two foam and bulk water pairs and a background foam were subjected to ^{1}H NMR in an effort to characterize the functional groups present in foam and bulk water. Preliminary estimates of exposure and risk from incidental ingestion of the foam and surface water while swimming were calculated using individual and summed PFAS concentrations in the foam and water.

2.3 Materials and Methods

Standards and Reagents. All reagents used for sample preparation and LC-QToF analysis are described in the Supporting Information (SI). Native (50) and isotopically-labeled (33) standards were purchased from Wellington Laboratories (Guelph, ON, Canada; Table S1). Analytes for target analysis included: carboxylates (C4-C14,C16); sulfonates (C3-10,12); Cl-PFOS; cyclic sulfonate (PFEtCHxS); unsubstituted perfluoroalkyl sulfonamides (C4,6,8); substituted sulfonamides (MeFOSA and EtFOSA); sulfonamido acetic acids (FOSAA, MeFOSAA, EtFOSAA); x:2 telomer sulfonates (C4, 6 ,8, 10); saturated telomer acids x:2 (C6, 8 ,10) and x:3 (C3, 5, 7); unsaturated telomer acids x:2 (C6, 8 ,10); HFPO-DA (Gen-X), ADONA, F53-B (Cl 9, 11); and diPaps x:2 (C6, 8). For a full list of PFAS analytes and their acronyms and stable-isotope labeled standards, see Table S1.

Sample Collection. Foam and bulk water were collected from nine locations around a freshwater lake (Figure 1). Foams 1-5 were located on the western short near areas of PFAS plumes, likely originating from AFFF sources, while Foams 6-8 were located on the eastern shore. Foam 6 was collected near the mouth of a stream impacted by a former municipal dump (e.g., unlined landfill) and Foam 7 and Foam 8 were collected in a location with residential septic tanks. In a separate sampling trip, a foam was collected west of the lake of interest as a possible background sample (Figure 1). Bulk water at this location was collected in a smaller amount, allowing for only PFAS analysis.

Foam samples were collected using a procedure developed for the state of Michigan.[32] Briefly, foam was manually scooped into Ziploc bags (previously determined to be blank for PFAS) and then allowed to condensate to a liquid. All of the collapsed liquid was then poured into 250 mL HDPE bottles which were filled below capacity. Underlying bulk water was also collected at each site in a 250 mL HDPE bottle by submerging the closed bottle 30 cm below the foam, opening the bottle to collect water, then closing the bottles underwater before bringing it up and through the surface. The bulk water from the background site was collected by the same procedure but using a 15 mL centrifuge tube. No field or trip blanks were collected at the time of sampling. All samples were then stored on ice until shipped overnight to OSU and then kept frozen until analysis.[33]

Foam and Bulk Water Sample Preparation. Foam was prepared by homogenizing the bottle slowly to avoid foaming, then diluting 800 µL into a 15 mL polypropylene centrifuge tube (VWR, Radnor, PA) containing 3,200 µL of MeOH. The solution was then centrifuged at 3000 g for 30 min to remove the visible debris in the sample. The solution was then transferred to an autosampler vial where 0.75 ng of each isotopically-labeled standard was added (Table S1). Prior to injection, 0.75 ng of M2PFOA and M8PFOS were also added. Bulk water was prepared with a micro liquid-liquid extraction described previously,[34] where 6 mL of bulk water, 1.94-2.0 g of sodium chloride, 20 µL of 6N HCl, and 1.5 ng of each isotopically-labeled standard were added to a 15 mL polypropylene centrifuge tube then extracted three times with a total of 2 mL 10% (v/v) 2,2,2-trifluoroethanol in ethyl acetate. Then, 1.5 ng of M2PFOA and M8PFOS in methanol were added along with 950 µL of methanol for a 3mL final extract.

Quality Control. Because isotopically labelled surrogates, MPFOA and MPFOS, were added to each foam (n=12) and each surface water (n=12), accuracy and precision were assessed by their ratio to M2PFOA and M8PFOA in samples relative to their ratios in calibration and quality control standards (foam n=19, surface water n=13). In addition, four replicates of Foam 6 and Bulk Water 2 (unspiked) were analyzed for a measure of whole method precision and a single aliquot was overspiked with 50 PFAS native standards (see SI). Foam and bulk water blanks were also performed (see SI) and gave no PFAS concentrations at or above the limit of detection (LOD).

Instrument and Data Analysis. Foam dilutions and bulk water extracts were analyzed by LC-QTOF-MS (X500R; SCIEX, Framingham, MA) in negative mode by injecting (900 μL) onto an orthogonal LC system as described in the SI.[34] The QToF was operated in TOF-MS mode for quantification based on the accurate mass of the parent ion, but MS/MS mode for PFBA and MPFBA to reduce background. Although extracts were analyzed in positive mode, no positive-mode PFAS were detected.

Five point calibration curves were constructed over the range of 20-10,000 ng/L except for FBSA, FHxSA, and FOSA which ranged from 100-50,000 ng/L. Values for a third party reference standard (Absolute Standards, Hamden, CT) containing carboxylates (C6-14), sulfonates (C4, 6, 8), MeFOSAA, and EtFOSAA were required to fall within 70-130 % of the expected values. Continuing calibration verification standards were analyzed every 10 samples and required to fall within 70-130 % of the expected value. Target compounds included the 50 PFAS for which native standards were available, while suspects included >1400 compounds from a custom XIC list.[31, 35] Criteria regarding mass errors, isotope ratios, and library matching for target and suspect screening are found in Nickerson et. al.[31]

Dissolved Organic Carbon Characterization. For DOC analysis, the foams were first diluted 1:10 v/v into HPLC-grade water. Both foams and bulk waters were filtered through a Whatman no. 1 paper filter prior to analysis for total organic carbon on a Schimadzu TOC-$V_{cph/cpn}$ (Kyoto, Japan) total organic carbon analyzer.
Two pairs of foam and bulk water (location 5 and 7) were analyzed by NMR since there was adequate sample volume for analysis and from locations of higher and lower PFAS concentrations (Figure 1). NMR analysis was performed using a Bruker

Avance IIIHD 800 MHz spectrometer equipped with a 5mm triple resonance cryogenic probe. Solution ^{1}H NMR spectra were acquired with 8,192 scans and 76,922 time domain points (acquisition time of 4 seconds). The recycle delay was 1 s, for a total experiment time of ~11.5 h per sample. All NMR data were collected at 25 °C. NMR data were apodized, zero filled, Fourier transformed and base line corrected using nmrPipe.[36] Regions were integrated using nmrglue and custom python scripts.[37] Regions were defined according to previously published work.[38]

Exposure and Risk Assessment. Preliminary estimates of exposure and risk were estimated for children and adults incidentally ingesting water via foam and surface water while playing or swimming in the lake. To estimate exposure, the concentrations of ΣPFAS in the surface water were multiplied by the ingestion rate, bioavailability, exposure factor and divided by body weight (see SI). Geometric mean and maximum ΣPFAS were multiplied by geometric mean and maximum ingestion rates, respectively, to yield central tendency and upper bound exposure estimates. A 19:1 ratio was assumed for foam to collapsed liquid, as observed during collection, and was applied by dividing the ingestion rate by 19. Children and adults were assumed to play or swim in the lake 2 hours per day, 5 days per week, for 12 weeks of the year (summer). Hazard quotients were calculated by dividing the estimated exposure by the reference dose for PFOS (2 ng/kg-day), which constituted up to 90% of total PFAS in the foam.[39]

2.4 Results and Discussion

Foam Method Validation. Since no published method exists for PFAS analysis in foam, the first step was to develop a reliable analytical method. In the case of foams, micro liquid-liquid extraction with ethyl acetate and trifluoroethanol resulted in a viscous emulsion that could not be handled with confidence. For this reason, dilution was selected as an alternative approach. A 1:5 v/v dilution into methanol was selected because it gave the least ion suppression as indicated by internal standard area counts and reduced peak splitting for PFBA. Spiking stable-isotope labeled internal standards before or after centrifugation was evaluated (Table S2); all subsequent samples were spiked post-centrifugation. Twenty five of the 31 isotopically labeled standards in n=12 foams (diluted 1:5) gave average area counts that were within 30% of the average area count for n=19 calibration standards (Table S3), which indicates minimal ion suppression or enhancement. For n=12 bulk water extractions, 27 of the 31 isotopically labeled standards gave average area counts that were within 30% of the average area counts of n=19 calibration standards (Table S3). The recoveries of MPFOA and MPFOS (surrogates) were 91 ± 5.8% and 92 ± 5.6%, respectively, in eight foams and 90 ± 6.3% and 105 ± 7.2%, respectively, in eight bulk waters (Table S4). Precision for three naturally occurring PFAS in replicate analyses of Foam 6 ranged from 2.3 – 23% (See SI) and the recovery of the 50 target PFAS overspiked into Foam 7 (Table S5) and Bulk Water 2 (Table S6) are reported and discussed in the SI.

Overview PFAS Composition and Concentration. Of the 50 target analytes, 16 analytes encompassing eight PFAS classes were found above the LOQ in foams, while only five analytes were quantified above the LOQ in underlying bulk water (Table 1; Table S7).

Perfluoroalkyl Carboxylates. Foams 1-5 and Background Foam had long-chained PFCAs ranging from PFOA – PFUnDA at concentrations above the EPA HAL for PFOA, while only one foam (Foam 2) had PFHxA above its LOQ (Table 1). Foam 6, Foam 8, and Background had PFUdA. To the best of our knowledge, this is one of the few reports of long-chain PFCAs associated with surface waters. Long-chain PFCAs typically are associated with sediments or biota rather than surface water.[9] Background Foam was comprised of PFNA, PFDA, and PFUdA, but the source of these PFCAs is unknown. Only PFHxA and PFOA were found in three of the underlying bulk waters (Bulk Water 1, 2 and 4; Table 1). Background Bulk Water had no PFCAs > LOQ (Table 1).

Perfluoroalkyl Sulfonates. Foams 1-5 all contained PFHxS, PFHpS, and PFOS, while two foams also contained PFNS (Foam 2 and 3; Table 1). The concentrations of PFOS ranged from 2,300 - 97,000 ng/L. In the case of Foam 2, the combined PFOS and PFOA concentration (98,200 ng/L) is 1,400 times greater than the EPA HAL for PFOS and PFOA combined (70 ng/L) in drinking water. Foams 6-8 and Background Foam all had PFOS > LOQ (Table 1) but at concentrations an order of magnitude lower than Foams 1-5. Bulk Water 1-4 and Background Bulk Water all had PFHxS and PFOS at comparable concentrations, while only Bulk Water 8 across from the AFFF-impacted side of the lake only had PFOS (Table 1).

Other ECF-Derived PFAS. Other ECF-derived PFAS quantified in Foams 1-5 included PFEtCHxS, FHxSA, EtFOSAA, and Spr-FHxSA (Table 1). PFEtCHxS was originally reported in all five Great Lakes and associated with hydraulic fluids and wastewater treatment plant effluents.[40] The C6 sulfonamide, FHxSA, was first reported in AFFF-impacted groundwater[41] and in urban waters impacted by AFFF, although at much lower concentrations.[42] The sulfonamide-based precursor (SPr-FHxSA, Figure S3), a suspect PFAS, was found only in Foam 4. While this precursor was first reported in 3M AFFF[35] and recently in AFFF-impacted soil,[31] to the best of our knowledge it is the first report of this precursor associated with foam. In the case of EtFOSAA, it is typically associated with soil and sediment[43-45] and not surface waters. Of the ECF-based PFAS in foam, only PFHxS and PFOS were detected in underlying bulk water (Bulk Water 1-4; Table 1). Each of these ECF-based PFAS were only observed in foam and not in surface water. Thus, foam appears to enrich in hydrophobic PFAS and its analysis provides for a sensitive detection of PFAS that may be at or below detection in bulk water, allowing for a more comprehensive site assessment. Although foam is being considered as a remedial tool for recovering PFAS from water, it is unclear if collection of foam is a practical, cost effective means for removing PFAS from large fresh water lakes.[23, 24, 46]

The 6:2 fluorotelomer sulfonate (FTS) was detected in Foams 1-5, while the 8:2 FTS was found above the LOQ in only Foams 2 and 4 (Table 1). The 6:2 FTS was detected in three underlying bulk waters but not the more hydrophobic 8:2 FTS. The detection of FTSAs and predominantly linear PFCAs in foams near known PFAS plumes (Figure 1) is consistent with groundwater data that indicates fluorotelomer-based AFFFs were used at the site.[47] Only one observation of the fluorotelomer-derived 5:3 FTCA was recorded for Foam 6.

Branched and Linear Isomers. The PFCAs in foam were predominantly linear with 0-12% branched isomers (88-100% linear isomer), which is significantly less than the 22-25% branching expected if produced by electrofluorination (ECF).[48-51] Greater than 75% linear PFCA isomers is attributed to the biotransformation of linear telomer-based precursors to only linear PFCAs at this site.[47]

The PFHxS in foam is predominantly linear isomers (86-94%) with the fraction of branched isomers ranging from 6-14%, which is below the 25-27% expected for ECF-based PFAS.[51] The fraction of the branched isomers in bulk water is higher (13-27%) compared to that for Foams 1-4 (Table 1). In the case of PFOS, all nine foams and six bulk waters have a greater percentage of branched isomers (41-49% for foam and 55-65% in bulk water), which indicates enrichment of branched over linear PFOS isomers compared to the manufactured ratio (25:75 to 27:73).[48-51] Although PFHpS, FHxSA, and EtFOSAA were not measured in bulk water, branched and linear isomers were observed in foam (Table 1). The percent branched PFHpS isomers was intermediate between than that of PFHxS and PFOS and for and FHxSA it was between PFHpS and PFOS.

When the ECF-based PFAS are ordered by retention time, which is a proxy for hydrophobicity,[47, 52] there is a decline in the percent linear isomers with increasing retention time (Table S8). The percent branched isomers in foam (and bulk water to a lesser extent) shift from below 25% (e.g., PFHxS < PFHpS) to greater than 25% (FHxSA < PFOS < PFNS) with the exception of EtFOSAA. In the case of PFHxS, less than 25% branched in foam and surface water indicates that branched PFHxS may have been preferentially transported through groundwater over time and discharged into the lake such that PFHxS today is enriched in linear isomers. Any discharged PFAS that remained in the water column were likely flushed out of the lake due to water movement from north to south (Figure 1). In contrast, > 25% branched isomers for PFHxSA, PFOS, and PFNS in foam (and PFOS in bulk water) indicates retardation of linear isomers during groundwater transport and present-day discharge of branched isomers into lake. Branched isomers of PFOS exhibit lower soil:water partition coefficients[53, 54] and less sorption to granulated activated carbon relative to linear isomers.[47]

Spatial Distribution. Foams 1-5, which were located near the toe of several known PFAS plumes (Figure 1) were comprised of the greatest number of PFAS as well as the highest concentrations (Table 1). In contrast, Foams 6-8 and Background Foam, which were not located near known PFAS plumes (Figure 1) had fewer PFAS with significantly lower PFOS concentrations (Table 1). The occurrence of PFUdA in Foam 6, Foam 8, and Background Foam at concentrations similar to those of AFFF-impacted Foams 1-5 is notable. The only detection of 5:3 FTCA in Foam 6 may be a marker of the former township dump, since 5:3 FTCA is the PFAS of greatest concentration in landfill leachates.[6, 55, 56] Of the foams from the eastern side of the lake, only Foam 8 had PFOS > LOQ in the underlying bulk water (Table 1). Foam 7 and 8 locations are potentially impacted by septic discharge to the lake since other known sources have not been identified. The source of PFAS to Background Foam and Bulk Water collected from another lake is unknown but they have PFAS profiles that are more similar to Foams 5-8 than Foams 1-4, which are impacted by AFFF discharge. The apparent differences in PFAS concentration and composition in AFFF-impacted foams (Foams 1-5) from Foams 6-8 on the eastern shore indicates that the water flow in the lake, which runs from northwest to southeast, may prevent the lake from being well mixed. The analysis of foam near sources other than AFFF plumes contain PFAS that may be useful for source identification.

Dissolved Organic Carbon Concentration and Composition. DOC concentrations in the foam and bulk water were on average 250 mg/L and 15 mg/L (Table 1) and indicate a generally uniform distribution of DOC around the lake (Figure 1). Integration of the NMR spectrum also indicated that the DOC of foams was considerably higher than the bulk water (Figure S1), in agreement with the DOC analysis (Table 1). Compared with PFAS concentrations, the DOC values are orders of magnitude larger. For example, in the case of Foam 2, the total PFAS concentration was < 0.1% of the DOC concentration. Thus, measuring DOC is not a good proxy for PFAS concentrations in foam. It is unlikely that PFAS are the primary cause of foam formation because the concentration of PFOS is five orders of magnitude lower than its critical micelle concentration (2.7×10^9 - 4.2×10^9 ng/L).[20] While it appears that PFAS concentrations are unlikely to be the primary cause of foaming, it is unknown if PFAS contribute to the stability of foams that form on surface water. Despite speculation that the color of foam is indicative of PFAS,[13, 14] color is unlikely to correlate with the relatively low PFAS concentrations, but rather to the naturally derived DOC.

NMR analysis was conducted on two different pairs of foam and bulk water samples and one foam collected from a location considered as background. Integration of the NMR spectra over regions corresponding to various chemical functional groups common to dissolved organic matter [36] revealed similar functional group types and proportions in the lake and background foams (Figure 2). The aliphatic and nitrogen/oxygen substituted aliphatic bands ('Aliphatic near NO') accounted for about 80% of the total functional groups present in all of the foam samples (Figure 2). Focusing on these two classes, their presence suggests that the organic matter fraction is comprised of both non-polar (e.g. lipids) and polar (e.g. peptidoglycans or chitinaceous materials) functionality.[57-59] Both the non-polar and polar functional groups may contribute to the formation of larger, organic matter structures with amphiphilic properties. Larger organic matter strucutres are corroborated by the presence of broader peaks in the NMR spectra which are indicative of large, slow tumbling structures with higher molecular weights.[60]The spectra collected from the foam samples contained broad peaks suggesting that both the non-polar and polar functional groups may contribute to the formation of larger organic matter structures with amphiphilic properties within the DOC fraction. Such amphiphilic structures may provide both a hydrophobic environment and electrostatic interactions with the capacity to drive PFAS retention. Though a corollary relationship, the functional groups, larger organic matter structures, and higher concentration of DOC could explain the enrichment of DOC and PFAS in the foam over the bulk water phase. Though DOC is much lower in abundance, (Figure S1), the primary DOC functional groups in the bulk water samples were also aliphatic (Figure 3) in nature. However, in contrast to the foams, the bulk water samples exhibited narrower NMR peak shapes (Figure 2), indicating that the DOC is likely comprised of smaller, potentially 'free-phase' organic compounds (e.g. short chain fatty acids or aliphatic amino acids).[61] In Bulk Water 5, there was a single resonance around 3.55 ppm which is associated with oxygen containing alkyl type ('O-alkyl; Figure 2) functional groups. Despite comprising a large fraction of the functional group composition in this sample (~70%; Figure 3), this class of functional groups is more likely from another source (or sources) of contamination as opposed to originating from naturally derived DOC. Lower concentrations of DOC and a lack of large organic matter structures likely result in lower PFAS concentrations in bulk water.

Enrichment Factors for PFAS and DOC. Enrichment factors were generated by dividing the PFAS and DOC concentrations in a foam over that of its associated underlying bulk water. Enrichment factors (Figure 4, Table S9) were calculated only for those PFAS (e.g., PFHxA, PFHxS, 6:2 FTS, PFOA, and PFOS) that were > LOQ in both foam and bulk water (Table 1 and Table S7). The EF of L-PFHxA and Br-PFHxS were less than the average EF of DOC (18), while the EF of PFAS including L-PFHxS, 6:2 FTSA, L-PFOA, and Br/L PFOS gave EFs that were greater than that of DOC (Figure 4; Table S9). For branched and linear PFHxS and PFOS, the average EF of linear isomers was a factor of 2-3 higher than that of their branched isomers (Table S9), which is consistent with greater hydrophobicity[53, 54] and longer chromatographic retention times of linear isomers (Table S9).

Johansson et al. speculated that natural organic matter (e.g., DOC) would be less surface active compared to PFAS.[28] The observed EFs for PFAS in foam on this freshwater lake are consistent with the range of EFs for PFAS in foam produced from

AFFF concentrate with values ranging from 386-7,991 for PFOS.[23] Meng et al. obtained even higher EFs (4,200-8,400) for PFOS when a hydrocarbon surfactant was added, which indicates that additional surface active constituents enhance the EFs of PFAS. The EFs in the present study are greater than EFs for PFOS (2-109) and PFOA (1.2-4.7) in natural[29, 30] and synthetic seawater surface microlayers,[28] and for a range of PFSAs (1.3 - >204)[26] and PFCAs (5-<118)[26, 27] in aerosols generated from synthetic fresh and saline waters under laboratory conditions. For example, Johansson et al. reported EFs (normalized to sodium) of up to 62,000 (PFUnDA) in aerosols that formed from the surface microlayer as a function of particle size.[28] A single report exists for 6:2 FTSA EFs (45-1,700) in aerosols generated from industrial wastewater,[24] encompasses the EFs observed for 6:2 FTSA (17-87) in the present study (Figure 2; Table S9).

A plot of EF vs. PFAS chromatographic retention time, a proxy for relative hydrophobicity (Figure 4),[47, 52] and the number of fully fluorinated carbons (Figure S2) revealed log relations, which is consistent with increased PFAS partitioning to the air-water interface.[62, 63] Back-transforming the estimate of slope results in a value of 6.9, which indicates that for every minute of retention time, there is a predicted 6.9 increase in PFAS EF. Likewise, the slope of the relation between EF and number of fully fluorinated carbons (Figure S2) indicates a 5.5 increase in EF for every fully fluorinated carbon. In the present study, EFs for PFAS that are more hydrophobic than PFOS, as indicated by chromatographic retention time including PFNA, PFUnDA, 8:2 FTSA, and EtFOSAA, were not calculated because concentrations in underlying bulk water were <LOQ (Table S7), but the EFs are likely higher than that of PFOS.[28] However, it is also clear that there is a spread in the reported EF values for individual PFAS (Figure 4), with lower EF values for Location 8 and the Background sample and higher values for the AFFF-impacted locations (1-5; Figure 1). Because the DOC values are similar across locations, we speculate that it is the DOC composition (e.g., molecular weight and functional groups) that determines the EF value.

Exposure and Risk Assessment. Estimates indicate a potential health risk from ingesting foam, as indicated by hazard quotients exceeding 1 (Table 2). Maximum exposures and hazard quotients were over an order of magnitude higher than geometric mean estimates, and especially elevated for children ages 1 to 6. This conclusion is similar to previous reports and the basis of an advisory on the lake for foam, which relied on maximum concentrations of PFOA, PFOS, PFHxS and PFNA previously measured in the foam.[15] Maximum exposures for young children also indicated ingestion of bulk water to pose a potential risk. See Table S10 and S11 for exposure estimates by individual PFAS. Sources of variability not considered in these estimates include body weight and frequency of use as we assumed geometric mean body weight and frequent, but not daily, use during the summer months. An important source of uncertainty is how much foam a child or adult would ingest while playing or swimming in the lake. The dermal and inhalation exposure routes were not considered in this preliminary assessment.

2.5 Conclusion

Implications. Foam in surface water settings has long been attributed to natural surface active agents,[16, 19] as well as to anthropogenic sources.[16] Waste spills associated with foaming events prior to the development of analytical methods for PFAS were attributed to non-surface active components and biologically derived surfactants.[64] The analysis of foam may prove useful for identifying the origins of wastes in future waste releases (see SI for more discussion).

The observed foams on this freshwater lake are comprised largely of DOC, which is orders of magnitude higher in concentration than the individual or summed PFAS concentrations. However, the foam concentrates PFAS well above the EPA HAL, especially for PFOS and PFOA, as well as longer-chained PFAS. The high concentrations (μg/L), especially for longer-chained PFAS, are a concern because foam may serve as a direct route of exposure to humans through ingestion or to organisms that live in the lake's surface where foam forms. Anthropogenic hydrocarbon surfactants, which are found in AFFF, may also be present in the foam but were not analyzed for this study. A robust analysis of the surface microlayer for PFAS and hydrocarbon surfactants is needed to confirm that the surface microlayer is the source material for the foam that forms on the lake. Lastly, when sampling (bulk) surface water, foam should be avoided because it is enriched with longer-chained PFAS including PFOS and PFOA which significantly exceed the EPA HAL. Preliminary estimates indicate that PFAS-enriched surface water foam can be an important exposure route that poses potential risk for children and adults playing and swimming in the lake.

Supporting Information Available

The supporting information contains information about instrumental analysis for LC-MS/MS and exposure risk assessment. This information is available free of charge on the ACS Publications website.

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Table 2.1 Concentrations of dissolved organic carbon (DOC; mg/L) and individual PFAS (ng/L) in foams and underlying bulk water (BW), branched: linear isomer ratio, and chromatographic retention time (Rt).[a-c]

Sample ID	DOC	PFHxA	PFOA	PFNA	PFDA	PFUnDA	PFHxS	PFHpS	PFOS	PFNS	PFEtCHxS	FHxSA	EtFOSAA	SPr-FHxSA[c]	5:3 FTCA	6:2 FTS	8:2 FTS
Foam 1	**250**	<LOQ	**840 (8:92)**	**340 (9:91)**	**260 (5:95)**	**250 (8:92)**	**1,200 (7:93)**	**610 (13: 87)**	**32,000 (41:59)**	<LOQ	**340**	**950 (30:70)**	<LOQ	ND	ND	**830**	<LOQ
Foam 2	**240**	**140 (0:100)**	**1200 (7:93)**	**850 (7:93)**	**630 (5:95)**	**510 (9:91)**	**2,000 (6:94)**	**2,300 (12:88)**	**97,000 (49:51)**	**130 (70:30)**	**730**	**1,000 (29:71)**	<LOQ	ND	ND	**1300**	**100**
Foam 3	**330**	<LOQ	**1300 (7:93)**	**1500 (7:93)**	**960 (6:94)**	**660 (10:90)**	**1,700 (6:94)**	**2,800 (10:90)**	**68,000 (46:54)**	**130 (72:28)**	**560**	**1,100 (28:72)**	**130 (16:84)**	ND	ND	**1000**	<LOQ
Foam 4	**240**	<LOQ	**530 (6:94)**	**320 (6:94)**	**290 (5:95)**	**260 (8:92)**	**890 (7:93)**	**690 (12:88)**	**49,000 (41:59)**	<LOQ	**220**	**690 (36:64)**	<LOQ	**140**	ND	**770**	**130**
Foam 5	**260**	ND	**280 (10:90)**	**380 (11:89)**	**420 (12:88)**	**410 (9:91)**	**330 (14:86)**	**160 (13:87)**	**32,000 (49:51)**	<LOQ	<LOQ	<LOQ	**100 (21:79)**	<LOQ	ND	<LOQ	<LOQ
Foam 6	**250**	ND	ND	<LOQ	<LOQ	**110 (6:94)**	<LOQ	ND	**2,300 (43: 57)**	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	**190**	ND	ND
Foam 7	**230**	ND	ND	ND	<LOQ	<LOQ	<LOQ	ND	**2,300 (40:60)**	<LOQ	<LOQ	<LOQ	<LOQ	ND	ND	ND	ND
Foam 8	**210**	ND	ND	<LOQ	<LOQ	**190 (7:93)**	<LOQ	ND	**3,700 (40:60)**	<LOQ	<LOQ	<LOQ	<LOQ	ND	ND	ND	ND
Background Foam	**260**	ND	<LOQ	**130 (0:100)**	**420 (4:96)**	**340 (16:84)**	ND	ND	**1500 (34:66)**	ND	ND	ND	ND	ND	ND	ND	ND
BW 1	**12**	**13 (0:100)**	**15 (5:95)**	ND	ND	ND	**46 (15:85)**	<LOQ	**36 (56:44)**	ND	<LOQ	<LOQ	ND	ND	ND	**24**	ND
BW 2	**16**	**14 (0:100)**	**13 (7:93)**	ND	ND	ND	**52 (16:84)**	<LOQ	**43 (59:41)**	ND	<LOQ	<LOQ	ND	ND	ND	**15**	ND
BW 3	**15**	<LOQ	<LOQ	ND	ND	ND	**27 (27:73)**	<LOQ	**24 (65:35)**	ND	ND	ND	ND	ND	ND	<LOQ	ND
BW 4	**15**	**15 (0:100)**	**18 (6:94)**	ND	ND	ND	**59 (13:87)**	<LOQ	**51 (60:40)**	ND	<LOQ	<LOQ	ND	ND	ND	**45**	ND
BW 5	**21**	<LOQ	<LOQ	ND	ND	ND	<LOQ	ND	<LOQ	ND	ND	ND	ND	ND	ND	ND	ND
BW 6	**14**	ND	<LOQ	ND	ND	ND	<LOQ	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
BW 7	**14**	ND	<LOQ	ND	ND	ND	<LOQ	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
BW 8	**15**	<LOQ	<LOQ	ND	ND	ND	<LOQ	ND	**13 (55:45)**	ND	ND	ND	ND	ND	ND	ND	ND

Back-ground BW	--[d]	ND	<LOQ	ND	ND	ND	**17 (0:100)**	ND	**28 (67:33)**	ND	ND	ND	ND	ND	ND	ND	ND

[a]LOQ for each analyte and matrix is found in Table S7. [b]ND was defined as below the limit of detection (LOD) which was defined as 1/3 LOQ. [c]Analyte found in suspect list at confidence level of 2. [d]Insufficient sample was available, so no DOC analysis.

Table 2.2 Preliminary estimates of exposure (ng/k-day) and risk (hazard quotient, unitless) to PFAS from daily incidental ingestion of foam and bulk water, geometric mean (max).

	Exposure		Hazard Quotient	
Age	Foam	Bulk Water	Foam	Bulk Water
1 to <2	4.9 (70)	0.42 (3.0)	**2.4 (35)**	0.21 (**1.5**)
2 to <3	4.7 (92)	0.41 (4.0)	**2.4 (46)**	0.21 (**2.0**)
3 to <6	2.6 (47)	0.23 (2.0)	**1.3 (23)**	0.11 (**1.0**)
6 to <11	1.8 (25)	0.15 (1.1)	0.88 (**13**)	0.08 (0.54)
11 to <16	1.1 (22)	0.10 (0.96)	0.57 (**11**)	0.05 (0.48)
16 to <21	0.68 (12)	0.06 (0.53)	0.34 (**6.1**)	0.03 (0.26)
21+	0.51 (9.5)	0.04 (0.41)	0.26 (**4.7**)	0.02 (0.21)

Figure 2.1 Foam and underlying bulk water sampling locations relative to known PFOS + PFOA contamination plumes indicated in color (plume data from AECOM)

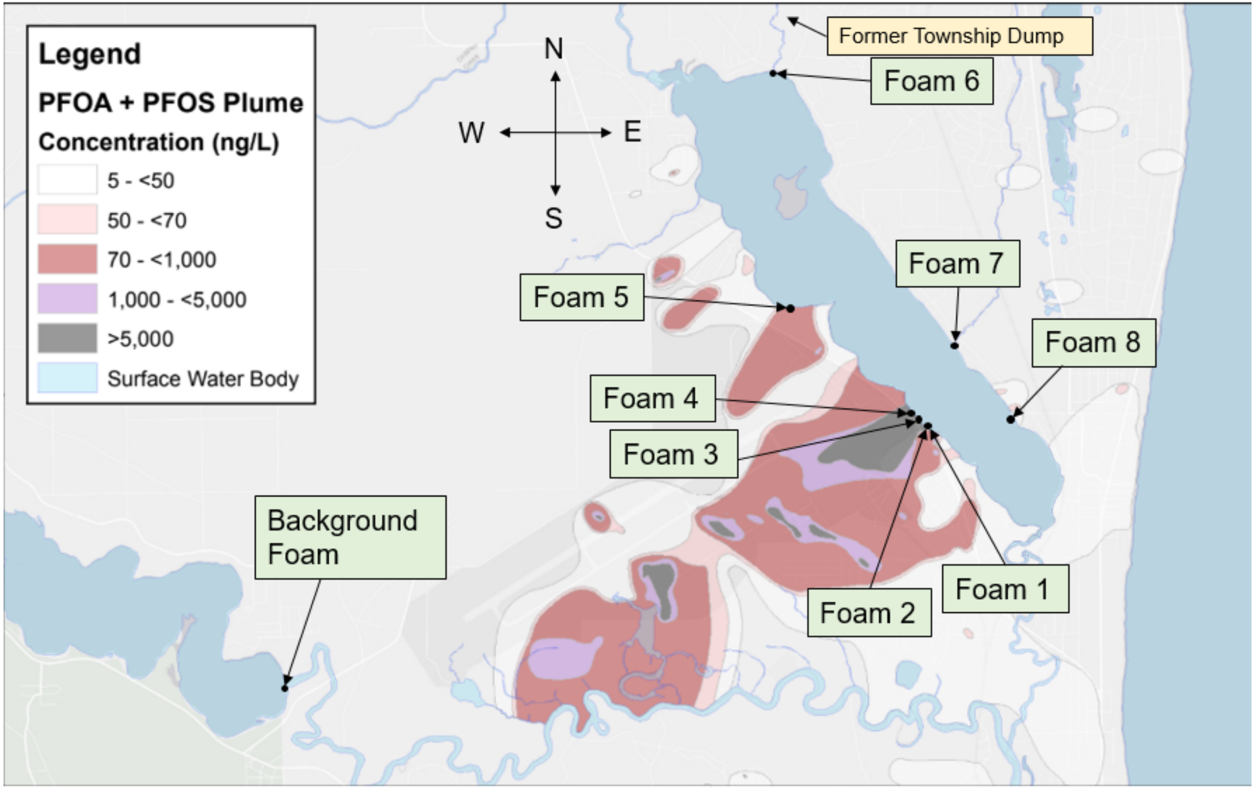


Figure 2.2 Representative ^{1}H NMR spectra used to identify functional groups present on DOC fraction. The regions are: 1. aliphatic methyl and methylene, 2. aliphatic methyl and methylene near O and N, 3. O-alkyl, 4. H-alpha protons from protein, 5. aromatic, from lignin and protein, 6. amide protein.

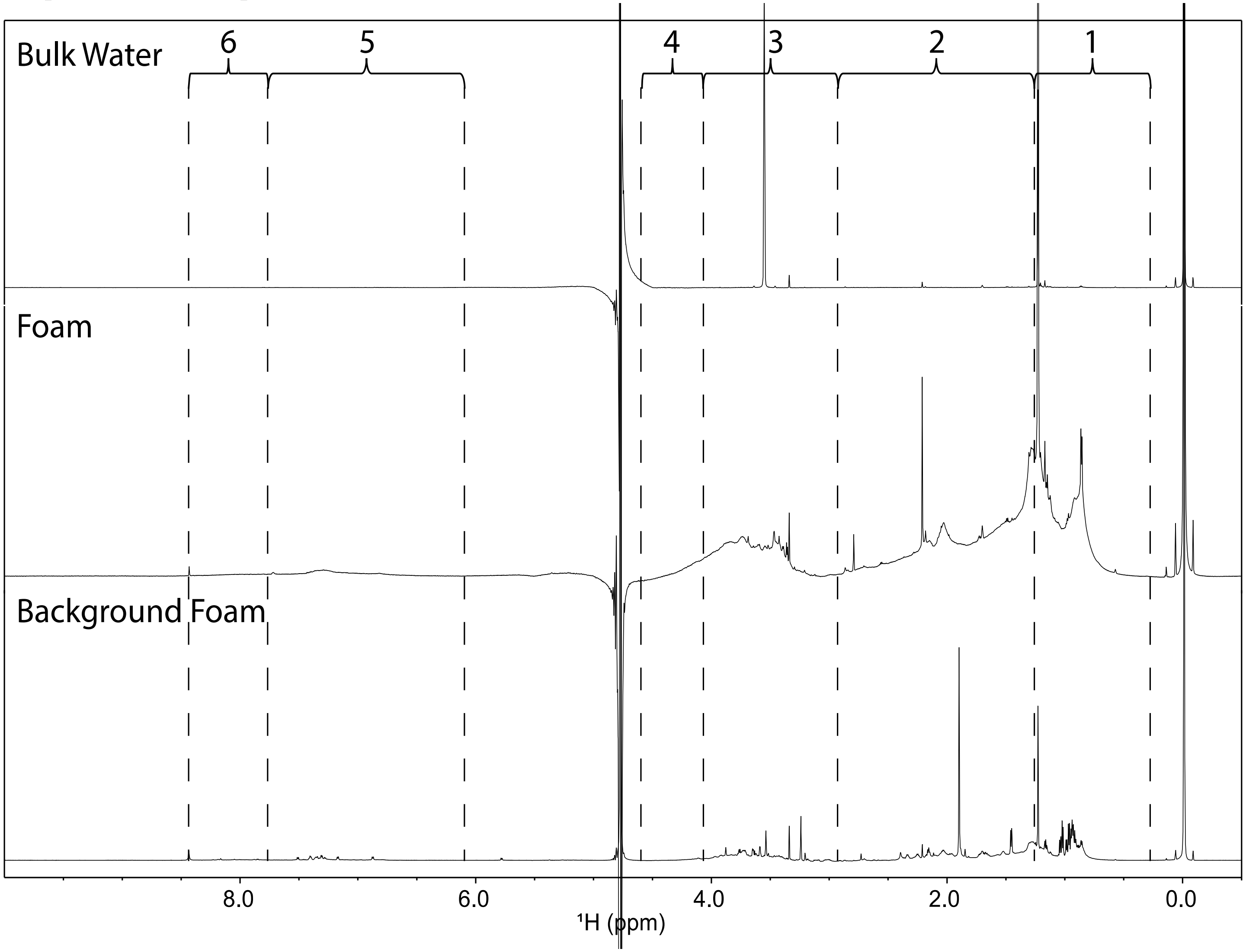


Figure 2.3 Percent composition of identified functional groups in foam and bulk water. Functional groups were identified using ^{1}H NMR. Percent contribution was calculated for each peak region associated with different functional groups (functional group peak area/total integral area).

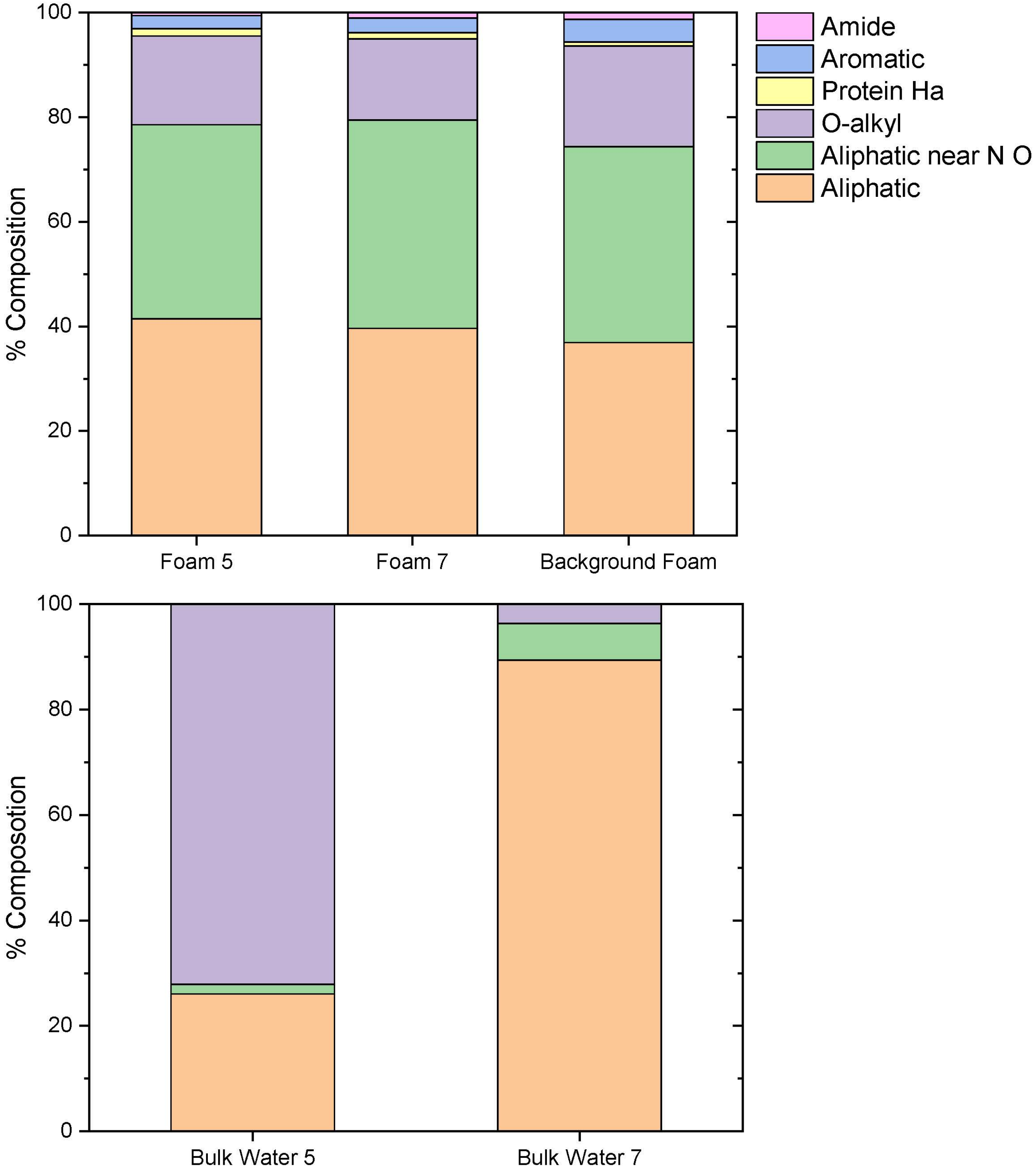
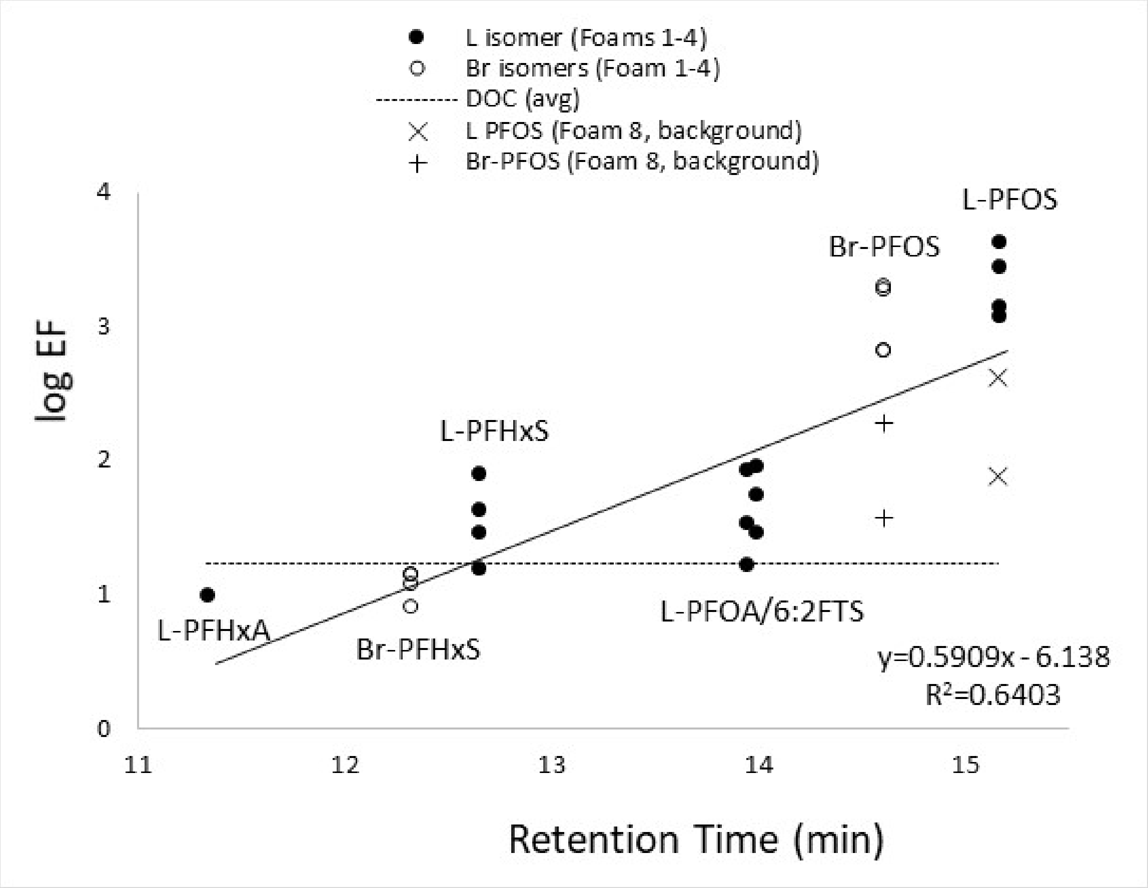


Figure 2.4 Linear regression of the log of enrichment factors for Br- and L-isomers for Foams 1-4 impacted by AFFF for Foam 8 and Background Foam plotted against chromatographic retention time. See Table S9 for individual enrichment factor values.



CHAPTER 3 – VALIDATION AND DEMONSTRATION OF SURFACE MICROLAYER SAMPLING TECHNIQUES FOR PFAS ON AN AFFF-IMPACTED FRESHWATER LAKE

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3.1 ABSTRACT

Per- and Polyfluoroalkyl substances (PFAS) have a known affinity for air-water interfaces and the surface microlayer (SML) is an example of an air-water interface in the environment. Various methods exist for sampling the SML for constituents other than PFAS, yet no study has systematically evaluated SML sampling protocols for PFAS. Three methods for sampling the SML were tested across 10 sites on a freshwater lake impacted by aqueous film-forming foam (AFFF) and analyzed for 50 target PFAS by liquid chromatography quadrupole time-of-flight mass spectrometry (LC-QToF). The SML sampling methods were evaluated for their accuracy, precision, and detection/quantification limits as well as their suitability for practical deployment in the field. Enrichment factors, calculated as the PFAS concentration in the SML divided by the PFAS concentration in bulk water, increased with PFAS chromatographic retention times, a proxy for PFAS hydrophobicity. Enrichment factors were obtained for PFOS ranged from 4-12 and higher for PFAS with chromatographic retention times greater than PFOS. Enrichment factors obtained for the SML were significantly lower than those for naturally occurring foams and sea spray aerosols. Finally, air-water partitioning coefficients were calculated from the PFAS concentration in SMLs and compared to existing laboratory derived air-water partitioning coefficients.

3.2 INTRODUCTION

Per- and Polyfluoroalkyl substances (PFAS) are a group of synthetic organic contaminants with global distribution with both known and unknown risks to environmental systems.[1, 2] Concentrations of PFAS in surface waters are important since surface waters can serve as a drinking water source and bioaccumulation of PFAS by organisms from water occurs.[3]

As surfactants, PFAS accumulate at air-water interfaces,[4] where uptake is explained by the Gibbs Adsorption Equation. The excess surfactant concentration at the surface is the difference between the bulk concentration and the concentration at the surface.[4, 5] Laboratory studies utilize surface tension measurements at relatively high surfactant concentrations and fit the data with a Freundlich isotherm to extrapolate interfacial partitioning coefficients (K_i)[6, 7] at lower environmental concentrations. To the best of our knowledge, there are no measurements of K_i in natural systems.

The surface microlayer (SML) is operationally defined as the thin, top layer of open surface waters that has distinct characteristics from underlying bulk water.[8] Decades of SML research indicates that the SML is a distinct microbial- and carbon-rich environment that supports chemical reactions and that has important implications for air-sea interactions.[8] Aquatic insects living in and passing through this layer in marine and freshwater ecosystems are exposed to chemicals contained in this layer.[9, 10] The thickness of the SML is operationally defined by the selected sampling approach and is typically between 1-1,000 μm. A conceptual SML model includes a volume of water underlying the two-dimensional (2-D) air-water interface.[11] Measurements of the PFAS concentrations in SML and bulk water are need to compute field-derived K_i values, which can then be compared to laboratory-derived values of K_i.

There are only two reports of measurements of PFAS in the SML of natural surface waters. To date, only members of the perfluoroalkyl carboxylates (PFCAs) and perfluoroalkyl sulfonates (PFSA) classes are reported for SML in the open ocean.[12, 13] Ju et al., report the first published SML measurements for PFOS and PFOA. Casas et al. reported the first field data for both the SML and sea spray aerosols (SSAs) in the same location, but did not draw any conclusions about the spatial variability in the SML nor to estimate K_i values. Sea spray aerosols (SSAs) are implicated as a source of PFAS undergoing long range transport.[14]

Analysis of naturally occurring SMLS is needed for a larger number of PFAS from a greater number of PFAS classes. While various methods exist for SML sampling,[15-18] including glass plates, wire mesh, and rotating drums, sampling protocols have not been evaluated systematically for PFAS. In the case of Casas and Ju et al., glass plates were deployed to obtain SML samples; however, little information is provided on the performance of the sampling protocol, including accuracy, precision, and detection limits. Withdrawal speeds and drainage time potentially impact glass plate sampling, yet placing a mesh on a moving surface is also problematic. Using an organic solvent to rinse PFAS from glass plates or meshes poses health and safety issues in the field. In addition, SML sampling methodology for PFAS has not been deployed in a manner that can offer insight into the spatial variability of PFAS in SMLs in freshwater systems at a small (1m) and larger (km) scale. Bulk water sampling at multiple levels below the SML would yield insight into how well the bulk water is mixed. Although the occurrence and enrichment of PFAS in foam[19, 20] was reported for a freshwater lake impacted by AFFF, no information on PFAS concentrations in natural freshwater systems impacted by AFFF are reported.

For this study, three SML sampling techniques were deployed at 10 sites on a freshwater lake impacted by aqueous film forming foams (AFFF).[19] Techniques included a large glass plate, a glass microscope slide, and three glass microscope slides. Bulk water was also obtained with a plastic pipette, at two separate depths of 3 and 30 cm. All samples were analyzed by liquid chromatography quadrupole time-of-flight mass spectrometry (LC-QToF) for 50 target PFASs. Accuracy, precision, limits of detection and quantification were determined to support recommendation of optimal field sampling techniques. The PFAS concentrations in the SML were ratioed to the underlying concentration of PFAS in bulk water to obtain enrichment factors (EFs). The average EFs obtained by the three SML sampling methods were compared to EFs obtained from salt water (e.g., oceans), SSAs, and foam. The precision associated of SML measurements of PFAS concentrations obtained by the large glass plate were interpreted as a measure of SML variability at the 1m scale and at the field (km) scale. Finally, PFAS concentrations in the SML and bulk water were used to estimate K_i values.

3.3 MATERIAL AND METHODS

Standards and Reagents. All reagents used for sample preparation and LC-QToF analysis are described in the Supporting Information (SI). Native (50) and isotopically-labeled (33) standards were purchased from Wellington Laboratories (Guelph, ON, Canada; Table S1). Analytes for target analysis included: carboxylates (C4-C14,C16); sulfonates (C3-10,12); Cl-PFOS; cyclic sulfonate (PFEtCHxS); unsubstituted perfluoroalkyl sulfonamides (C4,6,8); substituted sulfonamides (MeFOSA and EtFOSA); sulfonamido acetic acids (FOSAA, MeFOSAA, EtFOSAA); x:2 telomer sulfonates (C4, 6 ,8, 10); saturated telomer acids x:2 (C6, 8 ,10) and x:3 (C3, 5, 7); unsaturated telomer acids x:2 (C6, 8); HFPO-DA (Gen-X), ADONA, F53-B (Cl 9, 11); diPaPs x:2 (C6, 8) and diSamPaP. For a full list of PFAS analytes and their acronyms and stable-isotope labeled standards, see Table S1.

Sample Collection. Samples of SML and bulk water samples were collected in and around an AFFF-impacted site that had been the site of a previous sampling campaign for foam[19] (Figure 1). Site 1 was west of known PFAS plumes and treated as a background site.-Sites 2-4 on the east side of the lake potentially receive impacts from residential septic tanks and Site 4 is impacted by an unlined former municipal dump.[19] Site 5 was situated on a larger body of fresh water at the outlet of the freshwater body surface. Sites 6 and 7 are positioned on the western shore closest to known PFAS plumes (Figure 1). Sites 8-10 are within a marsh impacted by AFFF from a firefighter training site and landfill leachate. Samples were analyzed only for PFAS, but not dissolved organic carbon.

The three SML techniques evaluated included a 1] large glass plate, 2] a microscope slide, and 3] three microscope slides. At each sampling site, each SML sampling technique was used four times to obtain four replicates, for a total of 12 samples. Glass plates, rubber scrapers, and microscope slides were cleaned with methanol prior to deployment in the field. While used for other SML sampling, screen samplers were not used because they are not suitable for moving surface water bodies in the field and also required the use of methanol in the field to rinse sample off the mesh.

For the glass plate method, a 10 cm x 10 cm glass plate was dipped vertically into the surface water and then slowly pulled up. A single glass plate and rubber scraper were dedicated to a single site and used to obtain multiple replicates within the site. A rubber scraper was used to scrape the adhered water into a 15 mL centrifuge tube. Multiple dips were located within cm distance to obtain a single SML sample (e.g., replicate), but the multiple replicates of SML were obtained within an arm's reach (~ 1m). The dipping process was repeated until a total of 6 mL were collected (4-6 dips were required to obtain a 6 mL sample). The field equipment blank for the large glass plate included dipping a glass plate into a Ziploc® bag filled with deionized water to obtain a volume of 6 mL.

The microscope slide methods utilized single 25 mm x 75 mm glass microscope slides. Microscope slides contained within a 50 mL HDPE centrifuge tube were weighed prior to deployment in the field. For SML sampling, a single glass microscope slide was dipped and withdrawn like the glass plate, but instead of scraping off the adhered water, the whole slide was placed directly into a 50 mL HDPE centrifuge tube. Similarly, for three microscope slides sampling, individual slides were dipped one at a time but then placed together in a single 50 mL HDPE centrifuge tube. All centrifuge tubes containing either one or three slides were weighed back in the laboratory in order to compute the total volume of water collected. For the slides, the field equipment blank consisted of a microscope slide in a centrifuge tube that was taken to the field but not dipped. Whole bottle extractions were performed on the 50 mL centrifuge tubes. Bulk water was obtained at depths of 3 and 30 cm below the surface at each sampling site, using a plastic pipette. For each depth, two 3 mL aliquots were combined into a 15 mL HDPE centrifuge tube. A total of four 6 mL samples were obtained at each of the two depths. Field blanks consisted of 6 mL of deionized water in a 15 mL HDPE centrifuge tubes opened during sampling. Trip blanks (6 mL in 15 mL HDPE centrifuge tubes) were shipped along with the field samples but remained unopened. All samples were shipped on ice overnight to the laboratory and stored frozen until analysis. All equipment, trip, and field blanks gave PFAS that were below limits of detection (LOD).

Sample Preparation. For bulk water and the liquid sample in 50 mL centrifuge tubes that had been obtained by the large glass plate was extracted using a micro liquid-liquid extraction modified after Backe et al. and described previously.[21] To each 6 mL sample, 2.0 g of NaCl, 20 µL of HCl, and 1.5 ng of each of the 33 isotopically labelled (surrogate) standards were added. Samples were extracted in triplicate using a total of 1.5 mL of 10% 2,2,2-trifluoroethanol in ethyl acetate (v/v). The extract was added to a 1.5 mL autosampler vial containing 20 µL of ethylene glycol and blown down under nitrogen, using ethylene glycol as a keeper solvent. The extract was reconstituted with 1.5 ng of M2PFOA and M8PFOS in 10 µL of methanol, 50 µL of DI water, and 70 µL of methanol for a final extract volume of 150 µL. The accuracy and precision of the analysis for 6 mL of SML or bulk water was determined by spiking four replicates of blank groundwater to achieve 500 ng/L concentrations of 50 target and 33 stable isotope labeled surrogates.

After weighing the microscope slides in their 50 mL HDPE centrifuge tubes, microscope slides (one or three) were rinsed with methanol (~ 5mL/slide) prior to withdrawing the slides from their centrifuge tube. Extractions were performed in the original 15 mL centrifuge tube by adding 20 µL of ethylene glycol and 1.5 ng of each of the 33 isotopically labelled (surrogate) standards. The mixture was blown down and then reconstituted with 1.5 ng of M2PFOA and M8PFOS in 10 µL of methanol, 2.3 mg of NaCl, 50 µL of DI water, and 70 µL of methanol for a final extract volume of 150 µL.

To determine the recovery of PFAS from glass slides using only methanol rinsing, n=4 individual glass slides were overspiked with 200 µL (1 slide) or 600 µL (3 slides) of PFAS standards in water (homogenized immediately before spiking) to mimic the volume of water collected in the field. Surrogate PFAS were added to the vial and sample extraction was performed as described above.

Instrument and Data Analysis. All extracts were analyzed by LC-QTOF (X500R; SCIEX, Framingham, MA) in negative mode with 100 µL injections onto a C18 LC system described in the. Calibration curves were weighted 1/x or $1/x^2$ and made with a minimum of 5 points. Solvent blanks and low-end check standards were ran every 10 samples to check for accurate quantitation within the run and instrument contamination.

3.4 RESULTS AND DISCUSSION

SML Sampling Method Performance. Experimentally determining the accuracy of the glass plate sampling method is difficult since it is challenging to control the composition and PFAS concentrations of a SML, even under laboratory conditions. Thus, because SML was removed from the glass plate and the liquid was treated thereafter as a water sample, the accuracy of the glass plate sampling method was assumed equivalent to the analytical extraction method where recoveries for 50 target PFAS ranged from 37-240% and precision ranged from 1.4 to 80% (Table S2). The LOD and LOQs ranged from 0.3 to 29.3 ng/L and from 1.0 to 96.7 ng/L, respectively (Table S2).

One and three microscope slides gave percent recoveries for native target PFAS that fell within 100% ± 30% for 39 and 33 of the 45 target PFAS. For one and three slides, 12 and 6 target PFAS gave recoveries < 70%, respectively (Table S3). Absolute recovery determined as the extracted surrogates, M2PFOA and M8PFOS, was 127% and 111%, and 114% and 115% for one and three slides, respectively. The precision of one and three microscope slides ranged were <20% for target PFAS that gave good recovery (Table S3). Greater handling of three slides may lead to the lower recovery and reduced precision compared to three slides. Microscope slides are limited by the volume of water collected (~200 μL of water per glass microscope slide). Since the microscope slide SML was determined as a methanol dilution, the LOQs were estimated as a factor of X higher than the water extraction method LOD and LOQs (Table S2). For more discussion, see SI.

SML PFAS Composition. Only two target PFAS (PFHpA and PFOA) were found in the SML at Site 1, the background site (Table S6), which is in contrast to foam collected in 2019 that had three PFCAs (130 – 340 ng/L) and PFOS up to 1,500 ng/L.[19] The SML at Sites 2-4 gave one to four individual target PFAS including PFOA, PFNA, PFHpS, PFOS, FOSA, and 6:2 FTS ranging from 2-43 ng/L (Table 1). Site 5 gave no PFAS in the SML >LOQ (Table S6). Sites 1 and 5 were away from the known PFAS plumes. However, Sites 2 and 3 are on the eastern side of the lake with potential impacts from residential septic systems, while Site 4 is located near the mouth of a stream impacted by a former municipal dump (Figure 1). At Sites 2-4, PFAS that were observed in foam (e.g. 5:3 FTCA)[19] were not observed in the SML in the present study. Six PFAS occurred in the SML at Sites 6 and 7, which receive discharge of AFFF-impacted groundwater, with PFOS concentrations reaching 200 ng/L (Table 1). In addition to PFOA, a homologous series of PFSAs (C6-C8) was quantified along with FHxSA, a C6 sulfonamide, and 6:2 FTS. The C6 sulfonamide, FHxSA, was observed at Sites 6-10, which is consistent with its occurrence in foam at these sites,[19] and reports of FHxSA in Canadian surface waters[22] and AFFF-contaminated groundwater.[23] The SML PFAS composition and concentration at Sites 6-7 was significantly lower that what was found in foam collected a year prior to this study that was characterized by 14 PFAS including long chain carboxylates up to C11 with PFOS concentrations ranging up to 97,000 ng/L.[19]

At Sites 8-10, up to 20 PFAS from five classes including homologous series of C4-C12 PFCAs; C6-C10 PFSAs; and C4, C6, and C8 FASAs; 6:2 and 8:2 FTS; and the 5:3 FTCA were quantified at higher concentrations ranging from 9 to 13,000 ng/L (Table 1). Contributions from

ECF (PFCAs, PFSAs, FASAs) and fluorotelomer-based (FTSs, 5:3 FTCA) chemistries are evident from the PFAS classes at these sites. Sites 8-10 were not included in the early foam study; thus, there are no comparative foam data. The landfill leachate indicator,[24-26] 5:3 FTCA, was observed at Sites 9 and 10 which are co-located near where an AFFF plume and landfill discharge to surface water. The 5:3 FTCA was not observed at Site 4, which is farther downstream of a municipal dump discharge.

Concentrations of PFOA were low at Sites 2-7 and branched isomers were not detected. At Sites 8-10, branched isomers comprised 10% of PFOA (data not shown), which is consistent with the foam composition collected in 2018[19] and indicates a telomer contribution to the PFOA found in the SML. However, both PFOS and FHxSA were present at Sites 2-10 with up to 25% branched isomers (data not shown). The isomer data for FHxSA in the SML is consistent with that in foam collected in 2018;[19] however, branched isomers for PFOS in foam were higher and ranged from 41-49%.

SML Sampling Considerations and Limitations. The glass plate method is practical for obtaining larger SML volumes in a reproducible way. During withdrawal of the glass plate (or microscope slides), quicker speeds may thin or stretch the air-water interface, which may decrease the actual air-water interface captured. In addition, if the time allowed for the plate to drain time is short, more bulk water is potentially incorporated, thus potentially diluting the SML sample, resulting in the underestimation of SML concentration.[27, 28] However, controlling the glass plate withdrawal speed on a moving surface and the precisely monitoring the glass plate drain time is challenging in the field. Regardless, given the limitations on the sampling approach reported herein, the estimated SML concentrations are likely underestimated.

Bulk Water. Bulk water was obtained from two different depths, 3 and 30 cm, at each of the 10 sites. Concentrations at 3 and 30 cm were not statistically different at the 95% CI (Figure S1). For this reason, discussion of bulk waters is limited to data from 3 cm (Table 2). For Sites 2-4, a maximum of two PFAS were found at concentrations ranging from 1.2-25 ng/L, while at Sites 6-7 there were three to six PFAS observed in bulk water (Table 2). Unlike PFOS, PFOA was observed in Sites 2-7. Bulk water from Site 7 contained FHxSA at the highest concentration for the PFAS bulk water concentration (41 ng/L) as well as the 6:2 FTS, indicating ECF and fluorotelomer PFAS at this site (Table 2). Bulk water from Sites 8-10 contained the greatest number of PFAS and highest concentrations of all sites.

Enrichment Factors. Enrichment factors were calculated by dividing the SML concentration (Table 1) obtained from the glass plate by the bulk water at 3 cm (Table 2). Enrichment factors were only generated for analytes with quantified values in both the SML and bulk water. In bulk water, because there is no apparent concentration difference between 3 and 30 cm, EFs were calculated using only values from a depth of 3 cm.

Average EFs were calculated for 13 PFAS for sites 8-10 (Figure 2) and ranged from 0.7 (PFHpA, Site 10) to 20 (FOSA, Site 9). Enrichment factors for PFAS from PFBA to PFOA were 1 ± 0.8, but for PFAS after PFOA increases with increasing hydrophobicity (Figure 2). Note that chromatographic retention times were used as a proxy for hydrophobicity and PFAS in Figure 2 are organized by increasing hydrophobicity.[19, 29] Sites 9 and 10, which were co-located, gave higher EFs than for Site 8 (Figure 2) for PFHxS and more hydrophobic PFAS. The lower EFs for PFOS and more hydrophobic PFAS as Site 8 are due to lower SML concentrations (Table 1) and not bulk water concentrations (Table 2). The lower EFs at Site 8, which is down gradient of Sites 9 and 10, may be due to mixing with surface water of a different PFAS composition and has not reached equilibrium with the SML.

The average field-derived EFs for PFOA (1.5) and PFOS (8.5) for Sites 8-10 are consistent with the only two published field studies of PFAS in open water SML. For example, Ju et al. reported PFOS EFs from 2.0 – 109 while PFOA EFs ranged from 1.2-1.8 and were based on eight observations across five sites.[13] Casas et al. reported average EFs less than 3 for PFBS and PFOS and four carboxylates (C6, 8-11) at 17 locations ocean locations near Antarctica.[12] This is the first report of EFs for C4, C5, and C7 PFCAs; C6 and C7 PFSAs; C4, C6, and C8 FASAs; 6:2 FTS; and 5:3 FTCA in the SML.

The EFs in SML (Figure 2) are significantly lower than those reported for field-collected SSAs[14] and foam from the same lake.[19] Field-collected SSAs have EFs in the tens of thousands, even for

PFOA and PFHxS. The EFs of natural foams (maximum 2,800) are also significantly larger than in the SML (10s) of the present study (Figure 2). Foams and SSAs have larger air-water interfaces compared to the SML, thus allowing for more enrichment of PFAS.[30, 31]Foam is generated from the SML, but once formed is further enriched due to drainage of the bulk water. Enrichment of PFAS in SSAs is high because PFAS are enriched by air bubbles rising through the sea surface and bursting into the air.[14]

Branched and linear isomers of PFAS have different hydrophobicities, as evidenced by longer chromatographic retention times for linear isomers on a reverse-phase C18 analytical column.[19, 29] There was no apparent enrichment of branched or linear isomers in the SML on this freshwater lake compared to the bulk water. In contrast, the linear PFOS isomer gave higher EFs in field-collected foam than branched isomers.[19] In laboratory-generated SML using seawater, the linear PFOS isomer was enriched over the branched isomers.[31] The lack of linear isomer enrichment may be due to low salinity conditions of the freshwater.

Air-water Partitioning Coefficients. The field-derived SML and bulk water concentrations provide a unique opportunity to calculate an air-water partitioning coefficients and compare them to those in the literature. The thickness of the SML sampled by glass plates and microscope slides was calculated by Equation 1:

$$\text{SML Thickness (cm)} = \frac{\text{Volume of Water Collected (cm}^3\text{)}}{\text{Surface area of both sides (cm}^2\text{)} * \text{ number of dips}} \qquad \text{Eqn. 1}$$

where the surface area of the plates and slides is the area that is fully submerged in the water.[17] In this study, the surface area of the glass plate was 160 cm^2 (10 cm x 8 cm x 2) and 3,000 mm^2 for the microscope slides (25 mm x 60 mm x 2). The large glass plates were dipped 4-6 times to get 6 mL of sample, resulting in an estimated SML thickness of 63-94 μm sampled. The microscope slides were dipped individually and with ~ 200 μL per dip, resulting in an estimated SML thickness of 63-78 μm. The computed SML thicknesses are consistent with those estimated by glass plates for low-wind conditions.[17]

Field-estimated values of Ki were determined from PFAS concentrations in SML and underlying bulk water (Equation 2).

$$\text{Ki (cm)} = C_{SML}\left(\frac{ng}{L}\right) * \left(\frac{1\ L}{1{,}000\ cm^3}\right) * \left(\frac{0.01\ cm}{1}\right) * \left(\frac{1}{C_{bulk\ (\frac{ng}{cm^3})}}\right)$$

Where C_{SML} is the SML PFAS concentration (ng/L), 0.01 cm is the SML thickness obtained by the glass plate method, and C_{bulk} is the PFAS concentration in the underlying bulk water (ng/cm^3). As an example, at Site 10 the SML concentration for PFOS was 9,900 ng/L (Table 1), the bulk water concentration was 1,100 ng/L (Table 2), and the SML thickness was between 63 and 94 ng/L (Equation 1). The resulting air-water partitioning coefficients ranged from 0.062-0.093 cm (Table 3) and were consistent with values of 0.10 cm from bench-scale experiments using a Freundlich-based model.[7] The good agreement between the field-estimated K_i and laboratory-derived K_i indicates that the SML is potentially in equilibrium with underlying bulk water. Good agreement with laboratory-derived Ki values also indicates that the SML concentrations are due to PFAS partitioning to the 2-D air-water interface and are not equally distributed over the entire SML volume. This study reports the first calculation of an air-water partitioning coefficient for PFOS from data obtained from surface waters (field conditions) and the first report of any value for FOSA (0.085-0.13 cm).

Supporting Information Available

The supporting information contains information about instrumental analysis for LC-MS/MS, QA/QC data, and full field data. This information is available free of charge on the ACS Publications website.

3.5 Acknowledgements

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"Oregon State University in Corvallis, Oregon, is located within the traditional homelands of the Mary's River or Ampinefu Band of Kalapuya. Following the Willamette Valley Treaty of 1855, Kalapuya people were forcibly removed to reservations in Western Oregon. Today, living descendants of these people are a part of the Confederated Tribes of Grand Ronde Community of Oregon (grandronde.org) and the Confederated Tribes of the Siletz Indians (

3.6 References

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Figure 3.1 SML and bulk water sampling sites relative to known PFAS contamination plumes indicated in color (including inset Site 5).

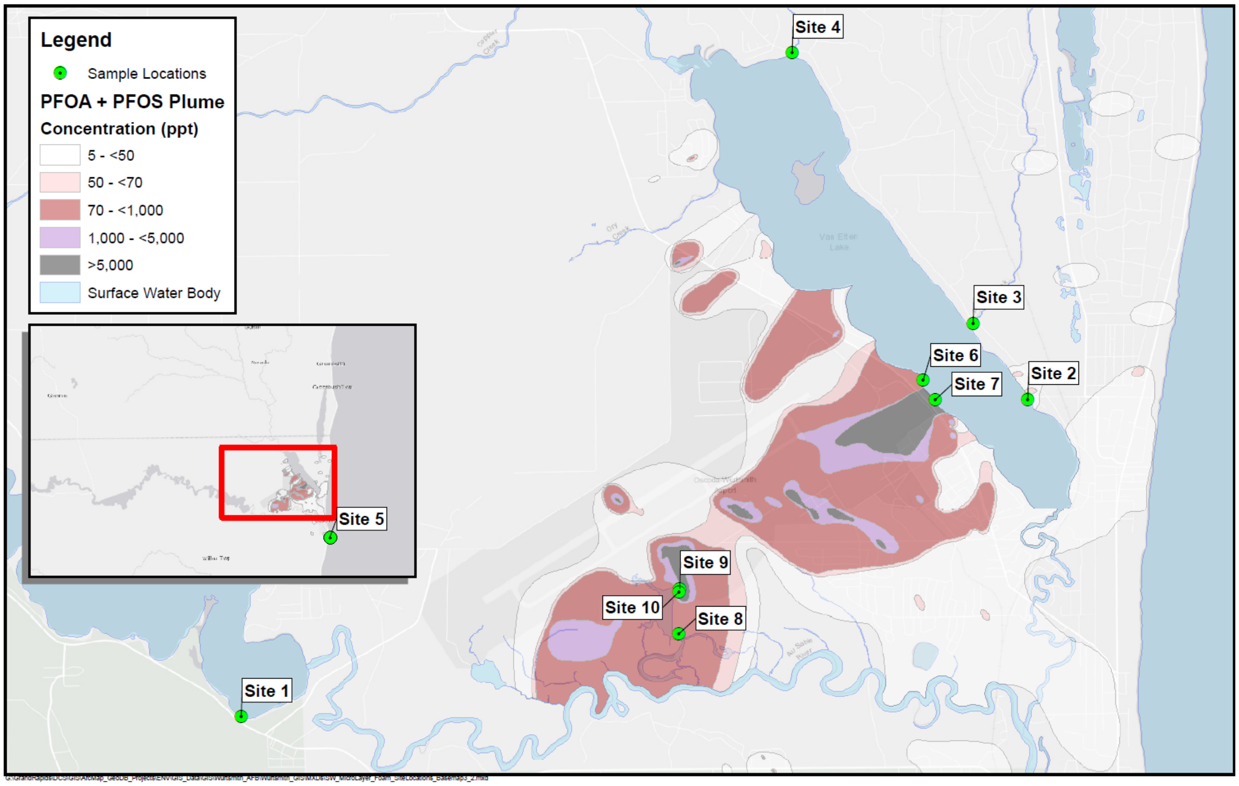

Figure 3.2 Average enrichment factors for analytes across sites 8-10 (error bars = propagated error of relative standard deviation). Analytes on x-axis are ordered by increasing hydrophobicity.

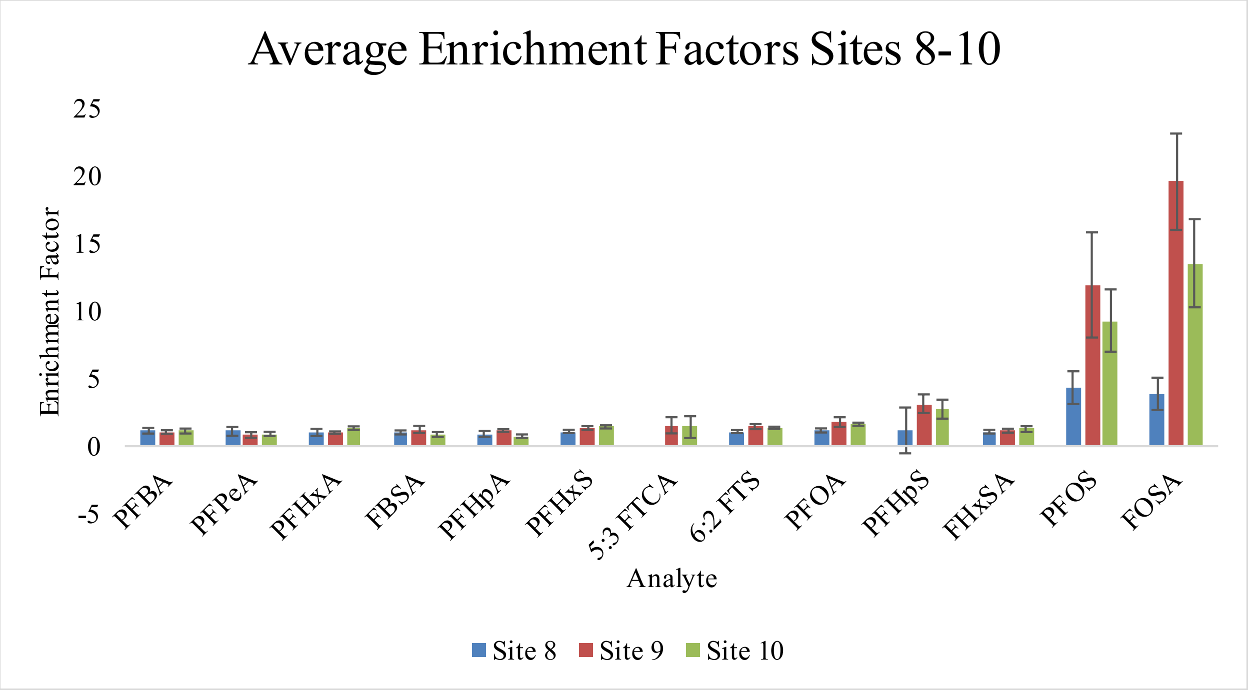

Table 3.1 Average concentrations in the SML from four replicates excluding site 1 and 4 (<LOD) from the glass plate sampling method. For the full data set, see Table S6.

Analyte	**LOC 2**	**LOC 3**	**LOC 4**	**LOC 6**	**LOC 7**	**LOC 8**	**LOC 9**	**LOC 10**
PFBA	<LOD	<LOD	<LOD	<LOD	<LOD	**39**	**30**	**29**
PFPeA	<LOD	<LOD	<LOD	<LOD	<LOD	**81**	**71**	**75**
PFHxA	<LOD	<LOD	<LOD	<LOD	<LOD	**120**	**120**	**120**
PFHpA	<LOD	<LOD	<LOD	**43**	<LOD	**72**	**42**	**42**
PFOA	**5.4**	**4.0**	**4.9**	**11**	**12**	**200**	**230**	**220**
PFNA	<LOD	<LOD	**43**	<LOD	<LOD	**28**	**36**	**27**
PFDA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**22**	**15**
PFUdA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**28**	**13**
PFDoA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**21**	<LOD
PFHxS	<LOD	<LOD	<LOD	**36**	**26**	**260**	**260**	**260**
PFHpS	**1.5**	<LOD	<LOD	**1.5**	**3.0**	**44**	**41**	**34**
PFOS	**34**	<LOD	<LOD	**200**	**200**	**4,200**	**13,000**	**9,900**
PFNS	<LOD	<LOD	<LOD	<LOD	<LOD	**9.3**	**120**	**66**
PFDS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**51**	**21**
FBSA	<LOD	<LOD	<LOD	<LOD	<LOD	**41**	**34**	**24**
FHxSA	<LOD	<LOD	<LOD	**14**	**19**	**430**	**630**	**450**
FOSA	<LOD	<LOD	**6.9**	<LOD	<LOD	**96**	**780**	**440**
6:2 FTS	**14**	<LOD	<LOD	<LOD	**14**	**120**	**160**	**150**
8:2 FTS	<LOD	<LOD	<LOD	<LOD	<LOD	**44**	**210**	**160**
5:3 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**10**	**120**

Table 3.2 Average concentrations in the bulk water (3 cm) from four replicates excluding site 1 and 4 (<LOD) from the glass plate sampling method. For the full data set, see Table S6.

Analyte	**LOC 2**	**LOC 3**	**LOC 4**	**LOC 6**	**LOC 7**	**LOC 8**	**LOC 9**	**LOC 10**
PFBA	<LOD	<LOD	<LOD	<LOD	<LOD	**39**	**30**	**29**
PFPeA	<LOD	<LOD	<LOD	<LOD	<LOD	**81**	**71**	**75**
PFHxA	<LOD	<LOD	<LOD	<LOD	<LOD	**120**	**120**	**120**
PFHpA	<LOD	<LOD	<LOD	**43**	<LOD	**72**	**42**	**42**
PFOA	**5.4**	**4.0**	**4.9**	**11**	**12**	**200**	**230**	**220**
PFNA	<LOD	<LOD	**43**	<LOD	<LOD	**28**	**36**	**27**
PFDA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**22**	**15**
PFUdA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**28**	**13**
PFDoA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**21**	<LOD
PFHxS	<LOD	<LOD	<LOD	**36**	**26**	**260**	**260**	**260**
PFHpS	**1.5**	<LOD	<LOD	**1.5**	**3.0**	**44**	**41**	**34**
PFOS	**34**	<LOD	<LOD	**200**	**199**	**4200**	**13000**	**9900**
PFNS	<LOD	<LOD	<LOD	<LOD	<LOD	**9.3**	**120**	**66**
PFDS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**51**	**21**
FBSA	<LOD	<LOD	<LOD	<LOD	<LOD	**41**	**34**	**24**
FHxSA	<LOD	<LOD	<LOD	**14**	**19**	**430**	**630**	**450**
FOSA	<LOD	<LOD	**6.9**	<LOD	<LOD	**96**	**780**	**440**
6:2 FTS	**14**	<LOD	<LOD	<LOD	**14**	**120**	**160**	**150**
8:2 FTS	<LOD	<LOD	<LOD	<LOD	<LOD	**44**	**210**	**160**
5:3 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**9.7**	**12**

Table 3.3 K_i values (cm) generated from field data, assuming a SML thickness of 63 μm. FOSA was <LOD in the bulk water for site 7 so no K_i value was calculated.

Site	6:2 FTS	PFOS	FOSA
7	0.30 x 10^{-2}	4.0 x 10^{-2}	ND
8	0.68 x 10^{-2}	2.7 x 10^{-2}	2.4 x 10^{-2}
9	0.91 x 10^{-2}	7.5 x 10^{-2}	12 x 10^{-2}
10	0.85 x 10^{-2}	5.9 x 10^{-2}	8.5 x 10^{-2}
Average	0.69 x 10^{-2} cm	5.0 x 10^{-2} cm	7.7 x 10^{-2} cm
%RSD	40%	42%	63%

CHAPTER 4 – PER AND POLYFLUOROALKYL SUBSTANCES IN FIELD-COLLECTED LIGHT NON-AQUEOUS PHASE LIQUIDS

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4.1 ABSTRACT

Per- and polyfluoroalkyl substances (PFAS) and fuels and solvents (e.g., nonaqueous phase liquid or NAPL) likely co-occur at sites where aqueous film forming foams (AFFFs) were used on burning fuel fires or in training where waste fuels and solvents were burned. No published data are currently available on PFAS in field-collected NAPL, whether light nonaqueous phase liquid (LNAPL) from fuels or dense nonaqueous phase liquid from chlorinated solvents. An analytical method was developed for target and suspect PFAS in NAPL along with a simple approach for estimating suspect PFAS concentrations. The validated method was then demonstrated on 17 LNAPL samples collected from five military installations where LNAPL releases date from 10 to 70 years ago. Target and suspect PFAS associated with AFFF of electrofluorination and telomerization origin were quantified in 11 out of the 17 LNAPLs. Perfluoroalkyl sulfonamides with pK_as ~ 6 occur in a higher percentage as their neutral (noncharged) forms gave the highest frequency of detection and the single highest concentration (C6 PFHxSA 67,600 ng/L) of the target PFAS. Suspect sulfonamide derivatives gave even higher estimated concentrations (74,000 ng/L) Perfluorooctane sulfonate (PFOS) occurred at the highest frequency, but not at the highest concentrations (110-110,000 ng/L). Given the PFAS composition in field-collected LNAPL, residual LNAPL at field sites may act as long-term sources of PFAS requiring additional *ex-situ* treatment.

4.2 INTRODUCTION

Aqueous film forming foams (AFFF) contains high concentrations (g/L) of per- and polyfluoroalkyl substances (PFAS) and are used to combat hydrocarbon-fueled fires.[1,2] As a result of widespread use of AFFF, PFAS are detected in soil and groundwater at military sites worldwide.[3-7] Fire-fighter training areas where AFFF were repeatedly released for training purposes and AFFF storage has resulted in hundreds of sites with PFAS contamination on US military installations.[8] In addition, petroleum products (e.g., diesel, waste oil, lubricants, gasoline) and chlorinated solvents such as trichloroethylene (TCE), were co-released with AFFF during fire-fighting exercises and waste disposal practices.[9,10] In many cases, sufficient quantities of petroleum products or chlorinated solvents were released during emergency response or firefighter training activities to result in the presence of light non-aqueous phase liquids (LNAPL) from fuels and dense non-aqueous phase liquids from solvents. Given the widespread use and larger quantities of flammable liquids for training, LNAPL is more prevalent in fire training areas. Given the challenges in treating PFAS, LNAPL containing PFAS recovered from the subsurface may require advanced treatment.

Laboratory studies indicate the potential for PFAS association with NAPL. For example, trichloroethylene (TCE) acted as a sorbent phase for PFAS in soil with low organic carbon content[10] and the number of fluorinated carbons impacts the degree of PFAS partitioning into the TCE.[11] Chen et al. (2009) reported increased loss of PFOS from solution onto oil-contaminated soil compared to soil without oil.[12] Others describe PFAS partitioning into TCE and decane[13] and to the water:NAPL interface in laboratory studies.[14-16] Kostarelos et. al. (2020) observed the formation of viscous, stable, microemulsions when mixing application-strength AFFF (3% in water) and Jet Fuel A.[17] The microemulsion that formed *in-situ* in sand columns served as a sink for up to 70% of the injected PFAS.[17] While there is ample evidence from laboratory studies that subsurface NAPL may act as a sink for PFAS, to the best of our knowledge, there are no data on the occurrence of PFAS in field-collected NAPL samples.

The dearth of data for PFAS and NAPL is likely due to the limited number of analytical methods. A suite of C4-C12 perfluoroalkyl carboxylates (PFCAs) and C4, 6, 8, and 10 perfluoroalkyl sulfonates (PFSAs) in automotive lubricants were extracted with a mixture of methanol and dichloromethane.[18] Others diluted lubricants in methanol and found fluorotelomer alcohols, but no PFCAs.[19] There are no reports for PFAS other than PFCAs and PFSAs in NAPL, yet many suspect PFAS are identified in AFFF.[1,20,21]

Assigning concentrations to suspect PFAS, which by definition do not have analytical-grade or stable-isotope labelled standards, is challenging. Strategies that employ ‘one-to-one’ matching assume an equal molar response between a suspect and a ‘borrowed’ target PFAS and its mass-labelled surrogate standard.[22,23] However, the number of suspect PFAS is growing rapidly{US National Institutes of Standards and Technology, 2021 #1742;Ruyle, 2021 #1737} and is outpacing the production of PFAS standards. Protocols for borrowing are complex and likely to lead to inconsistencies between laboratories and over time. Laboratories may also purchase different target and surrogate PFAS, limiting their ability to utilize published matching schemes. If a borrowed surrogate does not extract in a particular matrix, it cannot be used to quantify a suspect. For a suspect PFAS that ‘borrows’ a target PFAS (e.g., PFOS), which may occur in a sample at very high concentration, the borrowed target suppresses its mass labelled surrogate, which then leads to a potentially large over estimation of the suspect concentration. In addition, matching suspects to target PFAS requires a confirmed suspect structure, which isn’t always available. For these reasons, a simple, unifying alternative strategy for estimating suspect concentrations is needed.

The objective of this research was to develop an analytical method to quantify target PFAS and suspect PFAS in LNAPL recovered from groundwater wells at U.S. military sites. A micro liquid-liquid extraction method was combined with liquid chromatography quadrupole time-of-flight (QTOF) mass spectrometry to quantify 50 target PFAS and up to 800 suspect PFAS using a simple approach for estimating suspect concentrations. The validated method was then applied to 17 field-collected LNAPL samples.

4.3 MATERIALS AND METHODS

Materials. Methanol, water, and ethyl acetate used were HPLC grade from Fisher Scientific (Hampton, NH). All target and mass-labeled surrogate and internal standards (Table S1) were purchased from Wellington Laboratories (Ontario, Canada). Commercially available Jet Fuel A, was purchased from Corvallis Municipal Airport (Corvallis, OR) and was used for method development. Glass bottles (120 mL, VWR, Radnor, PA) were used for the collection, transport, and storage of LNAPL samples.

LNAPL Sample Collection. Individual sampling locations at five military installations were selected by site managers based upon previous detections of PFAS and records of LNAPL recovery. At these sites, LNAPL thicknesses ranged from 0.07 – 0.8 m and depth to LNAPL was < 3 m. The LNAPL composition included jet fuel, diesel, and other liquids and dates of last LNAPL release ranged from 1950 – 2010 (Table 1). LNAPL was collected in 60 mL glass amber bottles without polytetrafluoroethylene-lined lids. Trip and field blanks consisted of 50:50 water and Jet Fuel A that were shipped to field sites. The field blank was opened on-site during the time of sampling, while the trip blank remained closed during sampling and shipping. Water was added to the blank since no more than 30 mL LNAPL can be shipped to meet U.S.

Department of Transportation shipping regulations. All LNAPL samples were stored at room temperature upon receipt.

LNAPL Sample Preparation. A 10 mL aliquot of LNAPL was centrifuged at approximately 2000 g for 5 min. A 1.5 mL aliquot was then transferred to a 15 mL polypropylene centrifuge tube containing 10 μL of a mixture of 27 stable-isotope labeled surrogate standards (e.g., 30 μg/L of each surrogate standard, Table S1) and 10 μL ethyl acetate. Three rounds of extraction were performed by adding decreasing volumes of methanol (500, 375, and 325 μL), vortex mixing for 30 s, and then transferring the upper phase (e.g., 333 μL) to an autosampler vial for total extract volume of 1,000 μL. Twenty μL of ethylene glycol were added as a keeper solvent and then the mixture was blown down to 20 μL. The extract was reconstituted in 70 μL methanol and 50 μL 0.68 M sodium chloride in deionized water for a total volume of 140 μL. The final extract was transferred to a conical vial and spiked with 10 μL of 30 μg/L of two mass-labelled internal standards (M2PFOA and M8PFOS, see Supplemental Information (SI) Tables S1 and S2 for full list of acronyms).

Liquid Chromatography Quadrupole Time-of-Flight. Analyses were performed on an Agilent 1260 (Santa Clara, CA) liquid chromatograph interfaced with a SCIEX X500R QToF-MS/MS system (Framingham, MA) that was operated in negative electrospray ionization (ESI-) mode. Extracts were not analyzed in positive mode. A 90 μL aliquot of each LNAPL extract was injected onto an Agilent XDB-C18 (4.6 mm x 12.5 mm x 5 μm) guard and analytical column (4.6 x 75 mm x 5 μm). Data were collected in negative mode only, under SWATH® data-independent acquisition for both ToF-MS and MS/MS modes. Only perfluoro butanoic acid (PFBA) and its mass labeled surrogate (MPFBA) were analyzed in MS/MS mode to reduce background. Data acquisition was only performed in negative mode because under positive mode, high background was observed. Thus, the number of suspect PFAS is likely underestimated since many suspects are detected and give higher abundances in positive mode.[21,22]

Quantitative Analysis. All PFAS names, acronyms, neutral molecular formula, and surrogate standard are listed in Table S1. Target PFAS concentrations were determined by internal standard calibration and 1/x weighted linear regression over a 7-point calibration curve. The calibration curve spanned from 200-100,000 ng/L for all analytes except PFTrDA, PFDoS, all fluorotelomers, and HFPO-DA (up to 50,000 ng/L), and R^2 values were typically 0.99 or greater. Calibration standards (200 and 500 ng/L) were analyzed every 10 samples and were required to fall within 70-130% for the majority of target PFAS to ensure that sensitivity and calibration were maintained throughout analysis.

Criteria regarding mass errors, isotope ratios, and library matching for target and suspect screening are found in Nickerson et. al.[22] Briefly, target PFAS concentrations were only reported when they were at least three times higher than all instrument and method blanks (blank Jet Fuel A spiked with surrogates and internal standards) concentrations. Target analyte peaks were only considered when retention times were within 30 s of analytical standards, mass error <10 ppm from the nominal isotopic m/z (XIC window 0.01 Da), and the peak signal-to-noise ratio >10.

Suspect Screening and Semi-Quantification. Data from the LC-QToF were screened for the compounds on a NIST list,[24] which were assumed to be present as the deprotonated molecular ion ([M − H]−) in ESI−, to identify suspect matches. Suspect that gave library and NIST list matches were reported (Level 2b).[25] Suspect matches were reported only if the area counts were three times higher than all instrument and method blank area counts.

The new approach for semi-quantification of suspects consists of computing the average area counts for all target PFAS and surrogates for each point on a single ‘PFAS’ calibration curve. The average area count across all mass-labelled surrogates is then calculated. Response factors are generated by ratioing the average target area count to the average mass-labelled surrogate area count for each point in the calibration curve. Response factors are then plotted against target PFAS concentrations and fitted to a 1/x weighted linear model. This single linear model is then used as the ‘PFAS’ calibration curve to estimate the concentration of each suspect PFAS. To calculate concentrations from the curve, the area counts of the mass-labelled surrogates in a sample are averaged to form the denominator and the area count of the suspect analyte is placed in the numerator to generate a response factor that corresponds to the estimated suspect PFAS concentration. An example calculation that illustrates how the PFAS Curve is constructed and how a suspect concentration is determined appears as an excel file as Supporting Information. It is important to note that sulfonate-containing PFAS (e.g., PFSAs, Cl-PFOS, PFEtCHxS, 9Cl-PF2ONS, and 11 Cl-PF3OUdS, see SI for full list of acronyms) are excluded because they give significantly higher response factors than other classes of target PFAS (Figure S1), yet few suspect PFAS are perfluorinated sulfonates.[24] As such, PFSAs are not representative of most suspect PFASs and, thus, excluded from the 'PFAS' curve. For purposes of comparison, the semi-quantitative approach based on the 'PFAS Curve' was applied to a 3M AFFF, with a composition previously determined by a one-to-one matching approach.[22,26] For details on the agreement, see the SI.

The limit of detection (LOD) and limit of quantitation (LOQ) are calculated using the same procedure for targets outlined in Vial and Jardy,[27] except the average area counts of all target PFAS for each of the 7 points are used in the regression analysis. The example excel file in the SI contains information on how to use target PFAS raw area counts to compute the LOD using the method described by Vial and Jardy.

Quality Control. Whole method blanks consisting of commercial Jet Fuel A (previously determined to be blank) were extracted as described above. All blanks (field blank, trip blank, and whole method blanks) gave PFAS below the instrumental LOD. One LNAPL sample (no. 9) was analyzed as four replicates as a measure of whole method precision in a field-collected LNAPL. At the time of analysis, concentrations of PFBA were 70 ng/L in the process blank. Trip and field blanks and LNAPL gave values at or near this background value so samples did not exceed this value, therefore values for PFBA are not reported for field-collected LNAPL.

Method Performance. Spike and recovery experiments were used to determine method accuracy and precision for target PFAS. Accuracy, expressed as percent recovery, and precision, expressed as relative standard deviation, were obtained from four replicate samples of Jet Fuel A that were overspiked with 50 target PFAS (Table S2) to give a final concentration of 500 ng/L in blank Jet Fuel A. The LOD and LOQ were determined in accordance with methods described in Vial and Jardy (see SI for details).[27]

4.4 RESULTS AND DISCUSSION

Whole Method Accuracy, Precision, LOD/LOQ. Whole method accuracy for target PFAS, as indicated by the percent recovery, fell within 70-130%, with some exceptions including long-chain PFAS (e.g., C10 and C12 PFSAS, 11PF3OUdS, and diSAmPAP; Table S2) and some that lacked a matched surrogate (denoted with * in Table S2). Comparable recovery is reported for nine PFCAs and four PFSAs from lubricants (84.9 – 121%).[18] N-Methyl (MeFOSA) and N-ethyl perfluorooctane (EtFOSA) sulfonamide targets did not extract into methanol (0% recovery) and n:3 fluorotelomer carboxylic acids (FTCAs) exhibited very low recovery (<30%). Poor extraction recovery by methanol is attributed to greater solubility of the neutral sulfonamide and n:3 FTCA forms in LNAPL.

Precision, as indicated by percent relative standard deviation (% RSD), typically ranged from 1-20% (Table S2). Target PFAS that exhibited poor precision (> 20%) was observed for targets poor recovery. The average absolute recovery of the two surrogate standards from LNAPL was 70.4 ± 18.6 and 69.1 ± 17.3% for M4PFOA and MPFOS, respectively (Table S2). For more information on the accuracy and precision for all the target PFAS, see the SI. Whole method LOQs for target PFAS ranged from 73 to 302 ng/L (Table S2).

Semi-Quantification of Suspect PFAS. Target and suspects were quantified in a 3M AFFF previously characterized by ^{19}F-NMR and LC-QToF.[26] Compared to Hao et al., the total fluorine from this study accounted for 77% (542 mmol F/L) of the total fluorine by ^{19}F-NMR (700 mmol F/L).[26] Potential contributions from volatiles and any unidentified non-target PFAS would be included in total fluorine concentration determined by ^{19}F-NMR, but are not captured by target and suspect screening by LC-QTOF. See SI for a discussion on agreement with Hao et al. In the case of LNAPL, MeFOSA and EtFOSA are not extracted by methanol, thus the one-to-one matching approach.[22] could not be used for these samples. The 'PFAS Curve' offers a standardized way of reporting estimates of suspect concentrations that is reproducible across different matrices and extraction procedures. This approach can be used for positive mode detection where the few target PFAS detected in positive mode (no surrogates are commercially available yet) can be used to construct a positive-mode 'PFAS' curve. As target and their surrogate PFAS become available commercially, they can be added to create 'PFAS Curves' for used in estimating suspect PFAS detected in positive and negative mode.

Method Demonstration on Field-Collected LNAPL. Target and suspect PFAS from electrochemical fluorination (ECF) and fluorotelomer chemistry were detected in 11 out 17 LNAPLs. The greatest frequency of an individual PFAS was for PFOS (9 out of 11 samples), followed by the C6 perfluoroalkyl sulfonamide (PFHxSA) (8 out of 11 samples; Table 2). Overall, target PFAS made up the major fraction (>80%) of PFAS in LNAPL, with the exception of LNAPL 4 and 9 where suspect PFAS comprised 90% of the PFAS quantified (Table 2; Table 3). Trends with PFAS chain length are not readily apparent. However, long-chain PFAS are likely underrepresented in number and concentrations since they do not extract well from LNAPL into methanol.

Classes of target PFAS produced by ECF, including PFSAs, perfluoroalkyl sulfonamides and acetic acids, as well as four suspects including perfluoroalkyl sulfinates (Table 2) made up the majority of PFAS detected in LNAPL (Table 2). All of the detected target and suspect ECF-based PFAS (Table 2 and Table 3) are associated with AFFF,[26,28] which is consistent with known AFFF impacts, including firefighter training areas and aircraft maintenance, at the four out of the five field sites (the nature of the AFFF release is unknown for Site 2) where the LNAPL were collected. The PFOS quantified in LNAPL was 76% linear and 24% branched, which is similar to that of commercial 3M AFFFs.[29,30]

Perfluoroalkyl sulfonamides made up the largest fraction in six out of 11 LNAPLs (Table 2). However, sulfonamides make up only a small fraction of 3M AFFF.[26] Thus, higher concentrations of sulfonamides in LNAPL compared to PFSAs is not consistent with the reported composition of 3M AFFFs. Sulfonamides have a higher pKa (~6.2)[31] than PFSAs and PFCAs[32] such that a greater fraction of sulfonamides may be in their neutral form at environmental groundwater pHs and, thus, may partition more readily into LNAPL. Alternatively, precursors to sulfonamides may have undergone significant transformation to form sulfonamides,[7,33] thereby increasing sulfonamide concentrations, prior to partitioning into the

LNAPL. The four ECF-based suspects with library matches (Level 2b; Table 2 and Table 3), are C5- C6 zwitterions comprised of branched and linear isomers, which are also reported in 3M AFFFs.[26,28,34,35]

Members of the PFCA class were observed in only five of 11 LNAPL samples, with PFOA occurring at the third highest frequency of PFAS classes, but at significantly lower concentrations compared to ECF-based PFSAs and the sulfonamides (Table 2). The average percent PFOA isomer was 97% in LNAPL, which is greater than that of PFOS and indicates that fluorotelomer precursor degradation likely contributed to the observed PFCAs in LNAPL.[36] Fluorotelomer sulfonates were the third most detected class, but they and four fluorotelomer-based suspects made up only a minor fraction (<5%) of the PFAS, with the exception of LNAPL 4 and 17 (Table 2). The four fluorotelomer-based suspects (Table 3) are anionic and are found in fluorotelomer-based AFFFs at mg/L levels, but are not major (g/L) components.[1,26,34,35]

4.5 Implications

The concentration and composition of target and suspect PFAS in field-collected LNAPL indicates that LNAPL may serve as a long-term source of PFAS. It is not known if PFAS were co-released or if co-mingling occurred after AFFF was released in areas with LNAPL. Sites that remain impacted by LNAPL require more thorough characterization to gain a better understanding of the PFAS mass associated with the LNAPL present. Further, LNAPL containing PFAS recovered from active petroleum contamination remediation sites may require special treatment prior to disposal. The potential for additional treatment and limitations on the ultimate disposition of PFAS-impacted LNAPL as a waste product will evolve in the future as the US Environmental Protection Agency pursues hazardous substance designation under their October 2021 PFAS Strategic Roadmap.[37] Determination of partition coefficients for a broader array of PFAS is needed for a better understanding of which PFAS structural properties, including chain length, and headgroup, and pKa impact partitioning into LNAPL. Finally, the semi-quantitation technique (PFAS curve) used to estimate suspect PFAS concentrations is a promising technique for standardizing the approach to reporting suspect concentrations and the number of suspects continues to raise while the number of PFAS standards remain limited.

4.6 ACKNOWLEDGMENTS

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Table 4.1 – Number of military installations and wells sampled along with the limited information available on fuel (LNAPL) type and year(s) released.

Military Installation: Sample #	**AFFF-Related Activity**	**Fuel Type**	**LNAPL Release Year(s)**
1: 1,2	FFTA	Petroleum	1950-1960
1: 3,4	Aircraft maintenance, FFTA	Diesel	1984
1: 5	Aircraft maintenance	Jet Fuel 5	1960s, 1979, 1981, 2010
1: 6	unknown	Petroleum	unknown
2: 7	Not identified	Jet Fuel 5	1982, 1996
3: 8	unknown	No. 2 Fuel Oil	1996
4: 9,10	unknown	Diesel, No.5/No.6 Oil	2012
2: 11-14	Not identified	Jet Fuel 5	1982, 1996
5: 15-17	unknown	Jet Fuel 5, naval special fuel oil, diesel fuel marine	1980

FFTA = firefighter training area

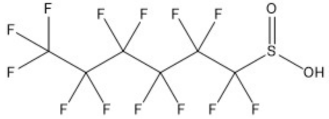
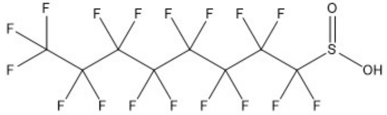
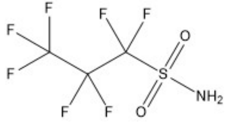
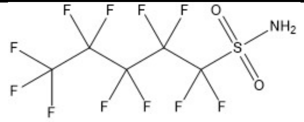
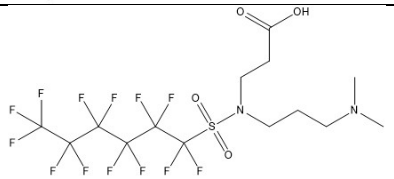
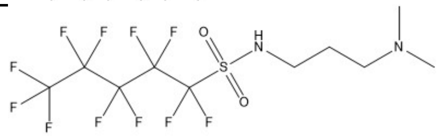
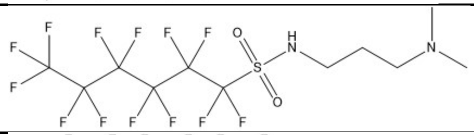
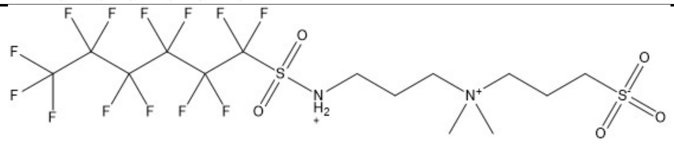
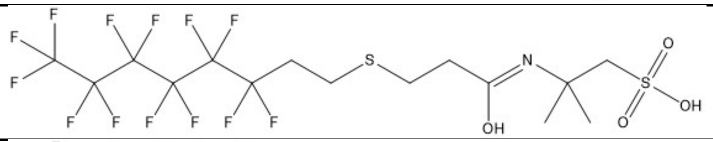
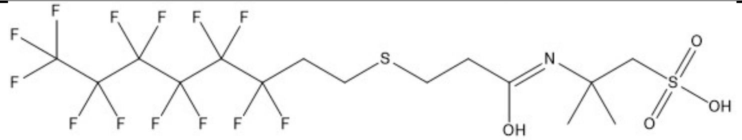
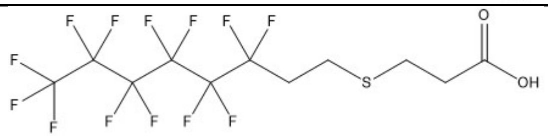
Table 4.2 Concentrations (ng/L) of target and suspect (S) PFAS in field-collected LNAPL samples. LNAPL samples 5,7,11,15, and 16 were <LOQ or <LOD (Table S2).

	PFAS	**1**	**2**	**3**	**4**	**6**	**8**	**9**	**10**	**12**	**14**	**17**
ECF	PFHxS	**204**	<LOQ	**91**	<LOQ	124	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	PFOS	**11100**	<LOQ	**3180**	**262**	**3990**	**1430**	**379**	**2660**	<LOQ	**110**	**1020**
	PFHxSi (S)	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**3500**	<LOD	<LOD	<LOQ	<LOD
	PFOSi (S)	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**630**	<LOD	<LOD	<LOD	<LOD
	FPrSA (S)	<LOQ	<LOD	<LOD	<LOD	**420**	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	FBSA	**981**	<LOD	**1770**	<LOD	**3040**	<LOD	<LOQ	<LOQ	<LOD	<LOD	<LOD
	FPeSA (S)	**1900**	<LOD	<LOD	<LOD	**3400**	<LOD	**250**	**1700**	<LOD	<LOQ	<LOD
	FHxSA	**39100**	<LOQ	**67600**	<LOQ	**55200**	**546**	**6830**	**16900**	**206**	**1490**	<LOD
	FOSA	<LOQ	<LOD	**2500**	<LOQ	**2040**	<LOD	**1490**	**1670**	**104**	<LOD	<LOD
	AmPr-FHxSA-PrA (S)	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**1000**	<LOD	<LOD	<LOD	<LOD
	AmPr-FPeSA (S)	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**1900**	<LOD	<LOD	<LOD	<LOD
	AmPr-FHxSA (S)	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**74000**	<LOD	<LOD	**400**	<LOD
	SPrAmPr-FHxSA (S)	<LOD	<LOD	<LOD	<LOD	**810**	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	PFHxA	<LOQ	<LOQ	<LOD	**152**	<LOQ	<LOD	<LOQ	<LOQ	<LOD	<LOD	<LOQ
	PFHpA	<LOQ	<LOQ	<LOD	**1010**	<LOQ	<LOD	<LOQ	<LOD	<LOD	<LOD	<LOQ
	PFOA	**457**	<LOQ	**106**	<LOQ	**304**	<LOQ	<LOQ	<LOQ	<LOD	<LOD	**100**
	PFDA	**116**	<LOD	<LOQ	<LOQ	<LOQ	<LOD	<LOQ	<LOQ	<LOD	<LOD	<LOQ
Fluorotelomer	6:2 FTS	<LOQ	**1640**	<LOD	**6040**	<LOQ	<LOQ	**321**	**349**	<LOD	<LOD	**1130**
	8:2 FTS	**488**	<LOQ	<LOD	**248**	<LOQ	<LOD	**366**	**587**	<LOD	<LOD	**712**
	10:2 FTS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	**141**	<LOD	<LOD	<LOQ
	6:2 UFTCA	<LOD	<LOQ	<LOD	**5640**	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	6:2 FTTh-PrAd-DiMeEtS (S)	<LOD	<LOD	<LOD	**3000**	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	6:2 FTThPrA (S)	<LOD	<LOD	<LOD	**160000**	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	8:2 FTThA (S)	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**1100**	<LOD	<LOD	<LOD	<LOD

[1] See Table S3 for data on all 17 LNAPL samples.

Table 4.3 Electrofluorination (ECF)- and fluorotelomer (FT)-based suspect structures (Level 2b).

Structure

Suspect	Structure	Reports occurence in AFFF
PFHxSi (ECF)		21
PFOSi (ECF)		38[a]
FPrSA (ECF)		21
FPeSA (ECF)		21
AmPr-FHxSA-PrA (ECF)		39
AmPr-FPeSA (ECF)		35
AmPr-FHxSA (ECF)		21
SPrAmPr-FHxSA (ECF)		21
6:2 FTTh-PrAd-DiMeEtS (FT)		1,35,39
6:2 FTThPrA-FT		39
8:2 FTThA-FT		39

[a] not reported in AFFF but in degradation pathway of ECF-based N-ethyl sulfonamido ethanol.

Chapter 5 – Conclusion

Providing insights into PFAS enrichment in environmental air-water interfaces allows for a better understanding of the fate and behavior of PFAS in the environment. An understanding of PFAS concentrations in NAPL near AFFF-impacted sites will inform remediation techniques and site assessment methods.

In Chapter 2, the enrichment of PFAS in naturally occurring foams was assessed. Reported sightings of foam near PFAS impacted sites had been reported in local news reports, but no published measurements for PFAS in foam existed, nor was it known how naturally occurring DOC might contribute to foam formation. The information in Chapter 2 is the first report of an analytical method for quantifying PFAS concentrations in naturally occurring foams and the first to attribute foam formation to the natural DOC rather than to PFAS. Enrichment of PFAS in the foam was up to 2,800-fold for PFOS, compared to the PFOS concentration of underlying bulk water. Enrichment was correlated with hydrophobicity, and for specific PFAS, the more hydrophobic linear isomer was more enriched than the branched isomers. Of the measured DOC, PFAS concentrations contributed to <0.1%, indicating that DOC as the overall driver of foaming. Foam and bulk water were further characterized by ^{1}H NMR, which showed a distinct DOC profile in the foam compared to the underlying bulk water. Exposure estimates indicated foam to be a potential route of exposure for PFAS to humans. Calculations indicated a risk to populations through recreational contact with PFAS-containing foam, which is consistent with local ordinances that warned against exposure to foam. Finally, foam should be avoided during surface water sampling to ensure that the measured concentrations for bulk water are not biased high.

In Chapter 3, methods for sampling the SML for PFAS were evaluated and the data was compared to measurements of the air-water partition coefficient. Field data for the SML were published previously, but this study included more PFASs and had the explicit goal of evaluating various sampling techniques for collecting SML containing PFAS. The data provided insights into sampling techniques and ultimately a glass plate for SML sampling was recommended. A potential low bias in SML concentrations may have resulted due to the use of nonideal withdrawal speeds and drainage times under field conditions. Enrichment of PFAS in the SML compared to the bulk water was significantly smaller than that of foam and sea spray aerosols. The SML has a much smaller surface-to-volume ratio compared to sea spray aerosols and foam, which leads to lower measured PFAS concentrations in the SML. Field data were used to calculate air-water partitioning coefficients (K_i) for select PFAS and were then compared to laboratory-generated values. The field data for PFAS concentrations in the SML and underlying bulk water were used to estimate field-derived K_i values. The field-derived values were consistent with laboratory derived values fit with a Freundlich isotherm. Good agreement indicates that the Freundlich model is likely treatment of surface tension data than the Langmuir model, which underestimates K_i values.

In Chapter 4, a micro liquid-liquid extraction method was developed to analyze PFAS in LNAPL. The matrix of LNAPL is a complex matrix that creates analytical challenges. Characterizing PFAS in LNAPL was of interest since there is often a co-occurrence of PFAS and LNAPL at sites impacted by AFFF. Application of the analytical method revealed a mix of ECF- and fluorotelomer-based chemistries in 17 field-collected LNAPL samples. The extraction method was also accompanied by a novel quantitation method to estimate concentrations of PFAS that lack authentic analytical standards. The suspect semi-quantification method was developed to harmonize the approach to estimating suspect PFAS concentrations across many matrices, especially for those difficult to work with, such as LNAPL. The semi-quantification method gave good agreement with another more detailed and time-consuming suspect semi-quantitation method. The new semi-quantification method is simpler, easier to implement, and is adaptable as more new PFAS are discovered and as additional authentic analytical standards become commercially available.

Future research needs for surface-water foams include the need to developing an analytical method to quantify hydrocarbon surfactants, which are also present in AFFF-impacted sites and likely in foam and the SML. Further characterization of the overall DOC, beyond ^{1}H-NMR, would offer insight into chemical nature of the DOC that promotes foaming. Particulate matter, in both foam and the SML, should be evaluated for its role in PFAS retention and enrichment. Future research on the SML should include quantifying the enrichment of DOC in the SML. In-depth geochemical characterization of the SML and underlying water, including salinity, turbidity, and pH, is needed for sites that give K_i values that do not appear to be at equilibrium.

The SML data resulting in the first report of a K_i value for FOSA, from either a field or laboratory measurement. A laboratory measurement of K_i for FOSA is now needed to support the field data. The analytical method for analyzing PFAS in LNAPL should be optimized for improved performance for long-chained PFAS and for PFAS detected in positive mode LC-QToF. The PFAS composition of LNAPLs should be further interpreted with respect to field site history, the nature of the LNAPL (e.g., jet fuel, diesel fuel, etc), and sample collection locations (e.g., depth to water and distance downgradient of fire-fighter training areas). The new semi-quantification curve developed for estimating suspect PFAS concentrations should be further validated on more AFFFs characterized by ^{19}F-NMR. Good agreement between total fluorine and the total PFAS concentrations estimated by target and suspect quantification strategies would further strengthen the value of the new semi-quantification approach.

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Appendix A – Chapter 2 Supplemental Information

Materials and Methods

Reagents. For LC-MS/MS analysis HPLC grade water (>99%, high purity, Burdick and Jackson brand), hydrochloric acid (BDH Chemicals), and ammonium acetate (regent grade, Macrom Chemicals) were purchased from VWR (Radnor, PA). Ethyl acetate (99.9%, reagent grade), and 2,2,2-Trifluoroethanol (99%, Fluka Analytical) were purchased from Sigma Aldrich (St. Louis, MO). Methanol (>99%, LC/MS grade) was purchased from Fisher Scientific (Hampton, NH). Sodium chloride was purchased from Mallinckrodt Chemical (> 99%).

Quality Control. Foam 6 and Bulk Water 2 were treated in replicate (n=4) to calculate a %RSD as an indication of precision for naturally occurring PFAS (not spiked). A single aliquot of Foam 7 and Bulk Water 6 were overspiked with 50 PFAS native standards at 500 ng/L and 1.5 ng of each isotopically-labeled standard prior to extraction and spiked 0.75 ng of M2PFOA and M8PFOS just prior to analysis. A foam method blank was performed by carrying 800 µL of DI water through the dilution and centrifugation process while a bulk water method blank was performed by extracting 6 mL of deionized water as described. Both blanks were spiked with 1.5 ng of each isotopically-labeled standard prior to extraction and spiked 0.75 ng of M2PFOA and M8PFOS just prior to analysis. Both foam and bulk water method blanks gave no PFAS greater than the LOD.

PFAS Analysis by Liquid Chromatography Quadrupole Time of Flight. Chromatographic separations were achieved using an Agilent 1260 HPLC (Santa Clara, CA) and 2 Zorbax NH2 guard columns (4.6 x 12.5 mm, 5 µm; Agilent), 1 Zorbax SIL guard column (4.6 x 12.5 mm, 5 µm; Agilent), and a Zorbax Eclipse Plus analytical column (4.6 x 50 mm, 1.8µm; Agilent) as modified after Backe et al.[1] The aqueous mobile phase (A) was 3% v/v HPLC-grade methanol in HPLC-grade water and the organic mobile phase (B) was 10 mM ammonium acetate (Fisher Scientific) in HPLC-grade methanol.

A SCIEX X500R QToF-MS/MS system (Framingham, MA) was operated in negative mode electrospray ionization (ESI-) mode. Data were collected under SWATH® data-independent acquisition for both TOF-MS and MS/MS modes. PFBA and MPFBA were analyzed in MS/MS mode to reduce background. Over the entirety of the data acquisition period, precursor ion data (TOF-MS) were collected over a m/z range of 100 Daltons (Da; TOF start mass) to 1250 Da (TOF stop). The accumulation time was 200 ms and the ion spray voltage was -4500 V. The source and gas parameters included: a source temperature of 550 ^{o}C, ion source gasses at 60 psi, curtain gas at 35 psi, and collision gas at 10 psi. The declustering potential was -20 V (with 0 V spread) and the collision energy was -5 V (with 0 V spread). Product ion scan (TOF-MS/MS) data were collected for a m/z range from 50 Da (TOF start mass) to 1200 Da. The accumulation time for each SWATH® window was 50 ms.

PFAS Exposure Assessment. Preliminary estimates of exposure and risk were estimated for children and adults incidentally ingesting foam and surface water while playing or swimming in the lake. To estimate exposure, the concentrations of ΣPFAS in the surface water were multiplied by the ingestion rate, bioavailability, and exposure factor then divided by body weight. Individual PFAS that were <LOD in all foam or bulk water samples were not included in this assessment. For purposes of the exposure and risk assessment, concentrations below the LOQ were included as reported by the instrument (data not shown) and those below the LOD were estimated as the LOD/sqrt(2). Geometric mean (GM) and maximum ΣPFAS were multiplied by GM and maximum ingestion rates, respectively, to yield central tendency and upper bound exposure estimates. We applied ingestion rates from the EPA Child-Specific Exposure Factors Handbook,[2] and assumed playing or swimming in the lake for 2 hours/day. Ingestion rates were not available for children <6 years of age, so the next available age range (6 to <11) was applied for younger children. A 19:1 ratio was assumed for foam to collapsed liquid and was applied by dividing the injestion rate by19. This is based on in-the-field reports that 1 gallon of foam (3.8 L) yields approximately 0.2 L of liquid.[3] Bioavailability was assumed to be 100%. The exposure factor was calculated by multiplying the exposure frequency by the exposure duration and dividing by the averaging time. Due to the northern climate, exposure frequency was assumed to be 5 days per week for 12 weeks of the year (60 days). We assumed a one year exposure duration and the averaging time of 84 days (7 days per week for 12 weeks).

Results

Foam Method Validation. Internal standard area counts were compared between adding before centrifugation or after (n=4) to test whether a significant portion of PFAS are sorbing to particles that are centrifuged out. The percent difference was calculated as follows:

$$\%\ Difference = \left(\frac{(Mean\ of\ Before) - (Mean\ of\ After)}{Mean(Mean\ of\ Before\ and\ Mean\ of\ After)}\right) * 100$$

The % differences had 29 of the 31 internal standards +/- 30% (Table S2), with a mix of higher and lower (14 lower, 17 higher), indicating no difference between adding before or after centrifugation. Thus, internal standards were added after centrifugation to have a more efficient use of internal standards (0.75 ng/sample vs 2 ng/sample).

Internal standard area counts for samples compared to calibration standards were calculated as follows:

$$\% \, Difference = \left(\frac{(Mean\ of\ Samples) - (Mean\ of\ Calibration\ Stds)}{Mean(Mean\ of\ Samples\ and\ Mean\ of\ Calibration\ Stds)} \right) * 100$$

Four replicate analyses of Foam 6 gave % RSD values of 2.3, 3.8, and 23.0% for naturally occurring PFUdA, PFOS, and 5:3 FTCA, respectively. The more variable 5:3 FTCA values may be due to the lack of a matched internal standard (e.g., 8:2 FTCA). For n=4 replicates of Bulk Water 2, the % RSD values of 5.3, 2.3, 2.2, 3.2, and 2.5% were obtained for naturally occurring PFHxA, PFOA, PFHxS, PFOS, and 6:2 FTS, respectively.

The overspike of 50 target PFAS into Foam 7 gave 27 out of 50 analytes falling within 70-130% of the spike concentration, exceptions being PFPeA,* PFHxA,* PFHxDA,* PFPrS, PFBS,* PFHpS, Cl-PFOS, FHxSA, FOSA,* 10:2 FTS, 6:2 FTCA,* 10:2 FTCA,* 3:3 FTCA, 7:3 FTCA, 8:2 UFTCA,* 10:2 UFTCA,* HFPO-DA, ADONA, 9Cl-PF3ONS, 11Cl-PF3OUdS, 6:2 diPaP,* and 8:2 diPaP* (Table S5). Those marked with * have a matched stable-isotope labelled standard. The overspike of 50 target PFAS into Bulk Water 6 gave 44 PFAS that fell within 70-130% of the spike concentration, exceptions being PFHxDA,* PFHpS, PFEtCHxS, FBSA, FOSA,* and MeFOSAA* (Table S6). Those marked with * have a matched stable-isotope labelled standard.

Correlation of EF and PFAS Characteristics

Linear correlations of log EF with number of fully fluorinated PFAS carbons and chromatographic retention time are shown in Figure 2 and Figure S2. Although the R2 for the linear regression between EF and number of fully fluorinated carbons ($R^2 = 0.8408$; Figure S2) was greater than that ($R^2 = 0.7374$) for chromatographic retention time (Figure 2), chromatographic retention time treats Br- and L-isomers as separate molecules. However, it is important to keep in mind that L-isomer is a single molecule whereas Br-PFHxS and Br-PFOS are several branched isomers.[4-7]The lower R^2 for EF and retention time may arise, in part, due to the use of a non-linear gradient that results in non-linear changes in chromatographic retention. Alternatively, not all carbons in the hydrophobic tail are fluorinated, for example as in 6:2 FTS, so plots of EF against number of fully fluorinated carbons does not account for all contributions to the hydrophobic tail of polyfluorinated PFAS.

Implications

Fisenko suggested that the 'natural froth' that formed in Etobicoke Creek after a 1997 toxic waste spill was the creek's attempt at a 'self-purification process' and was caused by cyanide, heavy metals, and 'biological surfactants'.[8] Analytical methods for PFAS were not widely available in 1997 so there are no data on PFAS or other surfactants for the 1997 waste spill described by Fisenko et al. Today, Etobicoke Creek is recognized as impacted by AFFF releases from the Toronto International airport, which has resulted in PFAS contamination of water, sediment, and biota.[9-14] Thus, the foaming observed by Fisenko was likely due to the release of AFFF, which contains PFAS along with hydrocarbon surfactants, and not to inorganics or biological surfactants.

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Table A1. Targeted analytes for PFAS analysis.

Chemical Name	Acronym	Neutral Molecular Formula[1]	Internal Standard
Perfluoro-n-butanoic acid	PFBA[2]	C4HO2F7	MPFBA
Perfluoro-n-petnanoic acid	PFPeA	C5HO2F9	M3PFPeA
Perfluoro-n-hexanoic acid	PFHxA	C6HO2F11	M2PFHxA
Perfluoro-n-heptanoic acid	PFHpA	C7HO2F13	M4PFHpA
Perfluoro-n-octanoic acid	PFOA	C8HO2F15	M4PFOA
Perfluoro-n-nonanoic acid	PFNA	C9HO2F17	M5PFNA
Perfluoro-n-decanoic acid	PFDA	C10HO2F19	MPFDA
Perfluoro-n-undecanoic acid	PFUdA	C11HO2F21	MPFUdA
Perfluoro-n-dodecanoic acid	PFDoA	C12HO2F23	MPFDoA
Perfluoro-n-tridecanoic acid	PFTrDA	C13HO2F25	MPFDoA
Perfluoro-n-tetradecanoic acid	PFTeDA	C14HO2F27	M2PFTeDA
Perfluoro-n-hexadecanoic acid	PFHxDA	C16HO2F31	M2PFHxDA
Perfluoropropane sulfonate	PFPrS	C3HO3SF7	M3PFBS
Perfluorobutane sulfonate	PFBS	C4HO3SF9	M3PFBS
Perfluoropentane sulfonate	PFPeS	C5HO3SF11	M3PFBS
Perfluorohexane sulfonate	PFHxS	C6HO3SF13	MPFHxS
Perfluoroheptane sulfonate	PFHpS	C7HO3SF15	MPFHxS
Perfluorooctane sulfonate	PFOS	C8HO3SF17	MPFOS
Perfluorononane sulfonate	PFNS	C9HO3SF19	MPFOS
Perfluorodecane sulfonate	PFDS	C10HO3SF21	MPFOS
Perfluorododecane sulfonate	PFDoS	C12HO3SF25	MPFOS
8-chloro-perfluorooctane sulfonate	Cl-PFOS	C8HClF16SO3	MPFOS
Perfluoroethylcyclohexane sulfonate	PFEtCHxS	C8HO3SF15	MPFHxS
Perfluorobutane sulfonamide	FBSA	C4H2O2NSF9	M8FOSA
Perfluorohexane sulfonamide	FHxSA	C6H2O2NSF13	M8FOSA
Perfluorooctane sulfonamide	FOSA	C8H2O2NSF17	M8FOSA
N-methylperfluoro-1-octane sulfonamide	MeFOSA	C9H4O2NSF17	d-N-MeFOSA-M
N-ethylperfluoro-1-octane sulfonamide	EtFOSA	C10H6O2NSF17	d-N-EtFOSA-M
Perfluorooctane sulfonamido acetic acid	FOSAA	C10H4O4NSF17	d3-N-MeFOSAA
N-methylperfluorooctane sulfonamido acetic acid	MeFOSAA	C11H6O4NSF17	d3-N-MeFOSAA
N-ethylperfluorooctane sulfonamido acetic acid	EtFOSAA	C12H8O4NSF17	d5-N-EtFOSAA
4:2 fluorotelomer sulfonate	4:2 FTS	C6H5O3SF9	M2-4:2FTS
6:2 fluorotelomer sulfonate	6:2 FTS	C8H5O3SF13	M2-6:2FTS
8:2 fluorotelomer sulfonate	8:2 FTS	C10H5O3SF17	M2-8:2FTS

10:2 fluorotelomer sulfonate	10:2 FTS	C12H5O3SF21	M2-8:2FTS
6:2 fluorotelomer carboxylic acid	6:2 FTCA	C8H3O2F13	M6:2FTA
8:2 fluorotelomer carboxylic acid	8:2 FTCA	C10H3O2F17	M8:2FTA
10:2 fluorotelomer carboxylic acid	10:2 FTCA	C12H3O2F21	M10:2FTA
3:3 fluorotelomer carboxylic acid	3:3 FTCA	C6H5O2F7	M6:2FTA
5:3 fluorotelomer carboxylic acid	5:3 FTCA	C8H5O2F11	M8:2FTA
7:3 fluorotelomer carboxylic acid	7:3 FTCA	C10H5O2F15	M10:2FTA
2H-Perfluoro-2-octenoic acid (6:2)	6:2 UFTCA	C8H2O2F12	M6:2FTUA
2H-Perfluoro-2-decenoic acid (8:2)	8:2 UFTCA	C10H2O2F16	M8:2FTUA
2H-Perfluoro-2-dodecenoic acid (10:2)	10:2 UFTCA	C12H2O2F20	M10:2FTUA
Gen X	HFPO-DA	C6HF11O3	MHFPO-DA
ADONA	ADONA	C7H2O4F12	M5PFNA
9-chlorohexadecafluoro-3-oxanonane-1-sulfonate	9Cl-PF3ONS	C8HF16ClSO4	MPFOS
11-chloroeicosafluoro-3-oxaundecane-1-sulfonate	11l-PF3OUdS	C10HF20ClSO4	MPFOS
bis(1H,1H,2H,2H-perfluorooctyl)phosphate	6:2diPAP	C16H9F26O4P	M4 8:2 diPAP
bis(1H,1H,2H,2H-perfluorodecyl)phosphate	8:2diPAP	C20H9F34O4P	M4 8:2 diPAP

[1] $[M-H]^-$ adducts were used for quantification

[2] MRM transitions of 213 → 169 and 217 → 172 were used for quantification of PFBA and MPFBA, respectively, to reduce background.

Table A2. Percent difference between adding internal standards before or after centrifugation.

Internal Standard	% Difference
MPFBA	25.6
M3PFPeA	43.6
M2PFHxA	-5.0
M4PFHpA	-6.9
M4PFOA	-12.6
M5PFNA	3.5
MPFDA	-1.3
MPFUdA	9.2
MPFDoA	3.2
M2PFTeDA	6.6
M2PFHxDA	-18.8
M3PFBS	16.9
MPFHxS	0.3
MPFOS	-0.2
M2-4:2FTS	17.1
M2-6:2FTS	-9.4
M2-8:2FTS	-3.3
M8FOSA	28.7
d-N-MeFOSA-M	0.6
d-N-EtFOSA-M	8.2
d3-N-MeFOSAA	-10.7
d5-N-EtFOSAA	-5.1
M6:2FTA	0.02
M8:2FTA	1.4
M10:2FTA	-17.0
M6:2FTUA	-2.5
M8:2FTUA	1.3
M10:2FTUA	-5.9
MHFPO-DA	-18.9
M2 6:2 PAP	44.8
M4 8:2 diPAP	16.8

Table A3. Percent difference in area counts for isotopically labelled standards of Foam (n=12) and Bulk Water (n=12) from calibration standards and associated p-values from a two-tailed unequal variance t-test (type 3).

Internal Standard	Foam % Difference	Foam p-value	Bulk Water % Difference	Bulk Water p-value
MPFBA	33.3	6.57E-07	1.2	0.925
M3PFPeA	8.4	0.271	-13.1	0.228
M2PFHxA	12.6	0.071	-7.7	0.492
M4PFHpA	-16.3	0.022	-4.7	0.672
M4PFOA	-12.9	0.043	-11.0	0.256
M5PFNA	5.4	0.561	-11.4	0.160
MPFDA	-11.8	0.091	-9.1	0.234
MPFUdA	7.9	0.371	-7.2	0.300
MPFDoA	20.7	0.057	-3.0	0.626
M2PFTeDA	35.0	0.002	-2.4	0.669
M2PFHxDA	120.1	2.72E-10	7.2	0.045
M3PFBS	4.7	0.371	-16.6	0.135
MPFHxS	-12.7	0.028	-8.0	0.462
MPFOS	15.7	0.074	-6.5	0.397
M2-4:2FTS	43.8	2.43E-04	-2.9	0.783
M2-6:2FTS	-26.6	3.72E-04	-18.3	0.089
M2-8:2FTS	-35.5	4.43E-09	-14.6	0.045
M8FOSA	38.2	1.35E-04	15.1	0.332
d-N-MeFOSA-M	18.1	0.010	38.8	0.378
d-N-EtFOSA-M	17.8	0.027	35.1	0.397
d3-N-MeFOSAA	0.7	0.905	-1.7	0.771
d5-N-EtFOSAA	-5.0	0.531	-6.6	0.288
M6:2FTA	-14.0	0.002	1.7	0.818
M8:2FTA	-16.3	2.74E-04	-0.2	0.973
M10:2FTA	-5.0	0.382	3.6	0.390
M6:2FTUA	-3.0	0.491	3.0	0.721
M8:2FTUA	-16.4	0.001	0.2	0.978
M10:2FTUA	13.4	0.085	-4.4	0.502
MHFPO-DA	-2.9	0.695	-4.0	0.487
M2 6:2 PAP	14.2	0.072	7.7	0.764
M4 8:2 diPAP	28.1	0.030	35.3	0.001

Table A4. Average recoveries for MPFOA and MPFOS relative to M2PFOA and M8PFOS for n=8 foam samples and n=8 bulk water samples.

Internal Standard	Foam % Recovery ± %RSD	Bulk Water % Recovery ± %RSD
MPFOA	90 ± 6.3%	91 ± 5.8%
MPFOS	105 ± 7.2%	92 ± 5.6%

Table A5. Recovery of native PFAS spiked into a single replicate of Foam 7.

Analyte	% Recovery	Analyte	% Recovery
PFBA	120	MeFOSA	71
PFPeA	138	EtFOSA	124
PFHxA	137	FOSAA	121
PFHpA	107	MeFOSAA	118
PFOA	123	EtFOSAA	108
PFNA	116	4:2 FTS	115
PFDA	127	6:2 FTS	117
PFUdA	122	8:2 FTS	106
PFDoA	115	10:2 FTS	158
PFTrDA	127	6:2 FTCA	138
PFTeDA	121	8:2 FTCA	128
PFHxDA	62	10:2 FTCA	133
PFPrS	139	3:3 FTCA	55
PFBS	141	5:3 FTCA	109
PFPeS	130	7:3 FTCA	131
PFHxS	88	6:2 UFTCA	115
PFHpS	131	8:2 UFTCA	145
PFOS	113[1]	10:2 UFTCA	133
PFNS	121	HFPO-DA	140
PFDS	114	ADONA	132
PFDoS	118	9Cl-PF3ONS	142
Cl-PFOS	155	11Cl-PF3OUdS	135
PFEtCHxS	111	6:2diPAP	154
FBSA	122	8:2diPAP	149
FHxSA	139		
FOSA	173		

[1]PFOS was found in sample and was background subtracted to get a % recovery.

Table A6. Recovery of native PFAS spiked into single replicate of bulk water.

Analyte	% Recovery from Overspike	Analyte	% Recovery from Overspike
PFBA	86	MeFOSA	78

PFPeA	86
PFHxA	79
PFHpA	86
PFOA	75
PFNA	71
PFDA	75
PFUdA	74
PFDoA	71
PFTrDA	91
PFTeDA	71
PFHxDA	29
PFPrS	71
PFBS	81
PFPeS	94
PFHxS	73
PFHpS	64
PFOS	101
PFNS	94
PFDS	86
PFDoS	84
Cl-PFOS	80
PFEtCHxS	56
FBSA	64
FHxSA	79
FOSA	65
EtFOSA	89
FOSAA	112
MeFOSAA	63
EtFOSAA	73
4:2 FTS	104
6:2 FTS	108
8:2 FTS	102
10:2 FTS	75
6:2 FTCA	78
8:2 FTCA	87
10:2 FTCA	90
3:3 FTCA	88
5:3 FTCA	90
7:3 FTCA	83
6:2 UFTCA	98
8:2 UFTCA	85
10:2 UFTCA	95
HFPO-DA	91
ADONA	75
9Cl-PF3ONS	81
11l-PF3OUdS	93
6:2diPAP	86
8:2diPAP	97

Table A7. Target PFAS concentrations (ng/L) and dissolved organic carbon (DOC) concentrations (mg/L) in foam and bulk water.[1]

Sample ID	Foam 1	Foam 2	Foam 3	Foam 4	Foam 5	Foam 6	Foam 7	Foam 8	Background	LOQ
DOC (mg/L)	250	239	334	239	259	252	225	212	260	
PFBA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	100
PFPeA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	100
PFHxA	<LOQ	140	<LOQ	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOD	100
PFHpA	<LOD	<LOQ	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	100
PFOA	840	1200	1300	530	280	<LOD	<LOD	<LOD	<LOD	100
PFNA	340	850	1500	320	380	<LOQ	<LOD	<LOQ	130	100
PFDA	260	630	960	290	420	<LOQ	<LOQ	<LOQ	420	100
PFUdA	250	510	660	260	410	110	<LOQ	190	340	100
PFDoA	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOD	100
PFTrDA	<LOD	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOD	<LOD	<LOD	100
PFTeDA	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOD	100
PFHxDA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	100
PFPrS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	100
PFBS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	100
PFPeS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	100
PFHxS	1200	2000	1700	890	330	<LOQ	<LOQ	<LOQ	<LOD	100
PFHpS	610	2300	2800	690	160	<LOD	<LOD	<LOD	<LOD	100
PFOS	32000	97000	68000	49000	32000	2300	2300	3700	1500	100
PFNS	<LOQ	130	130	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOD	100
PFDS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	100
PFDoS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	100
Cl-PFOS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	100
PFEtCHxS	340	730	560	220	<LOQ	<LOQ	<LOQ	<LOQ	<LOD	100
FBSA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	500
FHxSA	950	1000	1100	690	<LOQ	<LOQ	<LOQ	<LOQ	<LOD	500
FOSA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	500
MeFOSA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	100
EtFOSA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	100
FOSAA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	100
MeFOSAA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	100
EtFOSAA	<LOQ	<LOQ	130	<LOQ	100	<LOQ	<LOQ	<LOQ	<LOD	100
4:2 FTS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	100
6:2 FTS	830	1300	1000	770	<LOD	<LOD	<LOD	<LOD	<LOD	100
8:2 FTS	<LOQ	100	<LOQ	130	<LOQ	<LOD	<LOD	<LOD	<LOD	100
10:2 FTS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	100
6:2 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	100
8:2 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	100
10:2 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	100
3:3 FTCA	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOD	<LOD	<LOD	<LOD	100
5:3 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	190	<LOD	<LOD	<LOD	100
7:3 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	100
6:2 UFTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	100
8:2 UFTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	100
10:2 UFTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	100
HFPO-DA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	100
ADONA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	100
9Cl-PF3ONS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	100
11l-PF3OUdS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	100
6:2diPAP	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	500
8:2diPAP	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	250

Sample ID	BW 1	BW 2	BW 3	BW 4	BW 5	BW 6	BW 7	BW 8	Background	LOQ
DOC (mg/L)	12	16	15	15	21	14	14	15	N/A	
PFBA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	10
PFPeA	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOD	25
PFHxA	13	14	<LOQ	15	<LOQ	<LOD	<LOD	<LOQ	<LOD	10
PFHpA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	10
PFOA	15	13	<LOQ	18	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	10
PFNA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	10
PFDA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	10
PFUdA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	10
PFDoA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	10
PFTrDA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	25
PFTeDA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	10
PFHxDA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	25
PFPrS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	25
PFBS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	25
PFPeS	<LOQ	<LOQ	<LOD	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOD	10
PFHxS	46	52	27	59	<LOQ	<LOQ	<LOQ	<LOQ	17	10
PFHpS	<LOQ	<LOQ	<LOQ	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOD	10
PFOS	36	43	24	51	<LOQ	<LOD	<LOD	13	28	10
PFNS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	10
PFDS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	10
PFDoS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	10
Cl-PFOS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	10
PFEtCHxS	<LOQ	<LOQ	<LOD	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOD	10
FBSA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	250
FHxSA	<LOQ	<LOQ	<LOD	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOD	50
FOSA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	50
MeFOSA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	25
EtFOSA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	10
FOSAA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	10
MeFOSAA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	10
EtFOSAA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	25
4:2 FTS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	10
6:2 FTS	24	15	<LOQ	45	<LOD	<LOD	<LOD	<LOD	<LOD	10
8:2 FTS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	10
10:2 FTS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	10
6:2 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	10
8:2 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	10
10:2 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	25
3:3 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	10
5:3 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	10
7:3 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	10
6:2 UFTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	10
8:2 UFTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	10
10:2 UFTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	25
HFPO-DA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOD	25
ADONA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	10
9Cl-PF3ONS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	10
11l-PF3OUdS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	10
6:2diPAP	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	10
8:2diPAP	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOD	25

[1] The limit of detection (LOD) is defined as 1/3 the limit of quantification (LOQ).

Table A8. Branched and linear isomer ratios for ECF-derived PFAS arranged by chromatographic retention time in foam and bulk water.

Sample ID	PFHxS	PFHpS	FHxSA	PFOS	PFNS	EtFOSAA
Rt (min)	12.65	13.95	14.67	15.16	16.30	17.42
Foam 1	7:93	13: 87	30:70	41:59	--	--
Foam 2	6:94	12:88	29:71	49:51	70:30	--
Foam 3	6:94	10:90	28:72	46:54	72:28	16:84
Foam 4	7:93	12:88	36:64	41:59	--	--
Foam 5	14:86	13:87	--	49:51	--	21:79
Foam 6	--	--	--	43: 57	--	--
Foam 7	--	--	--	40:60	--	--
Foam 8	--	--	--	40:60	--	--
Back-ground	0:100	--	--	34:66	--	--
BW 1	5:85	--	--	56:44	--	--
BW 2	16:84	--	--	59:41	--	--
BW 3	27:73	--	--	65:35	--	--
BW 4	13:87	--	--	60:40	--	--
BW 8	--	--	--	55:45	--	--
Back-ground	0:100	--	--	67:33	--	--

-- Omitted either due to ND or <LOQ

Table A9. Enrichment factors (unitless) used to generate Figure 2 and Figure S2.

Sample ID	Number fluorinated carbons	Retention Time	Foam 1	Foam 2	Foam 3	Foam 4	Foam 8	Back ground	Average EF for L:Br
DOC	--	NA	20	15	22	16	14	--	--
L-PFHxA	5	11.33	--	10	--	--	--	--	--
Br-PFHxS	6	12.32	12	14	14	8	--	--	3.2[a]
L-PFHxS	6	12.65	29	43	81	16	--	--	
6:2 FTS	6	13.94	35	87	--	17	--	--	--
L-PFOA	7	13.99	56	92	--	29	--	--	--
Br-PFOS	8	14.61	651	1873	2005	657	193	37	2.0[b]
L-PFOS	8	15.16	1192	2806	4371	1417	417	77	

-- no value reported because one or more concentrations (foam, bulk water) were <LOQ

[a]average of four EF values; [b]average of six EF value

Table A10. Preliminary estimates of exposure from daily incidental ingestion of water via foam (ng/kg-day).

PFAS	Foam PFAS (ng/L)		1 to <2 years old		2 to <3 years old		3 to <6 years old		6 to <11 years old		1 to <2 years old		16 to <21 years old		21+ years old	
	GM[1]	Max	GM	Max	GM	Max	GM	Max	GM	Max	GM	Max	GM	Max	GM	Max
PFPeA	27	68	0.01	0.04	0.01	0.06	0.00	0.03	0.00	0.02	0.00	0.01	0.00	0.01	0.00	0.01
PFHxA	45	140	0.01	0.09	0.01	0.12	0.01	0.06	0.00	0.03	0.00	0.03	0.00	0.02	0.00	0.01
PFHpA	29	57	0.01	0.04	0.01	0.05	0.00	0.02	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.00
PFOA	199	1300	0.05	0.82	0.05	1.09	0.03	0.55	0.02	0.29	0.01	0.26	0.01	0.14	0.01	0.11
PFNA	199	1500	0.05	0.94	0.05	1.25	0.03	0.63	0.02	0.34	0.01	0.30	0.01	0.16	0.01	0.13
PFDA	213	960	0.05	0.60	0.05	0.80	0.03	0.41	0.02	0.22	0.01	0.19	0.01	0.11	0.01	0.08
PFUdA	240	660	0.06	0.42	0.06	0.55	0.03	0.28	0.02	0.15	0.01	0.13	0.01	0.07	0.01	0.06
PFDoA	47	64	0.01	0.04	0.01	0.05	0.01	0.03	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.01
PFTrDA	33	56	0.01	0.04	0.01	0.05	0.00	0.02	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.00
PFTeDA	61	83	0.02	0.05	0.01	0.07	0.01	0.04	0.01	0.02	0.00	0.02	0.00	0.01	0.00	0.01
PFHxS	337	2000	0.08	1.26	0.08	1.67	0.04	0.84	0.03	0.45	0.02	0.40	0.01	0.22	0.01	0.17
PFHpS	220	2800	0.05	1.76	0.05	2.34	0.03	1.18	0.02	0.63	0.01	0.56	0.01	0.31	0.01	0.24
PFOS	16843	97000	4.20	61.05	4.07	81.02	2.23	40.92	1.50	21.89	0.98	19.40	0.58	10.63	0.44	8.34
PFNS	69	130	0.02	0.08	0.02	0.11	0.01	0.05	0.01	0.03	0.00	0.03	0.00	0.01	0.00	0.01
PFEtCHxS	243	730	0.06	0.46	0.06	0.61	0.03	0.31	0.02	0.16	0.01	0.15	0.01	0.08	0.01	0.06
FHxSA	489	1100	0.12	0.69	0.12	0.92	0.06	0.46	0.04	0.25	0.03	0.22	0.02	0.12	0.01	0.09
EtFOSAA	77	130	0.02	0.08	0.02	0.11	0.01	0.05	0.01	0.03	0.00	0.03	0.00	0.01	0.00	0.01
3:3 FTCA	35	53	0.01	0.03	0.01	0.04	0.00	0.02	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.00
5:3 FTCA	30	190	0.01	0.12	0.01	0.16	0.00	0.08	0.00	0.04	0.00	0.04	0.00	0.02	0.00	0.02
6:2 FTS	149	1300	0.04	0.82	0.04	1.09	0.02	0.55	0.01	0.29	0.01	0.26	0.01	0.14	0.00	0.11
8:2 FTS	47	130	0.01	0.08	0.01	0.11	0.01	0.05	0.00	0.03	0.00	0.03	0.00	0.01	0.00	0.01

SumPFAS	19634	110451	4.89	69.51	4.75	92.26	2.60	46.60	1.75	24.92	1.14	22.09	0.68	12.11	0.51	9.49

[1] GM concentration in foam calculated using the value reported by the instrument for those <LOQ and LOD/sqrt(2) for measurements <LOD. Only those PFAS with one or more detected value are included.

Table A11. Preliminary estimates of exposure from daily incidental ingestion of bulk water (ng/kg-day).

PFAS	Bulk Water PFAS (ng/L)		1 to <2 years old		2 to <3 years old		3 to <6 years old		6 to <11 years old		1 to <2 years old		16 to <21 years old		21+ years old	
	GM[1]	Max	GM	Max	GM	Max	GM	Max	GM	Max	GM	Max	GM	Max	GM	Max
PFPeA	14.56	20.84	0.07	0.25	0.07	0.33	0.04	0.17	0.02	0.09	0.02	0.08	0.01	0.04	0.01	0.03
PFHxA	5.47	15.00	0.03	0.18	0.03	0.24	0.01	0.12	0.01	0.06	0.01	0.06	0.00	0.03	0.00	0.02
PFHpA	2.35	2.35	0.01	0.03	0.01	0.04	0.01	0.02	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.00
PFOA	8.38	18.00	0.04	0.22	0.04	0.29	0.02	0.14	0.01	0.08	0.01	0.07	0.01	0.04	0.00	0.03
PFPeS	2.82	4.10	0.01	0.05	0.01	0.07	0.01	0.03	0.00	0.02	0.00	0.02	0.00	0.01	0.00	0.01
PFHxS	15.70	59.00	0.07	0.71	0.07	0.94	0.04	0.47	0.03	0.25	0.02	0.22	0.01	0.12	0.01	0.10
PFHpS	3.14	5.21	0.01	0.06	0.01	0.08	0.01	0.04	0.01	0.02	0.00	0.02	0.00	0.01	0.00	0.01
PFOS	12.31	51.00	0.06	0.61	0.06	0.81	0.03	0.41	0.02	0.22	0.01	0.19	0.01	0.11	0.01	0.08
PFEtCHxS	2.91	4.29	0.01	0.05	0.01	0.07	0.01	0.03	0.00	0.02	0.00	0.02	0.00	0.01	0.00	0.01
FHxSA	15.58	28.96	0.07	0.35	0.07	0.46	0.04	0.23	0.03	0.12	0.02	0.11	0.01	0.06	0.01	0.05
6:2 FTS	6.19	45.00	0.03	0.54	0.03	0.71	0.02	0.36	0.01	0.19	0.01	0.17	0.00	0.09	0.00	0.07
SumPFAS	89.4	253.7	0.42	3.03	0.41	4.03	0.23	2.03	0.15	1.09	0.10	0.96	0.06	0.53	0.04	0.41

[1] GM concentration in foam calculated using the value reported by the instrument for those <LOQ and LOD/sqrt(2) for measurements <LOD. Only those PFAS with one or more detected value are included.

Figure A1. ^{1}H NMR total integral area of foam and bulk water (BW) samples.

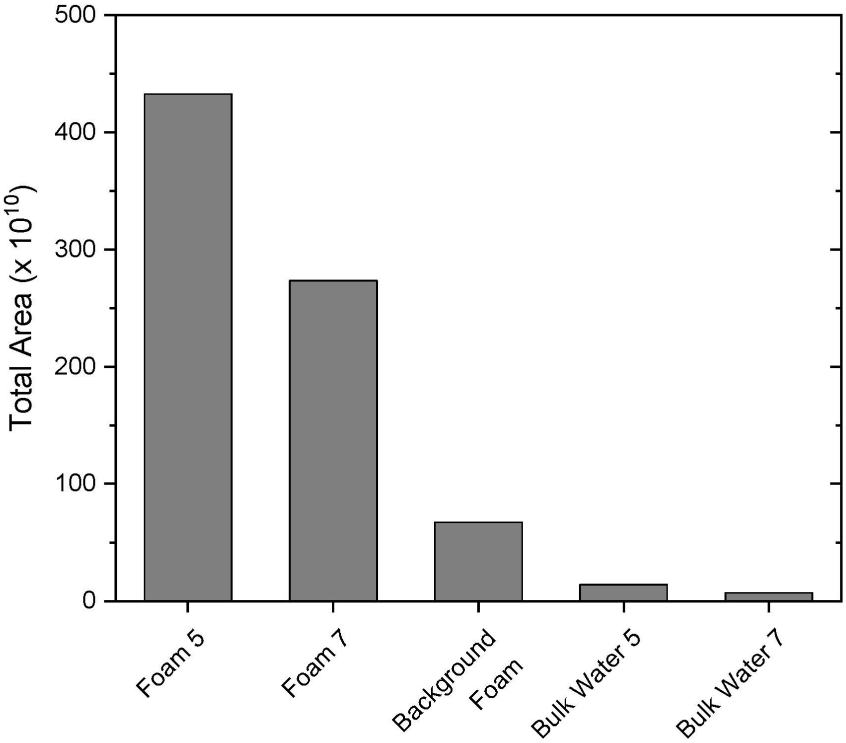


Figure A2. Linear regression of the log of enrichment factors plotted against number of fully fluorinated carbons.

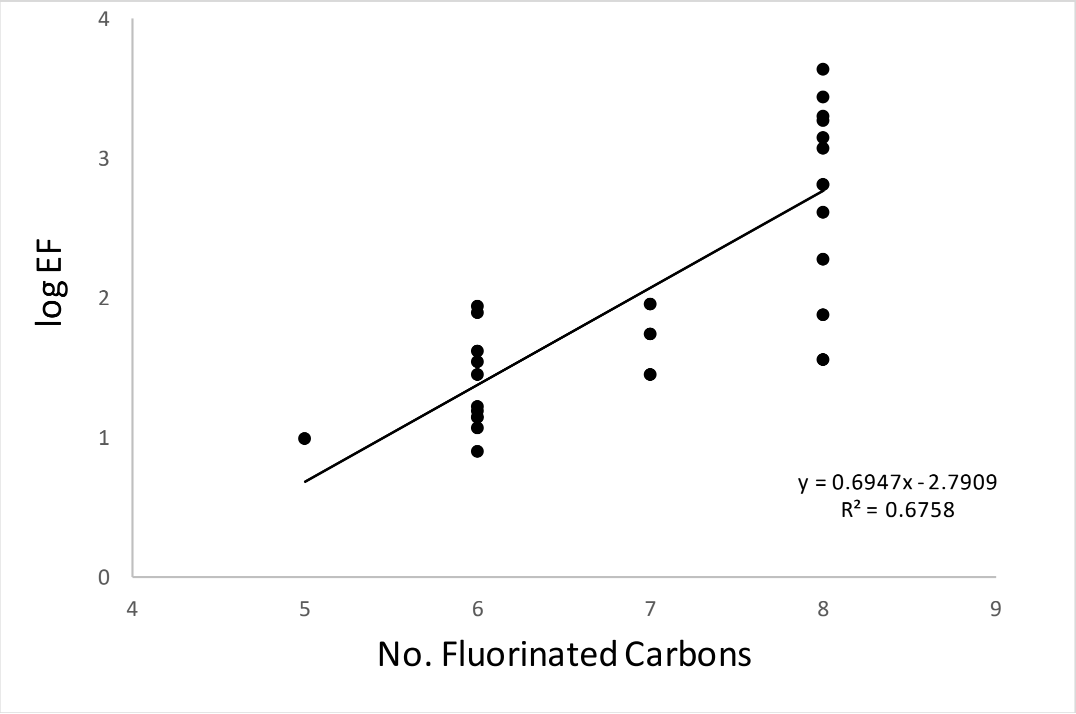
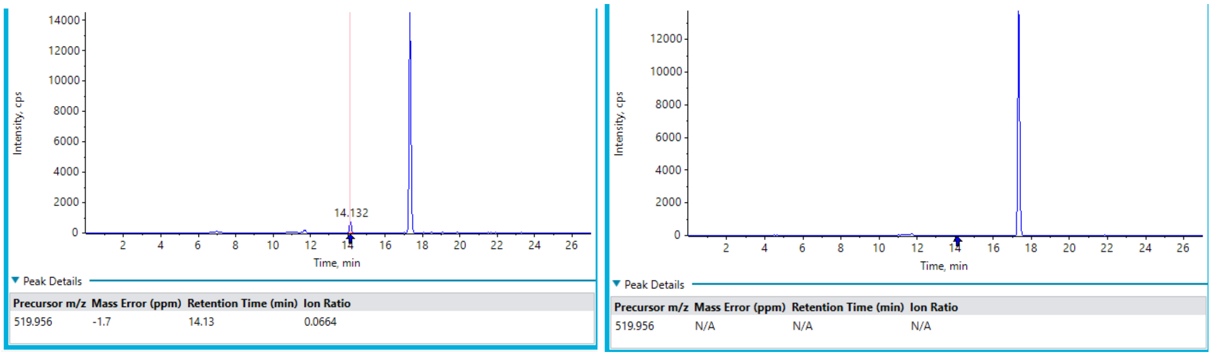


Figure A3. Chromatograms of the suspect SPr-FHxSA in (a) found in the sample and (b) its absence in the blank.



Precursor m/z	Mass Error (ppm)	Retention Time (min)	Ion Ratio
519.956	-1.7	14.13	0.0664

Precursor m/z	Mass Error (ppm)	Retention Time (min)	Ion Ratio
519.956	N/A	N/A	N/A

(a) (b)

Appendix B – Chapter 3 Supplemental Information

Materials and Methods

Reagents. For LC-MS/MS analysis HPLC grade water (>99%, high purity, Burdick and Jackson brand), hydrochloric acid (BDH Chemicals), and ammonium acetate (regent grade, Macrom Chemicals) were purchased from VWR (Radnor, PA). Ethyl acetate (99.9%, reagent grade), and 2,2,2-Trifluoroethanol (99%, Fluka Analytical) were purchased from Sigma Aldrich (St. Louis, MO). Methanol (>99%, LC/MS grade) was purchased from Fisher Scientific (Hampton, NH). Sodium chloride was purchased from Mallinckrodt Chemical (> 99%).

Quality Control. For the extraction method, n=4 groundwaters were spiked with all 50 natives at 500 ng/L to obtain accuracy and precision for the method. The limit of quantification (LOQ) for the extraction was done by the method outlined in Vial and Jardy 1999 and Backe 2013 by spiking all natives and surrogates at 7 concentrations near the estimated limit of detection in groundwater. When native was present in the groundwater, the value generated from the surrogate was used (Table S2). All samples were collected in replicates of n=4, thus precision as expressed by %RSD was assessed for each sample. Accuracy was obtained by second isotope-labelled PFOA and PFOS spiked as injection surrogates right before analysis.

PFAS Analysis by Liquid Chromatography Quadrupole Time of Flight. Chromatographic separations were achieved using an Agilent 1260 HPLC (Santa Clara, CA), 1 C18 Guard column, and a Zorbax Eclipse Plus analytical column (4.6 x 50 mm, 1.8µm; Agilent) as modified after Backe et al.[1] The aqueous mobile phase (A) was 3% v/v HPLC-grade methanol in HPLC-grade water and 10 mM ammonium acetate and the organic mobile phase (B) HPLC-grade methanol. A SCIEX X500R QToF-MS/MS system (Framingham, MA) was operated in negative mode electrospray ionization (ESI-) mode. Data were collected under SWATH® data-independent acquisition for both TOF-MS and MS/MS modes. PFBA and MPFBA were analyzed in MS/MS mode to reduce background. Over the entirety of the data acquisition period, precursor ion data (TOF-MS) were collected over a m/z range of 100 Daltons (Da; TOF start mass) to 1250 Da (TOF stop). The accumulation time was 200 ms and the ion spray voltage was -4500 V. The source and gas parameters included: a source temperature of 550 ^{o}C, ion source gasses at 60 psi, curtain gas at 35 psi, and collision gas at 10 psi. The declustering potential was -20 V (with 0 V spread) and the collision energy was -5 V (with 0 V spread). Product ion scan (TOF-MS/MS) data were collected for a m/z range from 50 Da (TOF start mass) to 1200 Da. The accumulation time for each SWATH® window was 50 ms.

Table B1. Targeted analytes for PFAS analysis.

Chemical Name	**Acronym**	**Neutral Molecular Formula[1]**	**Surrogate Standard**
Perfluoro-n-butanoic acid	PFBA[2]	C4HO2F7	MPFBA
Perfluoro-n-pentanoic acid	PFPeA	C5HO2F9	M3PFPeA
Perfluoro-n-hexanoic acid	PFHxA	C6HO2F11	M2PFHxA
Perfluoro-n-heptanoic acid	PFHpA	C7HO2F13	M4PFHpA
Perfluoro-n-octanoic acid	PFOA	C8HO2F15	M4PFOA
Perfluoro-n-nonanoic acid	PFNA	C9HO2F17	M5PFNA
Perfluoro-n-decanoic acid	PFDA	C10HO2F19	MPFDA
Perfluoro-n-undecanoic acid	PFUdA	C11HO2F21	MPFUdA
Perfluoro-n-dodecanoic acid	PFDoA	C12HO2F23	MPFDoA
Perfluoro-n-tridecanoic acid	PFTrDA	C13HO2F25	MPFDoA
Perfluoro-n-tetradecanoic acid	PFTeDA	C14HO2F27	M2PFTeDA
Perfluoro-n-hexadecanoic acid	PFHxDA	C16HO2F31	M2PFHxDA
Perfluoropropane sulfonate	PFPrS	C3HO3SF7	M3PFBS
Perfluorobutane sulfonate	PFBS	C4HO3SF9	M3PFBS
Perfluoropentane sulfonate	PFPeS	C5HO3SF11	M3PFBS
Perfluorohexane sulfonate	PFHxS	C6HO3SF13	MPFHxS
Perfluoroheptane sulfonate	PFHpS	C7HO3SF15	MPFHxS
Perfluorooctane sulfonate	PFOS	C8HO3SF17	MPFOS
Perfluorononane sulfonate	PFNS	C9HO3SF19	MPFOS
Perfluorodecane sulfonate	PFDS	C10HO3SF21	MPFOS
Perfluorododecane sulfonate	PFDoS	C12HO3SF25	MPFOS
8-chloro-perfluorooctane sulfonate	Cl-PFOS	C8HClF16SO3	MPFOS
Perfluoroethylcyclohexane sulfonate	PFEtCHxS	C8HO3SF15	MPFOS
Perfluorobutane sulfonamide	FBSA	C4H2O2NSF9	M8FOSA
Perfluorohexane sulfonamide	FHxSA	C6H2O2NSF13	M8FOSA
Perfluorooctane sulfonamide	FOSA	C8H2O2NSF17	M8FOSA
N-methylperfluoro-1-octane sulfonamide	MeFOSA	C9H4O2NSF17	d-N-MeFOSA-M
N-ethylperfluoro-1-octane sulfonamide	EtFOSA	C10H6O2NSF17	d-N-EtFOSA-M
Perfluorooctane sulfonamido acetic acid	FOSAA	C10H4O4NSF17	d3-N-MeFOSAA
N-methylperfluorooctane sulfonamido acetic acid	MeFOSAA	C11H6O4NSF17	d3-N-MeFOSAA
N-ethylperfluorooctane sulfonamido acetic acid	EtFOSAA	C12H8O4NSF17	d5-N-EtFOSAA
4:2 fluorotelomer sulfonate	4:2 FTS	C6H5O3SF9	M2-4:2FTS
6:2 fluorotelomer sulfonate	6:2 FTS	C8H5O3SF13	M2-6:2FTS
8:2 fluorotelomer sulfonate	8:2 FTS	C10H5O3SF17	M2-8:2FTS

10:2 fluorotelomer sulfonate	10:2 FTS	C12H5O3SF21	M2-8:2FTS
3:3 fluorotelomer carboxylic acid	3:3 FTCA	C6H5O2F7	M6:2FTA
5:3 fluorotelomer carboxylic acid	5:3 FTCA	C8H5O2F11	M6:2FTA
7:3 fluorotelomer carboxylic acid	7:3 FTCA	C10H5O2F15	M8:2FTA
6:2 fluorotelomer carboxylic acid	6:2 FTCA	C8H3O2F13	M6:2FTA
8:2 fluorotelomer carboxylic acid	8:2 FTCA	C10H3O2F17	M8:2FTA
10:2 fluorotelomer carboxylic acid	10:2 FTCA	C12H3O2F21	M10:2FTA
2H-Perfluoro-2-octenoic acid (6:2)	6:2 UFTCA	C8H2O2F12	M6:2FTUA
2H-Perfluoro-2-decenoic acid (8:2)	8:2 UFTCA	C10H2O2F16	M8:2FTUA
dodecafluoro-3H-4,8-dioxanonanoate	ADONA	C7H2O4F12	M5PFNA
9-chlorohexadecafluoro-3-oxanonane-1-sulfonate	9Cl-PF3ONS	C8HF16ClSO4	MPFOS
11-chloroeicosafluoro-3-oxaundecane-1-sulfonate	11Cl-PF3OUdS	C10HF20ClSO4	MPFOS
2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoro propoxy)-propanoic acid	HFPO-DA	C6HF11O3	MHFPO-DA
bis(1H,1H,2H,2H-perfluorooctyl)phosphate	6:2diPAP	C16H9F26O4P	M4 8:2 diPAP
bis(1H,1H,2H,2H-perfluorodecyl)phosphate	8:2diPAP	C20H9F34O4P	M4 8:2 diPAP
bis-[2-(N-ethylperfluorooctane-1-sulfonamide)ethyl]phosphate	diSAmPAP	C24H19F34N2O8PS2	M4 8:2 diPAP

[1] $[M-H]^-$ adducts were used for quantification

[2] MRM transitions of 213 → 169 and 217 → 172 were used for quantification of PFBA and MPFBA, respectively, to reduce background.

Table B2. Target PFAS, acronym, accuracy (% recovery), precision (% RSD), and limits of detection and quantification in low ionic strength **water** by LC-QToF. LOD/LOQ were derived from native target PFAS using the method of Jardy/Vial. The '*' indicates that the surrogate standard was used in place of the target to estimate the LOD/LOQ. A '**' indicates a surrogate was used and likely an overestimate.

Chemical Name	Acronym	Accuracy (% Recovery)	Precision (%RSD)	LOD (ng/L)	LOQ (ng/L)
Perfluoro-n-butanoic acid**	PFBA[2]	87.3	16.5	7.2	23.7
Perfluoro-n-pentanoic acid**	PFPeA	112	29.4	9.5	31.3
Perfluoro-n-hexanoic acid*	PFHxA	92.8	18.9	16.2	53.4
Perfluoro-n-heptanoic acid*	PFHpA	75.6	21.6	7.4	24.5
Perfluoro-n-octanoic acid*	PFOA	81.7	15.2	0.3	1.0
Perfluoro-n-nonanoic acid*	PFNA	93.5	16.5	7.6	25.2
Perfluoro-n-decanoic acid	PFDA	86.9	17.3	3.6	12.0
Perfluoro-n-undecanoic acid	PFUdA	88.1	18.8	3.7	12.2
Perfluoro-n-dodecanoic acid	PFDoA	93.4	15.7	4.2	13.7
Perfluoro-n-tridecanoic acid	PFTrDA	115	23.6	4.2	13.7
Perfluoro-n-tetradecanoic acid	PFTeDA	83.4	22.0	4.8	15.8
Perfluoro-n-hexadecanoic acid	PFHxDA	84.4	21.7	5.0	16.5
Perfluoropropane sulfonate	PFPrS	128	79.9	0.8	2.6
Perfluorobutane sulfonate*	PFBS	87.7	18.7	6.4	21.2
Perfluoropentane sulfonate	PFPeS	70.5	17.3	6.0	19.7
Perfluorohexane sulfonate**	PFHxS	79.5	20.1	6.6	21.6
Perfluoroheptane sulfonate	PFHpS	88.5	20.3	0.3	1.1
Perfluorooctane sulfonate*	PFOS	81.9	16.5	5.1	16.8
Perfluorononane sulfonate	PFNS	82.1	14.7	2.0	6.7
Perfluorodecane sulfonate	PFDS	80.5	16.6	2.6	8.6
Perfluorododecane sulfonate	PFDoS	64.9	21.7	3.3	11.0
8-chloro-perfluorooctane sulfonate	Cl-PFOS	83.7	16.8	2.5	8.4
Perfluoroethylcyclohexane sulfonate	PFEtCHxS	79.6	18.3	2.4	7.8
Perfluorobutane sulfonamide	FBSA	60.0	1.4	2.8	9.3
Perfluorohexane sulfonamide	FHxSA	66.5	1.9	3.7	12.4
Perfluorooctane sulfonamide	FOSA	71.3	5.5	1.1	3.6
N-methylperfluoro-1-octane sulfonamide	MeFOSA	80.8	19.5	3.8	12.7
N-ethylperfluoro-1-octane sulfonamide	EtFOSA	80.0	18.0	3.9	12.8

Perfluorooctane sulfonamido acetic acid	FOSAA	78.4	14.4	6.7	22.1
N-methylperfluorooctane sulfonamido acetic acid	MeFOSAA	92.4	15.0	6.6	21.8
N-ethylperfluorooctane sulfonamido acetic acid	EtFOSAA	63.5	34.1	6.6	21.9
4:2 fluorotelomer sulfonate	4:2 FTS	82.5	18.9	3.2	10.5
6:2 fluorotelomer sulfonate	6:2 FTS	93.3	15.5	2.7	8.9
8:2 fluorotelomer sulfonate	8:2 FTS	89.1	23.7	4.7	15.6
10:2 fluorotelomer sulfonate	10:2 FTS	104	24.7	5.8	19.3
3:3 fluorotelomer carboxylic acid	3:3 FTCA	79.8	28.7	3.3	10.9
5:3 fluorotelomer carboxylic acid	5:3 FTCA	81.7	8.4	1.9	6.4
7:3 fluorotelomer carboxylic acid	7:3 FTCA	87.8	23.1	5.8	19.0
6:2 fluorotelomer carboxylic acid	6:2 FTCA	82.1	17.3	8.0	26.4
8:2 fluorotelomer carboxylic acid	8:2 FTCA	64.1	7.8	11.3	37.3
10:2 fluorotelomer carboxylic acid	10:2 FTCA	77.8	23.6	8.9	29.5
2H-Perfluoro-2-octenoic acid (6:2)	6:2 UFTCA	80.4	8.3	4.2	13.9
2H-Perfluoro-2-decenoic acid (8:2)	8:2 UFTCA	89.5	7.4	6.1	20.0
dodecafluoro-3H-4,8-dioxanonanoate	ADONA	79.4	16.3	2.8	9.2
9-chlorohexadecafluoro-3-oxanonane-1-sulfonate	9Cl-PF3ONS	81.4	19.5	2.6	8.7
11-chloroeicosafluoro-3-oxaundecane-1-sulfonate	11l-PF3OUdS	83.3	19.9	2.5	8.2
2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoro propoxy)-propanoic acid	HFPO-DA	76.1	31.6	5.6	18.3
bis(1H,1H,2H,2H-perfluorooctyl)phosphate	6:2diPAP	241	34.0	24.3	80.1
bis(1H,1H,2H,2H-perfluorodecyl)phosphate	8:2diPAP	72.9	4.6	29.3	96.7
bis-[2-(N-ethylperfluorooctane-1-sulfonamide)ethyl]phosphate	diSAmPAP	36.8	8.9	25.7	85.0

Table B3. Accuracy, as indicated by percent recovery, and precision, as indicated by percent relative standard deviation (%RSD), for 1 and 3 microscope slides determined from spiking experiments. Absolute recovery for PFOS and PFOA as indicated by second mass labeled internal standards (M2PFOA and M8PFOS)

	1 slide		3 slides	
	Recovery (%)	Precision (% RSD)	Recovery (%)	Precision (% RSD)
PFBA	42	3	37	3
PFPeA	117	5	91	3
PFHxA	111	8	84	4
PFHpA	124	5	97	1
PFOA	112	6	90	4
PFNA	112	7	82	4
PFDA	113	8	77	2
PFUdA	113	9	73	3
PFDoA	113	8	73	1
PFTrDA	119	13	71	25
PFTeDA	106	7	84	1
PFPrS	134	15	87	5
PFBS	113	6	87	2
PFPeS	140	15	77	31
PFHxS	115	7	88	3
PFHpS	107	12	73	25
PFOS	113	11	88	4
PFNS	118	8	78	5
PFDS	127	14	64	14
Cl-PFOS	122	11	92	7
PFEtCHxS	106	19	81	8
FBSA	63	21	38	30
FHxSA	69	28	43	30
FOSA	105	7	64	3
MeFOSA	123	9	N/A	N/A

EtFOSA	97	20	70	11
MeFOSAA	122	9	78	5
EtFOSAA	110	6	71	6
4:2 FTS	131	9	101	2
6:2 FTS	121	9	93	1
8:2 FTS	111	7	78	5
3:3 FTCA	63	71	60	52
5:3 FTCA	71	18	57	26
7:3 FTCA	66	13	53	6
6:2 FTCA	55	33	45	28
8:2 FTCA	88	16	66	5
10:2 FTCA	93	11	60	8
6:2 UFTCA	99	7	74	5
8:2 UFTCA	100	4	77	4
ADONA	96	5	69	7
9Cl-PF3ONS	127	17	87	10
11l-PF3OUdS	112	10	80	9
HFPO-DA	111	10	66	32
6:2diPAP	72	10	63	11
8:2diPAP	84	17	77	6
M2PFOA	127	9.4	111	35
M8PFOS	114	7.8	115	6.7

Table B4. Field data across all 10 sites for SML (glass plate) and bulk water (3 cm).

Site	1	1	1	2	2	2	3	3	3
	SML	3 cm	EF 3 cm	SML	3 cm	EF 3 cm	SML	3 cm	EF 3 cm
PFBA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFPeA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFHxA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFHpA	31.7	29.5	1.1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFOA	4.3	1.4	3.2	5.4	3.5	1.5	4.0	3.2	1.2
PFNA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFDA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFUdA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFDoA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFTrDA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFTeDA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFHxDA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFPrS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

PFBS	<LOD	<LOD	<LOD	139.9	<LOD	<LOD	<LOD	<LOD	<LOD
PFPeS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFHxS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFHpS	<LOD	2.0	<LOD	1.5	1.2	1.2	<LOD	<LOD	<LOD
PFOS	<LOD	164.1	<LOD	34.0	<LOD	<LOD	<LOD	<LOD	<LOD
PFNS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFDS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFDoS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Cl-PFOS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFEtCHxS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
FBSA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
FHxSA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
FOSA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
MeFOSA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
EtFOSA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
FOSAA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

MeFOSAA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
EtFOSAA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
4:2 FTS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
6:2 FTS	<LOD	72.6	<LOD	14.3	<LOD	<LOD	<LOD	<LOD	<LOD
8:2 FTS	<LOD	16.9	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
10:2 FTS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
3:3 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
5:3 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
7:3 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
6:2 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
8:2 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
10:2 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
6:2 UFTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
8:2 UFTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
ADONA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
9Cl-PF3ONS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

11l-PF3OUdS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
HFPO-DA decarboxylated	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
6:2 diPAP	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
8:2 diPAP	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
diSAmPAP	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

Table B4 cont. Field data across all 10 sites for SML (glass plate) and bulk water (3 cm).

Site	**4**	**4**	**4**	**5**	**5**	**5**	**6**	**6**	**6**
	SML	**3 cm**	**EF 3 cm**	**SML**	**3 cm**	**EF 3 cm**	**SML**	**3 cm**	**EF 3 cm**
PFBA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFPeA	<LOD	36.4	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFHxA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFHpA	<LOD	<LOD	<LOD	21.1	<LOD	<LOD	43.4	39.4	1.1
PFOA	4.9	2.2	2.3	12.2	<LOD	<LOD	10.5	6.2	1.7
PFNA	43.0	25.4	1.7	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFDA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFUdA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFDoA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFTrDA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFTeDA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFHxDA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFPrS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFBS	<LOD	<LOD	<LOD	12.5	<LOD	<LOD	<LOD	<LOD	<LOD
PFPeS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFHxS	<LOD	<LOD	<LOD	12.2	<LOD	<LOD	36.4	5.5	6.6
PFHpS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	1.5	<LOD	<LOD
PFOS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	195.6	<LOD	36.2
PFNS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFDS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFDoS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Cl-PFOS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFEtCHxS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
FBSA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
FHxSA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	14.1	12.5	1.1
FOSA	6.9	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
MeFOSA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

EtFOSA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
FOSAA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
MeFOSAA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
EtFOSAA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
4:2 FTS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
6:2 FTS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
8:2 FTS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
10:2 FTS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
3:3 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
5:3 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
7:3 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
6:2 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
8:2 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
10:2 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
6:2 UFTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
8:2 UFTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
ADONA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
9Cl-PF3ONS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
11l-PF3OUdS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
HFPO-DA decarboxylated	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
6:2 diPAP	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
8:2 diPAP	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
diSAmPAP	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

Table B4 cont. Field data across all 10 sites for SML (glass plate) and bulk water (3 cm).

Site	7	7	7	8	8	8	9	9	9	10	10	10
	SML	3 cm	EF 3 cm	SML	3 cm	EF 3 cm	SML	3 cm	EF 3 cm	SML	3 cm	EF 3 cm
PFBA	<LOD	<LOD	<LOD	39.0	34.1	1.1	29.5	28.1	1.0	29.2	26.1	1.1
PFPeA	<LOD	<LOD	<LOD	80.7	73.5	1.1	70.5	85.3	0.8	74.8	82.5	0.9
PFHxA	<LOD	<LOD	<LOD	118.7	116.7	1.0	123.4	123.7	1.0	121.6	91.4	1.3
PFHpA	<LOD	<LOD	<LOD	71.9	79.2	0.9	42.1	36.4	1.2	42.0	56.5	0.7
PFOA	12.4	14.5	0.9	204.0	175.4	1.2	232.1	130.0	1.8	216.5	133.4	1.6
PFNA	<LOD	<LOD	<LOD	28.3	<LOD	<LOD	36.4	6.3	5.8	26.9	11.9	2.3
PFDA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	21.9	<LOD	<LOD	14.8	<LOD	<LOD
PFUdA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	28.3	<LOD	<LOD	13.4	<LOD	<LOD
PFDoA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	20.9	<LOD	<LOD	8.3	<LOD	<LOD
PFTrDA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFTeDA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFHxDA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFPrS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFBS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	7.1	5.3	1.3	9.0	<LOD	<LOD
PFPeS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	8.5	7.9	1.1	8.3	<LOD	<LOD
PFHxS	26.1	28.9	0.9	255.1	233.8	1.1	264.7	196.7	1.3	262.1	183.7	1.4
PFHpS	3.0	2.8	1.1	44.2	37.9	1.2	41.2	13.1	3.1	33.6	12.3	2.7
PFOS	199.0	31.6	6.3	4168.6	962.8	4.3	12796.5	1073.3	11.9	9887.2	1064.3	9.3
PFNS	<LOD	<LOD	<LOD	9.3	<LOD	<LOD	118.1	<LOD	<LOD	65.7	<LOD	<LOD
PFDS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	51.3	<LOD	<LOD	20.5	<LOD	<LOD
PFDoS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Cl-PFOS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFEtCHxS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	6.0	<LOD	<LOD	<LOD	<LOD	<LOD
FBSA	<LOD	<LOD	<LOD	40.7	40.1	1.0	34.3	27.7	1.2	23.8	27.4	0.9
FHxSA	18.6	40.7	0.5	433.6	403.2	1.1	633.6	553.3	1.1	451.1	358.1	1.3
FOSA	<LOD	<LOD	<LOD	96.1	24.8	3.9	777.4	39.7	19.6	443.1	32.8	13.5

MeFOSA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
EtFOSA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
FOSAA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
MeFOSAA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	19.2	<LOD	<LOD	7.8	<LOD	<LOD
EtFOSAA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	6.4	<LOD	<LOD	<LOD	<LOD	<LOD
4:2 FTS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
6:2 FTS	14.1	29.6	0.5	124.8	115.9	1.1	163.3	113.2	1.4	150.6	111.2	1.4
8:2 FTS	<LOD	<LOD	<LOD	43.5	<LOD	<LOD	208.6	10.4	20.1	164.7	12.0	13.8
10:2 FTS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
3:3 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
5:3 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	9.7	6.3	1.5	11.9	8.4	1.4
7:3 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
6:2 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	8.5	<LOD	<LOD	<LOD	<LOD	<LOD
8:2 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
10:2 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
6:2 UFTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
8:2 UFTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
ADONA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
9Cl-PF3ONS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
11l-PF3OUdS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
HFPO-DA decarboxylated	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
6:2 diPAP	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
8:2 diPAP	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
diSAmPAP	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

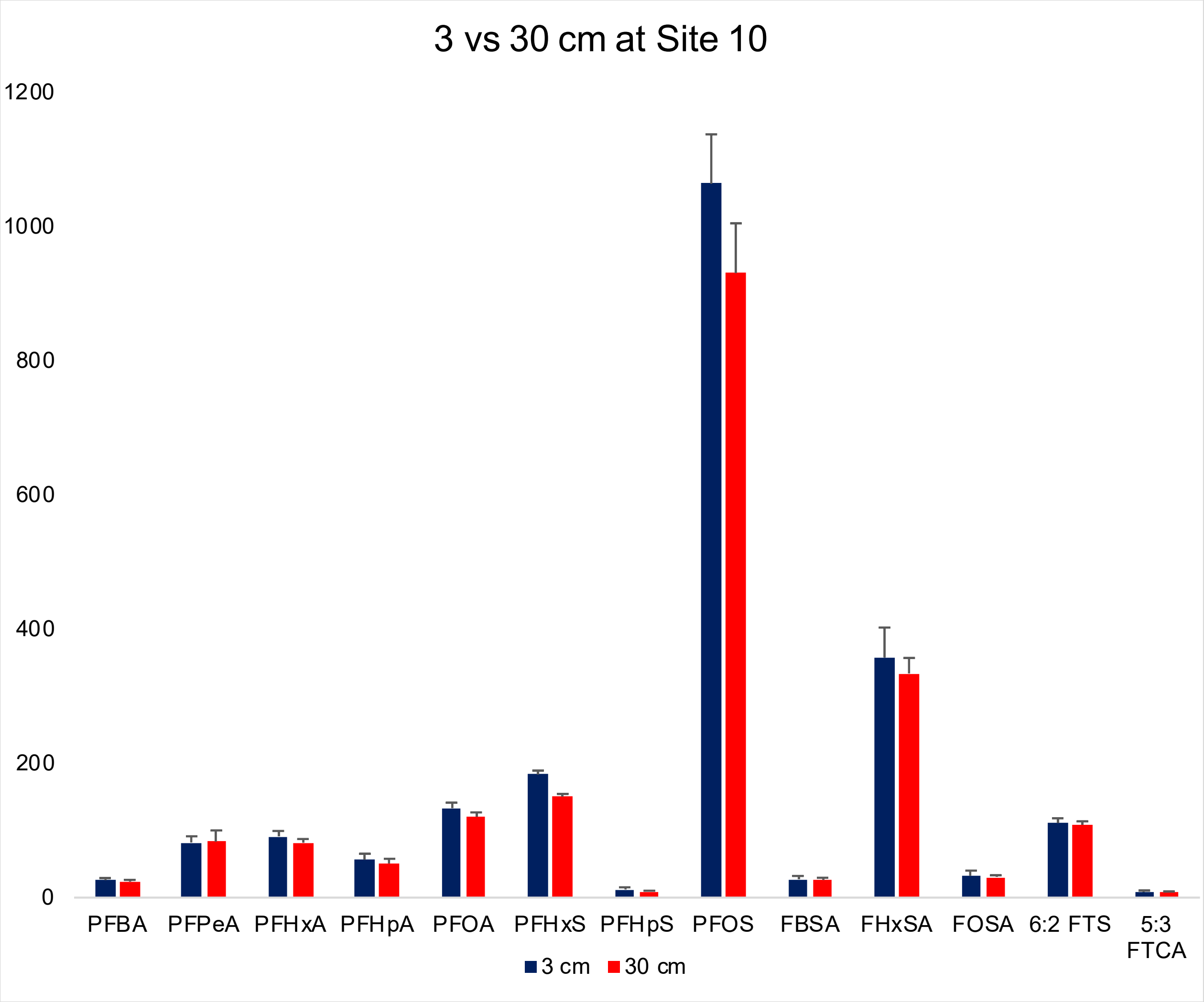


Figure B1. Concentrations in underlying bulk water at 3 and 30 cm below the surface at Site 10. Error bars depict the 95% CI PFAS concentrations for the two depths.

Appendix C – Chapter 4 Supplemental Information

MATERIALS AND METHODS

Liquid Chromatography Quadrupole Time-of-Flight Mass Spectrometry. The composition of the mobile phases are 3% methanol in water (A) and 10 mM ammonium acetate in methanol (B). All solvents are HPLC grade. Precursor ion data (ToF-MS) were collected over a m/z range of 100 Daltons (Da; TOF start mass) to 1250 Da with an accumulation time of 200 ms and an ion spray voltage of -4500 V. Source and gas parameters included a source temperature of 550 ^{o}C, ion source gasses at 60 psi, curtain gas at 35 psi, and a collision gas at 10 psi. A declustering potential of -20 V (with 0 V spread) and a collision energy of -5 V (with 0 V spread) was used. Product ion scan (ToF-MS/MS) data were collected for a m/z range from 50 Da (TOF start mass) to 1200 Da. The accumulation time for each SWATH® window is 50 ms.

Suspect Screening and Semi-Quantification. Mass spectral features were integrated with an XIC width of 0.01 Da, baseline subtraction over 2 min, and a Gaussian smoothing width of 1.0. Only peaks with a signal-to-noise ratio >25 were considered for compound matching. Mass spectral features were considered XIC matches when associated with a compound on the XIC list[1] with <5 ppm mass error, <10% isotope ratio difference, and <70% spectral library match based on the SCIEX OS algorithm (or a higher library score with only the precursor ion matching upon visual inspection). Mass spectral features were considered library matches when associated with a compound on the XIC list with <10 ppm mass error, <20% isotope ratio difference, and >70% spectral library match, as well as visual confirmation of at least one matching fragment. Since MS/MS spectral matching gives higher confidence in identification, library matches were allowed to have a wider range of acceptable values for mass error and isotope ratio difference. Broadly, a library match would be considered to have a confidence level of 2, while an XIC match is of level 4 confidence.[2] All structural isomers were reported when several fit the XIC match criteria and a single isomer could not be definitively identified. If a feature was associated with an XIC list compound as a library match, all other isomer matches for that feature were discarded. If a feature was matched with fluorotelomer (FT)- and electrofluorination (ECF)-derived compounds, the presence or absence of peak branching was used as an indication of which match was more likely (branching from ECF and linear only from FT). However, if the peak area was low (<104), the absence of branching was not used to rule out the FT match. All branched isomers were integrated when present and reported as a single area or semiquantitative concentration. Compound matching also considered other class members; for example, the presence of odd-numbered homologues (e.g., C5, C7) was used as evidence for the ECF-derived matches, as FT-derived compounds are typically present in even-numbered homologues. Finally, suspect matches were only considered valid if homologous series members eluted in reasonable order (increasing LC retention time with increasing chain length within a PFAS class).

The suspect list used for the AFFF analysis was the NIST "Suspect List of Possible Per- and Polyfluoroalkyl Substances (PFAS)" version 1.5.[3] After removing duplicates and molecules >1250 Da, the list was further sorted using the added RDKit function and filtering by the NumHDonors and NumHAcceptors (ESI- and ESI+, respectively). The negative and positive mode lists contained overlap with each other, and when an analyte is found in both modes, the one with the higher area count was used.

The semi-quantification approach was compared to a one-to-one matching approach described by Nickerson et al.[1] The 3M AFFF was diluted 1:1000 with methanol, spiked with surrogate standards as described for LNAPL and then analyzed in negative and positive mode LC-QToF. Targets were quantified as described in the Quantitative Analysis section. Level 2b (library match) and Level 4 suspects detected in negative and positive model were treated as described in the Semi-Quantification of Suspect PFAS section. The molecular formula were then converted to millimoles of fluorine and compared to the total fluorine determined by ^{19}F NMR (704 mmol F/L.[4]

Method Performance. Briefly, seven replicate Jet Fuel A samples were overspiked to give target PFAS concentrations in blank Jet Fuel A that spanned from 1 – 100 ng/L and then extracted. The data were treated using a 1/x weighted regression to calculate the LOD and then the LOQ was calculated as 3.3 x LOD.[5]

RESULTS AND DISCUSSION

Whole Method Accuracy, Precision, LOD/LOQ. Extracting non-volatile PFAS from LNAPL consisting of jet fuel, diesel, and other compounds (Table 1) required a solvent that formed an immiscible phase with Jet Fuel A. Methanol was selected[6] and generated two phases when mixed with Jet Fuel A. Dichloromethane[6] was avoided to eliminate chlorinated solvent use and waste. Initially, surrogate standards (sold in methanol) formed a separate phase, which was seen as a small bead, when spiked into Jet Fuel A. To avoid artificial high surrogate recoveries, surrogates were first mixed with ethyl acetate (10 uL) to promote mixing with Jet Fuel A. Attempts to improve accuracy by employing larger volumes of ethyl acetate or isopropanol reduced target PFAS recovery (data not shown).

Semi-Quantification of Suspect PFAS. The target PFAS concentrations and estimated suspect concentrations obtained by the semi-quantitation approach (e.g., 'PFAS curve') accounted for 77 ± 8.3% (95% CI) of the total fluorine as determined by ^{19}F-NMR (700 mmol F/L), which differs from the summed total of targets and suspect reported in Hao et al. (96 ± 10%).[4]

All target and suspect PFAS found by Hao et al.[4] were found in the present study with some exceptions. Suspect PFAS not found in the present study but reported in Hao et al. as minor components[4]include C5-C8, C10 H-PFSA and well as the class that included PFHx-OS, PFHp-OS, PFO-OS, the latter of which are not on the NIST list.

The summed total fluorine for just the *target* PFAS in this study (327 nmol F/L) was in good agreement (95%) with that of Hao et al. (311mmol F/L), which indicates that the difference in agreement rises from the estimated suspect concentrations. The lacks of agreement was attributed to two suspect classes that are major components of the AFFF: AmPr-FASA-PrA and CEtAmPr-FASA-PrA (Table S3). Concentrations estimated by Hao et al. were up to 20x higher than those estimated using the 'PFAS Curve' in the present study (Table S3). The surrogate used by Hao et. al.[4] for members of these two suspect classes was d5-N-EtFOSAA, which has a low molar response relative to other target PFAS (Figure S1). There is significant variability in molar response factors within the nitrogen-containing target PFAS (e.g., FOSAA, MeFOSA, FOSA; Figure S1). Choosing a target PFAS and its surrogate with low response factors will result in a higher suspect concentration estimate, while a high response factor will result in lower suspect concentration estimates. The two high abundance suspects (AmPr-FASA-PrA and CEtAmPr-FASA-PrA) may have low molar response factors, which would make d5-N-EtFOSAA an inappropriate surrogate. However, analytical standards are needed to confirm this hypothesis.

Table C1. Target PFAS, acronym, neutral molecular formula, and surrogate standard for analysis by QToF.

Chemical Name	**Acronym**	**Neutral Molecular Formula**[1]	**Surrogate Standard**
Perfluoro-n-butanoic acid	PFBA[2]	C4HO2F7	MPFBA
Perfluoro-n-pentanoic acid	PFPeA	C5HO2F9	M3PFPeA
Perfluoro-n-hexanoic acid	PFHxA	C6HO2F11	M2PFHxA
Perfluoro-n-heptanoic acid	PFHpA	C7HO2F13	M4PFHpA
Perfluoro-n-octanoic acid	PFOA	C8HO2F15	M4PFOA
Perfluoro-n-nonanoic acid	PFNA	C9HO2F17	M5PFNA
Perfluoro-n-decanoic acid	PFDA	C10HO2F19	MPFDA
Perfluoro-n-undecanoic acid	PFUdA	C11HO2F21	MPFUdA
Perfluoro-n-dodecanoic acid	PFDoA	C12HO2F23	MPFDoA
Perfluoro-n-tridecanoic acid	PFTrDA	C13HO2F25	MPFDoA
Perfluoro-n-tetradecanoic acid	PFTeDA	C14HO2F27	M2PFTeDA
Perfluoro-n-hexadecanoic acid	PFHxDA	C16HO2F31	M2PFHxDA
Perfluoropropane sulfonate	PFPrS	C3HO3SF7	M3PFBS
Perfluorobutane sulfonate	PFBS	C4HO3SF9	M3PFBS
Perfluoropentane sulfonate	PFPeS	C5HO3SF11	M3PFBS
Perfluorohexane sulfonate	PFHxS	C6HO3SF13	MPFHxS
Perfluoroheptane sulfonate	PFHpS	C7HO3SF15	MPFOA
Perfluorooctane sulfonate	PFOS	C8HO3SF17	MPFOS
Perfluorononane sulfonate	PFNS	C9HO3SF19	MPFOS
Perfluorodecane sulfonate	PFDS	C10HO3SF21	MPFOS
Perfluorododecane sulfonate	PFDoS	C12HO3SF25	MPFOS
8-chloro-perfluorooctane sulfonate	Cl-PFOS	C8HClF16SO3	MPFOS
Perfluoroethylcyclohexane sulfonate	PFEtCHxS	C8HO3SF15	MPFHxS
Perfluorobutane sulfonamide	FBSA	C4H2O2NSF9	M8FOSA
Perfluorohexane sulfonamide	FHxSA	C6H2O2NSF13	M8FOSA
Perfluorooctane sulfonamide	FOSA	C8H2O2NSF17	M8FOSA
N-methylperfluoro-1-octane sulfonamide	MeFOSA	C9H4O2NSF17	d-N-MeFOSA-M
N-ethylperfluoro-1-octane sulfonamide	EtFOSA	C10H6O2NSF17	d-N-EtFOSA-M
Perfluorooctane sulfonamido acetic acid	FOSAA	C10H4O4NSF17	d3-N-MeFOSAA
N-methylperfluorooctane sulfonamido acetic acid	MeFOSAA	C11H6O4NSF17	d3-N-MeFOSAA
N-ethylperfluorooctane sulfonamido acetic acid	EtFOSAA	C12H8O4NSF17	d5-N-EtFOSAA
4:2 fluorotelomer sulfonate	4:2 FTS	C6H5O3SF9	M2-4:2FTS
6:2 fluorotelomer sulfonate	6:2 FTS	C8H5O3SF13	M2-6:2FTS

8:2 fluorotelomer sulfonate	8:2 FTS	C10H5O3SF17	M2-8:2FTS
10:2 fluorotelomer sulfonate	10:2 FTS	C12H5O3SF21	M2-8:2FTS
3:3 fluorotelomer carboxylic acid	3:3 FTCA	C6H5O2F7	M6:2FTA
5:3 fluorotelomer carboxylic acid	5:3 FTCA	C8H5O2F11	M6:2FTA
7:3 fluorotelomer carboxylic acid	7:3 FTCA	C10H5O2F15	M8:2FTA
6:2 fluorotelomer carboxylic acid	6:2 FTCA	C8H3O2F13	M6:2FTA
8:2 fluorotelomer carboxylic acid	8:2 FTCA	C10H3O2F17	M8:2FTA
10:2 fluorotelomer carboxylic acid	10:2 FTCA	C12H3O2F21	M10:2FTA
2H-Perfluoro-2-octenoic acid (6:2)	6:2 UFTCA	C8H2O2F12	M6:2FTUA
2H-Perfluoro-2-decenoic acid (8:2)	8:2 UFTCA	C10H2O2F16	M8:2FTUA
dodecafluoro-3H-4,8-dioxanonanoate	ADONA	C7H2O4F12	MPFNA
9-chlorohexadecafluoro-3-oxanonane-1-sulfonate	9Cl-PF3ONS	C8HF16ClSO4	MPFOS
11-chloroeicosafluoro-3-oxaundecane-1-sulfonate	11Cl-PF3OUdS	C10HF20ClSO4	MPFOS
2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoro propoxy)-propanoic acid	HFPO-DA	C6HF11O3	MHFPO-DA
bis(1H,1H,2H,2H-perfluorooctyl)phosphate	6:2diPAP	C16H9F26O4P	M4 8:2 diPAP
bis(1H,1H,2H,2H-perfluorodecyl)phosphate	8:2diPAP	C20H9F34O4P	M4 8:2 diPAP
bis-[2-(N-ethylperfluorooctane-1-sulfonamide)ethyl]phosphate	diSAmPAP	C24H19F34N2O8PS2	M4 8:2 diPAP

[1] $[M-H]^-$ adducts were used for quantification

[2] MRM transitions of 213 to 169 and 217 to 172 were used for quantification of PFBA and MPFBA, respectively, to reduce background.

Table C2. Target PFAS acronym, accuracy as indicated by % recovery, precision as indicated by % relative standard deviation (RSD), and limits of detection and quantification in **L**NAPL by LC-QToF.

Chemical Name	Acronym	Accuracy (% Recovery)	Precision (%RSD)	LOD (ng/L)	LOQ (ng/L)
Perfluoro-n-butanoic acid	PFBA*[2]	89	24	28	92
Perfluoro-n-pentanoic acid*	PFPeA*	92	1	33	109
Perfluoro-n-hexanoic acid*	PFHxA*	106	4	27	89
Perfluoro-n-heptanoic acid*	PFHpA*	87	5	25	83
Perfluoro-n-octanoic acid*	PFOA*	95	4	25	84
Perfluoro-n-nonanoic acid*	PFNA*	93	4	28	92
Perfluoro-n-decanoic acid	PFDA	106	11	26	87
Perfluoro-n-undecanoic acid	PFUdA	105	8	28	93
Perfluoro-n-dodecanoic acid	PFDoA	113	6	29	95
Perfluoro-n-tridecanoic acid	PFTrDA*	75	9	31	102
Perfluoro-n-tetradecanoic acid	PFTeDA	114	7.7	37	123
Perfluoro-n-hexadecanoic acid	PFHxDA	103	18	32	106
Perfluoropropane sulfonate	PFPrS*	99	1	29	96
Perfluorobutane sulfonate*	PFBS	100	3	28	92
Perfluoropentane sulfonate	PFPeS*	86	9	25	83
Perfluorohexane sulfonate*	PFHxS*	87	5	27	91
Perfluoroheptane sulfonate	PFHpS*	95	12	25	83
Perfluorooctane sulfonate*	PFOS	85	9	26	85
Perfluorononane sulfonate	PFNS*	83	8	23	77
Perfluorodecane sulfonate	PFDS*	63	10	22	74
Perfluorododecane sulfonate	PFDoS*	34	20	25	83
8-chloro-perfluorooctane sulfonate	Cl-PFOS*	98	8	23	76
Perfluoroethylcyclohexane sulfonate	PFEtCHxS*	86	5	22	74
Perfluorobutane sulfonamide	FBSA[a]	139	11	NC	NC
Perfluorohexane sulfonamide	FHxSA*	106	14	30	98
Perfluorooctane sulfonamide	FOSA	79	15	26	85
N-methylperfluoro-1-octane sulfonamide	MeFOSA	NR	NR	NA	NA
N-ethylperfluoro-1-octane sulfonamide	EtFOSA	NR	NR	NA	NA
Perfluorooctane sulfonamido acetic acid	FOSAA*	131*	13	22	73

N-methylperfluorooctane sulfonamido acetic acid	MeFOSAA	98	3	42	138
N-ethylperfluorooctane sulfonamido acetic acid	EtFOSAA	97	3	31	102
4:2 fluorotelomer sulfonate	4:2 FTS	112	8	34	113
6:2 fluorotelomer sulfonate	6:2 FTS	102	4	29	96
8:2 fluorotelomer sulfonate	8:2 FTS	101	4	24	79
10:2 fluorotelomer sulfonate	10:2 FTS	65	15	26	84
3:3 fluorotelomer carboxylic acid	3:3 FTCA*,[a]	28	24	NC	NC
5:3 fluorotelomer carboxylic acid	5:3 FTCA*,[a]	14	70	NC	NC
7:3 fluorotelomer carboxylic acid	7:3 FTCA*	16	73	48	157
6:2 fluorotelomer carboxylic acid	6:2 FTCA	106	17	35	115
8:2 fluorotelomer carboxylic acid	8:2 FTCA	126	20	63	209
10:2 fluorotelomer carboxylic acid	10:2 FTCA	155	35	36	119
2H-Perfluoro-2-octenoic acid (6:2)	6:2 UFTCA	111	13	35	115
2H-Perfluoro-2-decenoic acid (8:2)	8:2 UFTCA	133	18	22	73
dodecafluoro-3H-4,8-dioxanonanoate	ADONA*	107	9	26	86
9-chlorohexadecafluoro-3-oxanonane-1-sulfonate	9Cl-PF3ONS*	80	7	24	79
11-chloroeicosafluoro-3-oxaundecane-1-sulfonate	11l-PF3OUdS*	55	8	24	79
2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoro propoxy)-propanoic acid	HFPO-DA	124	12	33	110
bis(1H,1H,2H,2H-perfluorooctyl)phosphate	6:2diPAP*	312	17	29	96
bis(1H,1H,2H,2H-perfluorodecyl)phosphate	8:2diPAP	88	14	37	124
bis-[2-(N-ethylperfluorooctane-1-sulfonamide)ethyl]phosphate	diSAmPAP*	15	45	91	302
M4PFOA surrogate (n=16)		70	13	NA	NA
MPFOS surrogate (n=16)		69	12	NA	NA

* does not have a matched stable-isotope labeled surrogate standard (see Table S1)

[a] an accuracy and precision are reported because the target spike concentration was 500 ng/L; no LOD or LOQ are reported since no area counts were observed for the spike range 0- 100 ng/L (see NC footnote)
NA = not applicable
NC = no area counts observed, so LOD was computed (and thus no LOQ)
NR = No recovery (analyte not extracted into methanol)

Table C3. Semi-quantification (mg/L) of select suspect sulfonamide-based PFAS in 3M AFFF determined from 'PFAS Curve' compared to one-to-one matching.[4] The NIST number can be used to look up the molecule on the NIST list, which has structural information (e.g., International Chemical Identifier or InChI).

Suspect	**NIST Number[3]**	**Estimated concentration from 'PFAS Curve'**	**Hao et al.[4]**
AmPr-FEtSA-PrA	3642	66.7	77.9
AmPr-FPrSA-PrA	3643	323	1672
AmPr-FBSA-PrA	3644	315	3052
AmPr-FPeSA-PrA	71	367	1442
AmPr-FHxSA-PrA	72	791	4966
AmPr-FHpSA-PrA	150	38.6	26.0
CEtAmPr-FEtSA-PrA	157	8.9	13.6
CEtAmPr-FPrSA-PrA	190	64.2	639
CEtAmPr-FBSA-PrA	280	54.6	1127
CEtAmPr-FPeSA-PrA	281	71.8	702
CEtAmPr-FHxSA-PrA	380	260	1924
CEtAmPr-FHpSA-PrA	519	0.4	16.8
CEtAmPr-FOSA-PrA	663	1.7	9.1

Table C4. Concentrations (ng/L) of target PFAS for all 17 LNAPL samples.

Sample Name	LNAPL 1	LNAPL 2	LNAPL 3	LNAPL 4	LNAPL 5	LNAPL 6	LNAPL 7	LNAPL 8	LNAPL 9	LNAPL 10
PFBA	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PFPeA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOQ	<LOD
PFHxA	LOD	<LOQ	<LOD	**152**	<LOD	<LOQ	<LOD	<LOD	<LOQ	<LOQ
PFHpA	<LOQ	<LOQ	<LOD	**1005**	<LOD	<LOQ	<LOD	<LOD	<LOD	<LOD
PFOA	**457**	<LOQ	**106**	31	<LOQ	**304**	<LOD	<LOQ	<LOQ	<LOQ
PFNA	<LOQ	<LOD	<LOQ	<LOQ	<LOQ	<LOQ	<LOD	<LOQ	<LOQ	<LOQ
PFDA	**116**	<LOD	<LOQ	<LOQ	<LOD	<LOQ	<LOD	<LOD	<LOQ	<LOQ
PFUdA	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOQ	<LOD
PFDoA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFTrDA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFTeDA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFHxDA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFPrS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFBS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFPeS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFHxS	**204**	<LOQ	**91**	<LOD	<LOQ	**124**	<LOD	<LOQ	<LOQ	<LOQ
PFHpS	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFOS	**11064**	<LOQ	**3180**	**262**	<LOQ	**3985**	<LOD	**1434**	**379**	2655
PFNS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ
PFDS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD
PFDoS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Cl-PFOS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFEtCHxS	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
FBSA	**981**	<LOD	**1765**	<LOD	<LOD	**3037**	<LOD	<LOD	<LOQ	**92**
FHxSA	**39096**	45	**67551**	<LOD	<LOQ	**55197**	<LOD	**546**	**6829**	**16921**
FOSA	<LOQ	<LOD	**2497**	<LOQ	<LOD	**2043**	<LOD	<LOD	**1487**	**1667**
MeFOSA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

EtFOSA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
FOSAA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
MeFOSAA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
EtFOSAA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD
4:2 FTS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOQ	<LOD
6:2 FTS	<LOD	**1643**	<LOD	**6041**	<LOQ	<LOQ	<LOD	<LOQ	**321**	**349**
8:2 FTS	**488**	<LOQ	<LOD	**248**	<LOD	<LOQ	<LOD	<LOD	**366**	**587**
10:2 FTS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	**141**
3:3 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
5:3 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
7:3 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
6:2 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
8:2 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
10:2 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
6:2 UFTCA	<LOD	<LOQ	<LOD	**5642**	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
8:2 UFTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
ADONA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
9Cl-PF3ONS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
11l-PF3OUdS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
HFPO-DA decarboxylated	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
6:2 diPAP	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
8:2 diPAP	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
diSAmPAP	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

Table C4 continued. Concentrations (ng/L) of target PFAS for all 17 LNAPL samples.

Sample Name	11	12	13	14	15	16	17
PFBA	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PFPeA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFHxA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ
PFHpA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ
PFOA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**100**
PFNA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFDA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ
PFUdA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFDoA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFTrDA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFTeDA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFHxDA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFPrS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFBS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFPeS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFHxS	<LOD	<LOQ	<LOD	<LOQ	<LOD	<LOQ	<LOQ
PFHpS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFOS	<LOD	<LOQ	<LOQ	**110**	<LOQ	<LOQ	**1020**
PFNS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFDS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFDoS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Cl-PFOS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFEtCHxS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
FBSA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
FHxSA	<LOQ	**206**	<LOQ	**1490**	<LOD	<LOD	<LOD
FOSA	<LOD	**104**	<LOD	<LOD	<LOD	<LOD	<LOD
MeFOSA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
EtFOSA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
FOSAA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

MeFOSAA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
EtFOSAA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
4:2 FTS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
6:2 FTS	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD	**1130**
8:2 FTS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**712**
10:2 FTS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ
3:3 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
5:3 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
7:3 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
6:2 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
8:2 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
10:2 FTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
6:2 UFTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
8:2 UFTCA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
ADONA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
9Cl-PF3ONS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
11l-PF3OUdS	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
HFPO-DA decarboxylated	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
6:2 diPAP	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
8:2 diPAP	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
diSAmPAP	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

Figure C1. Molar response factors for PFAS based on analytical standards