Uptake and transformation of per- and polyfluoroalkyl substances from aqueous film-forming foams in concrete

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In memory of my father

Abstract

The significant environmental occurrence of per- and polyfluoroalkyl substances (PFAS) due to their ubiquity in many consumer and industrial products combined with their potentially harmful health effects has caused increased attention from regulators in recent years. A significant source of PFAS contamination is the utilization of aqueous film-forming foams (AFFF) in combatting class B fires at airports, military bases, and firefighter training facilities. Extensive research has investigated PFAS contamination across solid and aqueous matrices, encompassing surface water, wastewater, groundwater, biosolids, and soils. Contamination of concrete - an often-overlooked matrix and potential PFAS source - remains underexplored, particularly at military bases and airports. As a ubiquitous construction material globally, concrete is directly exposed to AFFF during training exercises, particularly in the form of ground slabs at impacted sites. Limited studies examining concrete from these sites have revealed substantial PFAS presence stemming from both electrochemical fluorination (ECF)-based and fluorotelomer (FT)-based AFFFs, highlighting concrete's potential for long-term PFAS leaching even years after AFFF activities have ceased. Numerous questions persist regarding AFFF contamination of concrete, including diffusion rates, the influence of AFFF additives, and concrete-PFAS chemical interactions, warranting further investigation. This thesis aims to understand the physicochemical interactions between concrete and AFFF under conditions mimicking those at impacted sites to better understand the ultimate fate of PFAS upon initial exposure to concrete in the environment.

First, laboratory-based experiments were conducted to assess the artificial PFAS contamination of concrete using individual PFAS and ECF AFFF. Evaluation of PFAS uptake in concrete encompassed flat finished surfaces and chipped surfaces to simulate aged concrete variability. Additionally, various PFAS within an AFFF mix, including dominant perfluorosulfonic acids (PFSAs) and precursors, were examined using high-resolution mass spectrometry. Analysis of PFAS and AFFF solutions pooled onto concrete surfaces revealed no significant concentration decrease, while examination of powder from lab-contaminated cores indicated PFAS diffusion primarily within the top 0.5 cm of the core, with faster penetration observed in chipped surface concrete compared to flat surface. The contradiction was because PFAS mass in concrete cores only represented a small fraction (1.3% to 10.8%, mean 3.9%) of initial spiked PFAS. A correlation between decreasing PFAS chain length and increased mobility

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or diffusivity through cores was evident, suggesting that AFFF additives influence PFAS diffusion in concrete. Furthermore, intermittent wetting and drying cycles accelerated PFAS penetration, albeit equally for PFAS of differing chain lengths, probably due to the wicking effect. Cores from a Canadian military base contained a mix of ECF and FT PFAS, with 6:2 fluorotelomer sulfonate (6:2 FTSA) being most abundant in the top 1 cm of the core, with perfluoroctanesulfonic acid (PFOS) being dominant throughout the rest of the core suggesting a recent switch from ECF to FT foams.

A comprehensive extraction method for PFAS from AFFF-affected concrete, validated through spike-recovery trials, was also developed in this work. Seven solvent conditions were assessed for their efficiency in extracting perfluoroalkyl acids (PFAAs) and 14 distinct precursor classes present in ECF-based AFFF-contaminated concrete powder. Methanol with 100 mM ammonium acetate was the optimal solvent for extracting a broad spectrum of anionic, cationic, and zwitterionic compounds, although other solvent conditions exhibited comparable recovery rates for most PFAS. Recovery analysis of perfluorocarboxylic acids (PFCAs), perfluoroalkyl sulfonamides (FASAs), and perfluoroalkyl amido amines (PFAAAm) compounds indicated high recoveries for PFCAs and FASAs, contrasting with notably low recoveries for PFAAAm compounds, implying rapid degradation of amide-containing precursors during extraction. This degradation mechanism was attributed to alkaline hydrolysis facilitated by calcium hydroxide leaching from concrete. Additionally, investigations into sulfonamide precursors suggested salting-out effects rather than compound degradation as the primary cause for their rapid concentration decrease.

This work provides important findings on the kinetics of uptake of PFAS into concrete from AFFF, as well as potential transformations that can occur at concrete-water interfaces, within concrete, and during extraction.

Résumé

La présence importante dans l'environnement de substances per- et polyfluoroalkyles (PFAS) en raison de leur omniprésence dans de nombreux produits de consommation et industriels, combinée à leurs effets potentiellement nocifs sur la santé, a suscité une attention accrue de la part des autorités de réglementation au cours des dernières années. L'utilisation de mousses aqueuses filmogènes (AFFF) pour lutter contre les incendies de classe B dans les aéroports, les bases militaires et les centres de formation des pompiers constitue une source importante de contamination par les PFAS. Des recherches approfondies ont été menées sur la contamination par les PFAS dans les matrices solides et aqueuses, y compris les eaux de surface, les eaux usées, les eaux souterraines, les biosolides et les sols. La contamination du béton - une matrice souvent négligée et une source potentielle de PFAS - reste sous-explorée, en particulier dans les bases militaires et les aéroports. En tant que matériau de construction omniprésent dans le monde, le béton est directement exposé aux AFFF lors des exercices d'entraînement, en particulier sous la forme de dalles de sol sur les sites touchés. Des études limitées portant sur le béton de ces sites ont révélé la présence substantielle de PFAS provenant d'AFFF à base de fluorure électrochimique (ECF) et de fluorotélomère (FT), soulignant le potentiel de lixiviation à long terme des PFAS dans le béton, même des années après l'arrêt des activités AFFF. De nombreuses questions persistent concernant la contamination du béton par les AFFF, notamment les taux de diffusion, l'influence des additifs AFFF et les interactions chimiques entre le béton et les PFAS, ce qui justifie des recherches plus approfondies. Cette thèse vise à comprendre les interactions physico-chimiques entre le béton et l'AFFF dans des conditions reproduisant celles des sites impactés, afin de mieux comprendre le devenir ultime des PFAS lors de l'exposition initiale du béton dans l'environnement.

Tout d'abord, des expériences en laboratoire ont été menées pour évaluer la contamination artificielle du béton par les PFAS individuels et les AFFF ECF. L'évaluation de l'absorption des PFAS dans le béton a porté sur des surfaces finies planes et des surfaces écaillées pour simuler la variabilité du béton vieilli. En outre, divers PFAS dans un mélange AFFF, y compris les acides perfluorosulfoniques (PFSA) dominants et les précurseurs, ont été examinés à l'aide de la spectrométrie de masse à haute résolution. L'analyse des PFAS et des solutions AFFF déposées sur les surfaces en béton n'a révélé aucune diminution significative de la concentration, tandis que l'examen de la poudre provenant de carottes contaminées en

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laboratoire a révélé une diffusion des PFAS principalement dans les 0,5 cm supérieurs de la carotte, avec une pénétration plus rapide observée dans le béton à surface écaillée que dans le béton à surface plane. Cette contradiction s'explique par le fait que la masse de PFAS dans les carottes de béton ne représentait qu'une petite fraction (de 1,3 % à 10,8 %, moyenne de 3,9 %) des PFAS initialement dopés. Une corrélation entre la diminution de la longueur de la chaîne des PFAS et l'augmentation de la mobilité ou de la diffusivité à travers les carottes était évidente, ce qui suggère que les additifs AFFF influencent la diffusion des PFAS dans le béton. En outre, des cycles intermittents de mouillage et de séchage ont accéléré la pénétration des PFAS, bien que de manière égale pour les PFAS de différentes longueurs de chaîne, probablement en raison de l'effet de mèche. Les carottes provenant d'une base militaire canadienne contenaient un mélange d'ECF et de FT PFAS, le sulfonate de fluorotélomère 6:2 (6:2 FTSA) étant le plus abondant dans les 1 cm supérieurs de la carotte, l'acide perfluoroctanesulfonique (PFOS) étant dominant dans le reste de la carotte, ce qui suggère un passage récent des mousses ECF aux mousses FT.

Une méthode complète d'extraction des PFAS du béton contaminé par l'AFFF, validée par des essais de récupération de pointes, a également été mise au point dans le cadre de ce travail. Sept conditions de solvants ont été évaluées pour leur efficacité à extraire les acides perfluoroalkyles (PFAA) et 13 classes distinctes de précurseurs présents dans la poudre de béton contaminée par l'AFFF à base d'ECF. Le méthanol avec 100 mM d'acétate d'ammonium était le solvant optimal pour extraire un large spectre de composés anioniques, cationiques et zwitterioniques, bien que d'autres conditions de solvant aient présenté des taux de récupération comparables pour la plupart des PFAS. L'analyse de la récupération des acides perfluorocarboxyliques (APFC), des sulfonamides perfluoroalkyles (FASA) et des composés perfluoroalkyles amido amines (PFAAAm) a révélé des taux de récupération élevés pour les APFC et les FASA, contrastant avec des taux de récupération particulièrement faibles pour les composés PFAAAm, ce qui implique une dégradation rapide des précurseurs contenant des amides au cours de l'extraction. Ce mécanisme de dégradation a été attribué à l'hydrolyse alcaline facilitée par la lixiviation de l'hydroxyde de calcium du béton. En outre, les recherches sur les précurseurs sulfonamides ont suggéré que les effets de salage plutôt que la dégradation des composés étaient la cause principale de la diminution rapide de leur concentration.

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Ce travail fournit des résultats importants sur la cinétique d'absorption des PFAS dans le béton à partir de l'AFFF, ainsi que sur les transformations potentielles qui peuvent se produire aux interfaces béton-eau, à l'intérieur du béton et pendant l'extraction.

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List of Abbreviations

AFFF	Aqueous film-forming foam					
ASTM	American Society for Testing and Materials					
ATP	Adenosine triphosphate					
CIC	Combustion ion chromatography					
DESI MSI	Desorption electrospray ionization mass spectrometry imaging					
ECF	Electrochemical fluorination					
EPA	Environmental Protection Agency					
FAA	Federal Aviation Administration					
FASA	Perfluoroalkyl sulfonamide					
FT	Fluorotelomer					
FTA	Firefighter training area					
FTOH	Fluorotelomer alcohol					
FTSA	Fluorotelomer sulfonate					
HALT	Hydrothermal alkaline treatment					
HR-CS-AAS	High-resolution-continuum source-atomic absorption spectroscopy					
HRMS	High-resolution mass spectrometry					
IC	Ion chromatography					
LC-MS/MS	Liquid chromatography-mass spectrometry/mass spectrometry					
MS	Mass spectrometry					
PFAA	Perfluoroalkyl acid					
PFAAAm	N-dimethyl ammonio propyl perfluoroalkane amide					
PFAS	Per- and polyfluoroalkyl substance					
PFCA	Perfluorocarboxylic acid					
PFOA	Perfluorooctanoic acid					
PFOS	Perfluorooctanesulfonic acid					
PFSA	Perfluorosulfonic acid					
PFSAm	N-dimethyl ammonio propyl perfluoroalkane sulfonamide					
PFSAmS	N-trimethyl ammonio propyl perfluoroalkane sulfonamide					
SEM-EDS	Scanning electron microscopy-energy dispersive x-ray spectroscopy					
TF	Total fluorine					
ТОР	Total oxidizable precursors					
UHPLC	Ultra-high-performance liquid chromatography					

Contribution of Authors

This thesis is presented in a manuscript-based format. A general introduction and literature review are presented in Chapters 1 and 2. Chapters 3 and 4 comprise the two manuscripts that are in preparation for submission to peer-reviewed journals. Chapter 5 summarizes the work completed from the two manuscripts and proposes future research directions. Appendices A and B contain respective supplementary information for the two manuscripts presented.

The literature review, design and performing of experiments, analysis and interpretation of experimental data, and preparation of the manuscripts for publication were performed by the candidate, David Lutes, under the supervision of Drs. Jinxia Liu and Andrew Boyd. A detailed description of the efforts of contributing authors to each manuscript is presented below.

Chapter 3. Lutes, D.; Boyd, A.; Liu, J., Uptake of per- and polyfluoroalkyl substances into concrete from aqueous film-forming foams: Experimental investigations and comparison to field-impacted samples.

Lutes, D. Designed the study, conducted the experimental procedures, analyzed the results, and drafted and edited the manuscript.

Boyd, A. Contributed to the study design and revised the manuscript.

Liu, J. Acquired the funding, defined the research scope and objectives, contributed to the study design, contributed to the interpretation of results, and revised the manuscript.

Chapter 4. Lutes, D.; Boyd, A.; Liu, J., Abiotic transformation of per- and polyfluoroalkyl substances in the presence of concrete: Implications for chemical extraction and contamination characterization.

Lutes, D. Designed the study, conducted the experimental procedures, analyzed the results, and wrote the manuscript.

Boyd, A. Revised the manuscript.

Liu, J. Acquired the funding, defined the research scope and objectives, contributed to the study design, contributed to the interpretation of results, and revised the manuscript.

CHAPTER 1. Introduction

1.1 Background

Per- and polyfluoroalkyl substances (PFAS) are a group of synthetic chemicals that are characterized by the presence of carbon-fluorine bonds. First developed in the 1940s and 50s, they have been used in many consumer and industrial products for their water-repellant and surfactant properties, including cosmetics, cookware, textiles, and aqueous film-forming foams (AFFF).¹ PFAS has garnered considerable attention from the general public and government regulators in recent years due to abundant research on their environmental persistence, toxicity, and bioaccumulation in humans and wildlife.²⁻⁶ Despite this plethora of research, many questions on the environmental fate of PFAS remain unanswered, particularly in research areas with limited knowledge.⁷⁻⁹ The ubiquity and distribution of PFAS in various environmental matrices around the world,^{10, 11} coupled with their comparatively low regulatory maximum contaminant level (MCL),¹² underscore the pressing need to answer these questions. This urgency arises from identified and unidentified health effects and the potential for elevated exposure in areas surrounding PFAS-impacted sites.¹³

The most common source of PFAS contamination in the environment by the magnitude of mass is from AFFFs¹⁴, despite them being the smallest contributor to the number of presumptive contaminated sites in terms of contamination source.¹⁵ AFFF is a type of firefighting foam used to fight class B, or hydrocarbon fuel fires, that is used at airports, military bases, and other training areas due to its high performance at extinguishing these types of fires.¹⁶ The mechanism of action is that the foam forms a thin film that coats the surface of the fire, causing oxygen to be cut off from the active fire and preventing reignition. The foam is also used proactively in areas not yet consumed by fire to stop its spread by coating the object or surface in the foam, preventing breakthrough.¹⁷ The first major use of AFFFs was in the 1970s on military bases and naval vessels in the US, and the uses then expanded to major civilian airports and fire departments after its joint development by the US Navy and the 3M Company (3M).¹⁸

After the phase-out of perfluorooctanesulfonic acid (PFOS) by 3M in 2000~2022, production of electrochemical fluorination (ECF)-based foams that contained PFOS and related chemicals as the dominant PFAS ceased, and switch to fluorotelomer(FT)- based-AFFFs was made.¹⁹ However, fluorotelomer-based- AFFFs have also been used since the 1970s, though less for military installations and more for civic applications.²⁰ Interventions in the mid-2010s began limiting the uses of both types of AFFFs further, and PFAS-free or fluorine-free foams are

gaining popularity in the amidst of the global efforts to eliminate PFAS for non-essential uses continue.²¹ Up to this point, AFFFs had been released unhindered into the environment for nearly 50 years at various military, civic and industrial sites. As a result of this prolonged period of continuous usage, there was heavy contamination of the environment surrounding sites that used them.^{16, 22} Efforts are underway today to remediate these numerous sites that exist, while some sites are still using fluorine-based foams, continuously contributing to the existing contamination.²³

Accurate assessment of AFFF-contaminated sites can be highly challenging for many reasons. Fluorosurfactants used in AFFFs are considered proprietary and thus do not have to be disclosed, making it difficult to characterize them. At many sites, foams of different chemistry or manufacturing processes may have been used based on regulations, directives, or availability at the time, which could have included ECF, FT, short-chain, and fluorine-free foams, making analysis based on the presence of certain foam-specific compounds difficult.²⁴ Site-specific factors, such as co-contaminant presence, may also complicate investigations, which is frequently the case at military bases. Finally, geographical factors, including climate, underlying soil type, site proximity to aquifers, and water table, may make assessment difficult.²⁵

The seminal work by Moody and Field (2000) highlighted the need to begin examining the environmental fate of AFFF at impacted sites due to its unknown but potentially harmful toxicity. This work sparked several other early studies by researchers which primarily focused on the detection of common PFAS, including PFOS and perfluorooctanoic acid (PFOA) in aquatic environments such as surface waters, wastewaters, and landfill leachates surrounding contaminated sites,²⁶⁻³⁰ validating the initial work by Moody and Field (2000), creating a call to action on PFAS and AFFF research.^{31, 32} As regulatory concerns of PFAS grew, technology in analytical methods advanced further to allow an increasingly larger suite of PFAS to be analyzed by mass spectrometry (MS) based methods, which in turn drew more researchers into the field, cycling between these three phases, leading to an exponential increase in the published work on PFAS in the last few years.^{33, 34}

So far, extensive research has been conducted on the environmental fate and transport of PFAS from AFFF contamination into the surrounding soil, groundwater, and surface water at contaminated sites, as these matrices are where AFFF is either directly or indirectly released

during discharge events. Important matrices often not examined but of particular significance at military bases and airports are construction materials, namely concrete and asphalt. The areas surrounding military bases and airports are constructed either concrete or asphalt, with smaller facilities using gravel or compacted soil. As the construction of military bases is considered sensitive information, limited information on the design of firefighter training areas (FTAs) at these sites exists. Information on FTA design requirements for civilian airports is also limited. According to published case studies investigating PFAS contamination at FTAs in the United States, Canada, and Australia, a concrete slab is usually used as the training platform near the fire station, and sometimes asphalt and concrete are combined. If a dedicated area near the fire station is not available, not constructed, or the site does not have a fire station, a surrounding piece of tarmac has also been shown to be used as a training site for AFFF use. It is important to note that AFFFs are often stored and used in other areas outside the FTA. They can be released inside or outside airplane hangars and AFFF storage facilities for equipment testing, fire drills, or due to spills or leakages. AFFFs can also impact runways and taxiways in the event of an actual fire or emergency. It has been common in the past to handle AFFFs without many precautions due to a lack of awareness of the toxic properties of AFFFs or PFAS in general.

Few studies have been published on AFFF interactions with concrete and asphalt since the initial work outlining AFFF contamination at impacted sites by Moody and Field (2000). From the limited work published, PFAS has been demonstrated to leach from AFFF-impacted concrete long after fire training activities have ceased, indicating that concrete can behave as a sponge, slowly releasing PFAS over an extremely long period.³⁵ Preliminary information on the initial uptake of PFAS into concrete, including chain length relationships, dominant species present, and sealants to use to mitigate release from concrete, has been presented. However, many knowledge gaps remain on the physicochemical interactions between concrete and AFFF. Specifically, there is a lack of published work in the kinetics of sorption, desorption and leaching, abiotic transformation, transport, and interaction with the matrices surrounding construction materials, including soil and groundwater.

In light of these knowledge gaps, a series of lab-based experiments were performed to explore the interactions between PFAS/AFFF and concrete and to elucidate many of these unknowns. Research has been conducted to determine the uptake and penetration of PFAS into concrete, as well as to investigate abiotic transformations of certain PFAS compounds present in

AFFFs. In addition, preliminary tests were carried out on AFFF-contaminated concrete removed from a Canadian military base.

1.2 Research Objectives

The purpose of the thesis is to examine the physicochemical interactions between concrete and AFFF under conditions mimicking those at impacted sites in order to better understand the ultimate fate of PFAS upon initial exposure to concrete in the environment. Three specific objectives are presented and examined further below:

- 1. To determine the extent of PFAS uptake by concrete surfaces:
 - To compare AFFF vs PFAS solutions to observe the effect of additives in AFFF;
 - To determine the effect of two different concrete surface types: flat and chipped;
 - To determine if wetting and drying cycles affect PFAS uptake into the matrix;
 - To examine the depth of penetration profile of PFAS into the concrete matrix.
- 2. To develop a method for extraction of a wide range of anionic, cationic, and zwitterionic PFAS from AFFF-impacted concrete:
 - To comparatively assess solvent additives on PFAS recovery;
 - To determine the recovery performance of perfluoroalkyls vs polyfluoroalkyl compounds.
- 3. To assess the potential transformation of precursors in AFFF when exposed to concrete:
 - To establish the kinetics of the generation of perfluoroalkyl compounds and transformation of polyfluoroalkyl chemicals in uptake and extraction experiments;
 - To evaluate the transformation of relevant amine-containing precursor compounds present in ECF-based AFFF;
 - Determine reaction pathways and mechanisms responsible for transformations.

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CHAPTER 2. Literature Review

2.1 Overview of PFAS and AFFF

Per- and polyfluoroalkyl substances (PFAS) are synthetic fluorochemicals that contain a fully or partially fluorinated hydrophobic carbon tail and, very often, non-fluorinated hydrophilic functional groups. Identified by the presence of repeating carbon-fluorine bonds, products coated or embedded with PFAS are resistant to water, oil, and heat. Applications of PFAS can be found in many consumer products and industrial applications, such as water-proof clothing, food packaging, paints, cookware, cosmetics, specialty surfactants, and many others.¹ The extremely strong carbon-fluorine bond gives PFAS their non-reactive and non-transformative chemical characteristics.² As a byproduct of their design, PFAS are considered persistent in both the environment and biota. Toxicological and epidemiological studies performed have shown that exposure to certain PFAS can cause suppressed immune function, thyroid disease, liver disease and cancer, kidney disease, and other cancers, but all depend heavily on the circumstances of exposure and factors associated with the individuals exposed.³ It has been well documented that some compounds have particularly long half-lives in human blood,^{4, 5} so chronic exposure to low levels of PFAS may have significant health implications.

2.1.1 Classification, production, and occurrence

The definition of PFAS has evolved over time. They are also limited by global location based on federal, state/provincial, or even municipal regulations, as each level offers its own often conflicting and differing regulations and definitions of PFAS. The United States Environmental Protection Agency (EPA) defines PFAS as containing one of the following structures: $R-(CF_2)-CF(R')R''$, where both the CF₂ and CF moieties are saturated carbons, and none of the R groups can be hydrogen, $R-CF_2OCF_2-R'$, where both the CF₂ moieties are saturated carbons. None of the R groups can be hydrogen, or $CF_3C(CF_3)RR'$, where all the carbons are saturated, and none of the R groups can be hydrogen (Figure 2.1).



 R_1 , R_2 , R_3 = nonhydrogen atoms



This definition can be considered quite broad, as over 15,000 individual compounds fall under this definition.⁶ A prior less specific definition set in 2011 is also commonly accepted and defines PFAS as containing the perfluoroalkyl moiety C_nF_{2n+1} , similar to the new EPA definition but encompassing a much smaller subset of compounds that fall under the current definition.⁷ In 2017, OECD broadened the PFAS definition to include any organic compounds that contain at least fully fluorinated carbon, which led to over 1 million entries in a still-evolving PFAS database.

As there are a vast number of compounds that exist regardless of the definition, PFAS are further broken down into different groups. At the highest level, they are separated into non-polymeric PFAS and polymeric PFAS, which includes polytetrafluoroethylene (PTFE), a compound used in many industrial products.⁸ They can be further broken down into *perfluoroalkyls*, which contain a fully fluorinated carbon chain, and *polyfluoroalkyls*, which contain a partially fluorinated carbon chain. The global production volume of polymeric PFAS is significantly higher than non-polymeric ones, but the latter has huge chemical variations, which make a comprehensive assessment of their environmental presence challenging. In this thesis, the PFAS under investigation fall under the non-polymeric type and are mainly used as fluorosurfactants.

Historically, fluorosurfactants were manufactured by a process known as electrochemical fluorination (ECF), which was used exclusively by 3M. This process starts with a raw organic aliphatic material that undergoes electrolysis with hydrogen fluoride, replacing the hydrogen atoms with fluorine atoms.⁹ As the process generates free radicals, undesirable products are generated, including branched perfluorinated isomers and other unintended PFAS species. Another dominant manufacturing process is fluorotelomerization (FT), which is used by most fluorochemical producers. In this production method, a perfluoroalkyl iodide is reacted with tetrafluoroethylene, forming a longer starting product, which is further reacted with ethylene to form a fluorotelomer in the form of n:2 where n is the number of fully fluorinated carbons and two represents the two fully hydrogenated carbons.⁷ Further functionalization steps create a variety of chemical structures with different types of hydrophilic functional groups. Both methods of production have been used in the manufacturing of AFFFs.¹⁰ In recent years, another fluorotelomer chemical family in the form of n:1:2 chemistry (1 representing a methyl branch)

has also been used in AFFF products, but little is known about the new chemical synthesis process.¹¹

Release of PFAS into the environment can come from various sources, including storage and applications of AFFF, manufacturing facilities that use some variation of PFAS, landfills, wastewater treatment plants, etc. As a result of prolonged use in both industrial and consumer products, PFAS have been detected worldwide in a variety of environmental matrices, including soil, groundwater, and surface waters, etc.^{12, 13} Many of these matrices can collect in surface waters where they may ultimately end up in a lake or river, which can be used as an intake source for a wastewater treatment plant. Despite their phase-out and regulation in recent years, they are often detected in areas with no prior industrial manufacturing link to PFAS or AFFF.¹⁴

2.1.2. AFFF contamination and environmental fate

The environmental fate of PFAS from AFFF sources at impacted sites has been relatively well documented with several case studies published in the existing literature. Various aspects of site-specific contamination have been explored, including distribution and occurrence, transport within the vadose zone, biotic transformation of precursors, and environmental implications associated with a release.¹⁵⁻²¹

Data from historical AFFFs show that anionic perfluoroalkyl sulfonates (PFSAs) comprise a large component of ECF-based foams, specifically C₈ and C₆ perfluoroalkyl chains, while in contrast, only trace amounts of perfluoroalkyl carboxylates (PFCAs) were found.²² The majority of precursors (to perfluoroalkyl acids (PFAAs) including PFSAs and PFCAs) identified in these foams can be grouped into one of two groups based on the attached functional group separating the fluorinated and non-fluorinated section of the compound; these two groups are sulfonamide-based precursors and amide-based precursors (shown in Figure 2.2).²³ Dominant precursors found in some foams were those belonging to the quaternary ammonium compounds and amines in the sulfonamide class. Precursors from FT-based foams have also been discovered; however, as they are less often used in military installations than ECF-based foams and thus investigated, there are still many questions on the environmental fate of these compounds.²⁴ FT-based precursors may also transform biotically to terminal PFCAs, which complicates the differentiation of PFCA sources based on types of AFFF used, when using non-

high resolution traditional liquid chromatography-mass spectrometry/mass spectrometry LC-MS/MS methods.²⁵



 $R_1 \& R_2$ = nonhydrogen atoms

Figure 2.2 Base structures of ECF-based precursors.

Sulfonamide-based precursors have been demonstrated to compose a large portion of 3M ECF-based AFFFs. Select precursor compounds have been observed to transform in laboratory experiments and contaminated sites. This is especially true for the most dominant C₆ precursor, *N*-dimethyl ammonio propyl perfluorohexane sulfonamide (PFHxSAm), and the transformation has often been reported in groundwater and aquifer solids.²⁶ The biotransformation of PFHxSAm to first perfluorohexanesulfonamide (FHxSA) and then the terminal product of PFHxS through likely nitrifying microbial activity with the generation of a few other intermediates has been reported, further elucidating the breakdown pathyway.^{27, 28} Further microbial biotransformations of other PFAA precursors in AFFF has been reported including PFOAB, PFOSB, PFOAAm, PFOSAm, PFOAAmS, PFOSAmS, PFOANO, and PFOSNO at varying degradation rates at varying time scales.²⁹ Various precursors from both foam types are known to undergo transformation into PFAAs, so it is important to characterize their presence at impacted sites in order to determine the full potential burden of these compounds.

Other aspects, including sorption, partitioning, and transport, have been discussed with multiple individual published works that investigate these environmental phenomena that can occur with PFAS at these sites.^{26, 30-32} As the work on characterizing AFFF-impacted sites has been extensive and generated many research publications too lengthy to summarize, a few topics relevant to this paper are discussed below.

2.2 PFAS characterization methods

Analysis of PFAS requires sophisticated instruments and robust analytical methodology. The most common type of analytical instrumentation used is liquid chromatography-mass

spectrometry (LCMS).³³ Depending on the type and resolution of the mass spectrometer used, very useful data can be obtained to generate a full PFAS profile when combining results with software tools. Successful characterization of PFAS, including important precursors at impacted sites, can be difficult without high-resolution instruments with time-of-flight or OrbitrapTM detectors. Triple quadrupole mass spectrometers have also been widely used for quantitative analysis of PFAS with available chemical standards. As the science of mass spectrometry advances and the technology becomes quite accessible, abundant information on specific PFAS has been published, including detailed analyses on precursors, which are of vital importance as precursors can comprise up to 100% of the components in AFFF.²⁶ If such instrumentation is not available, other analytical methods, such as the total oxidizable precursor (TOP) assay, can be performed by chemically transforming precursors present in a sample to terminal PFCAs so that an equivalent amount of PFAS can be estimated.³⁴ Alternatively, high-temperature combustion may be used to mineralize all PFAS present into fluoride, which is then measured using ion chromatography (IC) in a technique known as combustion ion chromatography (CIC).³⁵

Developing robust sample preparation methods is as important as employing suitable analytical instruments with proper quality control and assurance. Methods for extracting a wide array of PFAS from soil are well documented due to the prevalence of AFFF-contaminated soil.³⁶⁻³⁹ However, these methods can take many years to perfect because of huge variations of PFAS structures (thus properties) and also soil properties, and thus should not be taken for granted. Developing a method in an area with little existing research, such as extracting PFAS from impacted construction materials, can be difficult because of the lack of existing knowledge and the contrasting chemistry of PFAS and concrete. Regardless, there have been many different methods developed for the extraction of PFAS in many environmental and non-environmental matrices, including waters and wastewaters, plants, mammalian tissues, plasma and serum, dairy milk, solids and sediments, bird feathers, and even human hair.⁴⁰⁻⁴⁹

Despite recently published works on the characterization of the numerous different classes of precursors in AFFF, there remain few analytical standards for these compounds, making accurate quantitative analysis impossible. Synthesis of all relevant precursors is technically challenging and prohibitively expensive, thus unrealistic in the short term. However, some compounds with analytical standards that structurally resemble the precursor analyte may

be used to semi-quantify the precursor of interest. Having full-scan data of a particular field sample from an impacted site, coupled with either total organofluorine data (via CIC) or equivalent total oxidizable precursors (via TOP assay), can determine the degree of contamination, regardless of the availability of analytical standards for precursors. Despite the limitations of both CIC and TOP assays, with the most noteworthy limitation being less than 100% conversion and recovery rates in complex matrices, these two methods can be useful as complementary methods to full-scan LCMS to regulators, remediation practitioners and other stakeholders.

2.3 Abiotic transformation of precursors

As stated previously, the naturally occurring biotic transformation of precursors at AFFFimpacted sites has been well-documented; however, the natural abiotic transformation of precursors, which is relevant to this thesis, is not well explored or understood. In contrast, as treatment technologies, many abiotic processes for both precursors and non-precursors, including oxidation processes, photolysis and photocatalysis, reduction processes, and thermal decomposition, have been intensively studied.⁵⁰ However, those engineered processes are usually achieved under conditions that deviate from natural redox environments and/or temperatures.

Abiotic transformation of PFOANO and PFOSNO (perfluoroalkyl amine oxides) has been reported with a short DT₅₀ (the time it takes for 50% mass to disappear) of 3-7 days for PFOANO and 15 days for PFOSNO and the unusually fast degradation is hypothesized to come from low stability arising from the amine oxide group.⁵¹ Potential transformation of PFHxSAm to FHxSA-PrA and PFHxSi in autoclaved controls in a biotransformation experiment has been demonstrated, indicating the possible abiotic transformation of this compound; however, quantitative estimates were not given by the authors.²⁸

Another abiotic process to consider for precursors is hydrolysis. Previous work of inducing hydrolysis reactions in alkaline conditions can form fluorotelomer alcohols (FTOHs) from some fluorotelomers in a fast reaction (<1 day).⁵² Further work published on side-chain fluoropolymers (SFPs) in textiles confirmed the earlier work that some fluoropolymers can abiotically transform to FTOHs but also found that some PFCAs can form through this reaction.⁵³ Specific rate kinetics showed that as pH increased linearly, the rate of hydrolysis products from fluoropolymers increased exponentially, with some fluoropolymers having a half-

life of ~0.7 years when pH reaches above 12. This was in contrast to neutral-mediated hydrolysis, which showed a half-life of 55-89 years for the same fluoropolymers tested.⁵⁴ It was also estimated that the generation of these FTOHs, which can transform into terminal PFCAs, will greatly increase the load of PFCAs detected in oceanic waters due to the volatile nature of FTOHs and their atmospheric transport potential.

Another process where base accelerates the decomposition of non-fluoropolymer PFAS at higher temperatures and pressures has been studied, known as hydrothermal alkaline treatment (HALT).⁵⁵ In this process, subcritical pressure and temperatures combined with strong alkaline conditions can destroy even the recalcitrant PFAS. Simple hydrothermal treatment alone can break down many PFAAs given sufficient time, but this reaction is much more efficient and rapid under alkaline conditions.⁵⁵

Depending on the amount of base added, these reactions can occur rapidly, leading to almost 100% defluorination in under one hour, often without any detectable intermediates or transformation products, yielding fluoride as the net result.⁵⁶ This technique has been applied to impacted groundwater and soil where destruction efficiencies remain high (94-99.9%), although slightly lower than benchtop experiments with spiked water.^{57, 58}. The degradation of AFFF precursors has also been tested and tends to break down to terminal PFCAs/PFSAs much faster (15 min) than PFAAs breakdown under the same conditions.⁵⁹ The effect of the added base to create alkaline conditions is hypothesized to result in nucleophilic substitution of OH⁻ present to F⁻ from the C-F bonds, resulting in an unstable hydroxylated structure that will undergo C-C bond cleavage. However, alkaline-induced hydrolysis of precursors without subcritical temperature or pressure has not yet been demonstrated in the literature.

2.4 Contaminant interactions with concrete

Concrete is one of the most widely used building materials in the world, with over 25 billion tons produced every year.⁶⁰ It is a relatively low-cost material that offers many desirable mechanical properties such as high strength, durability, and long service life; it is also readily available in most parts of the world.⁶¹ The environmental impact involved in the production of Portland cement, the binder present in concrete, is very considerable as large amounts of energy are required from the mining of raw materials and carbon dioxide generated during its production.⁶² In recent years, several more sustainable types of concrete have been developed

that retain similar structural properties but are manufactured in alternative ways or involve substituting Portland cement for other more naturally abundant additives.⁶³ Supplementary cementitious materials (SCMs) such as silica dust and fly ash, byproducts of other industrial activities that are otherwise disposed of, have been used for many years in concrete to partially replace Portland cement. Many new sustainable additives are being tested to lower the environmental impact of production including Celitement, calcined clays, natural pozzolanas, and metakaolin-based wastes.⁶⁴⁻⁶⁶

Another issue with concrete use that has not garnered significant attention is its environmental contamination and its ultimate reuse or fate after its service life. The interaction of concrete and salts such as chlorides has been well researched due to the prevalence of chlorides in road salts and marine environments and its potential to diffuse through concrete, corroding the steel reinforcing bars cast inside concrete.⁶⁷⁻⁷⁰ The documented interactions of other environmental contaminants and concrete, as well as lab-based studies on this topic, have not been well covered in the literature, despite its significance for concrete to potentially act like a sponge to the contaminant discharged, serving as a source for future long-term leaching. Additionally, if the concrete material has a history of contamination at the end of its life, then whether it is recycled or disposed of needs careful consideration. Due to its ubiquity as a building material, concrete may be found frequently at contaminated sites.

Haselbach et al. (2014) reported that zinc and copper metals tend to sorb to the surface of permeable concrete after washing with simulated rainwater. After up to 30 repeat applications of the fresh stock metal solution, the amount of metal retained on the concrete stayed consistent, suggesting that concrete surfaces have a high affinity for certain metals after multiple application and wetting cycles. Other studies investigating the removal and leaching of heavy metals in permeable concrete found that heavy metals tend to form complexes, sorb to the hydrated cement paste, or form some precipitates. Holmes et al. (2018) used heavily contaminated water with 400 µg/L of lead and cadmium and 45 mg/L of zinc to replicate the conditions of a Superfund site. Contaminated water was run through 6-30 kg permeable cores of 100 cm in length, but after 266 days, there was no breakthrough after the first concrete column. Earlier work by Hillier et al. (1999) studied the leaching of background levels of heavy metals from Portland cement and found that only vanadium leached from concrete in detectable quantities out of the primary heavy metals tested. Kaminski et al. (2019) examined cesium-137 sorption to concrete,

confirming earlier results of a high affinity of heavy metals for the cement matrix on the concrete surface. Exploring the desorption from different mineral aggregates in concrete, researchers found that solutions of potassium chloride and ammonium chloride can, within 1-h wash time, desorb varying amounts (10-88%) of the initial concentration of cesium-137 depending on the mineral type. Further studies confirmed that heavy metal sorption to concrete can be significant and thus a potential treatment method if pervious high-flow through concrete is used.^{75, 76} A review of select studies on contaminant sorption or diffusion into concrete is presented in Table 2.1.

According to a recent review paper by Azad (2024) limited information is available on concrete contamination with emerging contaminants such as PFAS or even other organic contaminants, as well as the ultimate fate of the contaminated concrete. Jiang et al. (2011) characterized the sorption and desorption of permethrin, an organic pesticide, using carbon-14 labeling to track its path through concrete. Initial sorption of the spiked solution to concrete reached a steady state concentration in the concrete after just 10 hours. Initial desorption was also rapid but then followed an exponential decrease pattern, with 20-30% of the initial concentration of spiked permethrin remaining on the concrete after 300 hours, which was attributed to a combination of breakdown of the contaminant and strong binding to the calcium silicate hydrate (CSH) matrix. However, with an initial contamination time (sorption time) to the concrete of only 70 hours and a desorption time of 300 hours yielding around a 70-80% recovery, this would suggest desorption is a much slower process than sorption. Ramwell (2005) examined herbicide sorption to concrete in a series of experiments where concrete and asphalt slabs were placed into dishes spiked with various herbicides so that the bottom 3 mm of the slab was in contact with the solution. Samples were taken regularly from the solution to observe if any decrease in concentration occurred, indicating potential sorption. Most of the tested herbicides remained in solution, with around 90% of the initial herbicide mass remaining after 144 hours. Of the small concentrations of herbicides that were sorbed to concrete, it was found that very little was released or desorbed after two consecutive 10-second washes with water, further suggesting strong binding or complexing of contaminant to the concrete surface or inner matrix.

Contaminant	Solvents	Sorption Mix	Extraction	Experiment	Sorption/	Reference
	Used	Method	Method	Time	Desorption	
Copper, zinc	Water	Column test	Analysis of	1 hour	87-93%	71
			leachate		sorption to	
					concrete	
Cadmium,	Water	Column test	Analysis of	266 days	99.9%	72
lead, zinc			leachate with		sorption to	
			nitric acid		concrete	
Permethrin	Acetone/	Shaken at	Analysis of	1–7 days	77-90%	78
	hexane	140rpm	liquid pooled		sorption in 24	
					hrs, 70-80%	
					desorption in	
					300 hrs	
Caesium-137	Ammonium	Gently mixed	Centrifugation	30 days	5-60%	74
	chloride/		and washing		desorption	
	potassium		with DI water			
	chloride					
Various	Water/	Bottom	Analysis of	6 days	~10%	79
herbicides	methanol	surface	liquid pooled		sorption in 6	
		contact			days, ~60%	
					desorption in	
					6 days	
Heavy metals	Hydrochloric	Gently mixed	Analysis of	256 days	>1% desorbed	73
	acid		liquid pooled		in 256 days	

Table 2.1 Summary of select studies on contaminant sorption to concrete.

2.5 PFAS interactions with concrete

Before 2022, only one study documented the presence of PFAS in concrete due to AFFF contamination.⁸⁰ A significant increase in attention to this topic since 2022 is partially due to the US DoD Strategic Environmental Research and Development Program's (SERDP) statement that an improved understanding of concrete and asphalt impacted by the historical release of AFFF is needed. As of January 17th, 2024, four additional papers have been published discussing experiments performed on AFFF and concrete and one review article.
Baduel et al. (2015), for the first time, described the level of PFAS contamination in concrete collected from an AFFF-impacted site through three independent experiments. First, concrete powder samples were collected at various spots on the concrete pad used for firefighter training exercises and extracted using methanol to determine PFAS spatial distribution across the pad. In the concrete pad, PFAS concentrations increased exponentially as the sample got closer to the drain, with a drain concentration of 244,294 ng/g of all PFAAs, indicating that the pads had drainage slopes and were appropriately drained. The following experiment quantified the vertical PFAS distribution in a 12-cm core taken from the pad at 1-cm intervals. Their results showed an exponential decrease in concentration after the first 0-1 cm depth of the pad and a strong correlation between increasing carbon chain length and decreasing concentration of PFAS measured, indicating longer chain PFAS are less mobile through concrete. The final experiment tested the desorption of PFAS from the core taken from the pad; water was ponded to the top surface of the core, and samples were taken regularly to observe potential PFAS leaching. The results showed that although the PFAS leaching reached steady-state concentration in the water in as little as 3 hours for PFOS and around 30 hours for 6:2 FTSA, only a small fraction of the PFAS in the core leached out, indicating that under repeated rainfall events the pad could serve as a source of long-term leaching. It was estimated that it would take 82 years to desorb 90% of PFOS present in the pad.

Thai et al. (2022) further examined the leaching behavior of PFAS from contaminated concrete in a series of simulated rainfall experiments and repeated the ponding experiments in Baduel et al. (2015) to ascertain the kinetic results from previous cores. Results from the rainfall simulations showed that after 60 minutes of rainfall, PFAS concentrations leaching from the concrete tended to plateau. However, after letting the core surface dry for 24 hours and then repeating the simulation, a similar profile in magnitude of concentration was observed. This trend held after a 130-day period where the cores were left wrapped at room temperature, suggesting that the wicking mechanism combined with Fickian diffusion is responsible for the consistently elevated levels of PFAS leaching after repeated simulations with intermittent wetting and drying.

Vo et al. (2023) assessed the utilization of sealants to mitigate the release of PFAS from concrete cores, the same cores obtained by Thai et al. (2022). Of the two commercially available sealants tested, both had strong performance in limiting PFAS release. The first product had

marginal performance, while the second one reduced the leaching of PFOS by over 100 times to a final concentration of 0-0.18 µg/L in the leachate. Using a forecast model, they also compared the cumulative PFAS mass loss of the pad to the surrounding environment with and without sealants. They found that using the second sealant product resulted in a negligible PFOS loss of <0.01 µg after two rainfall simulations. Using similar core samples as in a prior study, Vo et al. (2023) examined the vertical distribution of PFAS in a concrete core using a visual mass spectrometry method known as desorption electrospray ionization mass spectrometry imaging (DESI-MSI). DESI-MSI scans were taken of the surface of the core and compared with the amounts measured by traditional LCMS from subjecting concrete powder to extraction. The results agreed with earlier published studies and reiterated that most PFAS in concrete from AFFF-impacted sites tend to be located in the top few centimeters of the core. LCMS analysis of extracted powder samples is practically impossible at a high spatial resolution, but DESI-MSI provides a useful analytical tool for characterizing the scope of contamination from impacted concrete. DESMI-MSI has a few limitations. The first is a somewhat poor detection limit; although similar concentrations of 6:2 FTSA were present in the same samples, only PFHxS and PFOS could be detected via DESI-MSI. In addition, LCMS results for both samples showed very similar results for PFHxS, despite PFHxS appearing only in one of the two DESI scans. Further, despite the attempt to construct a calibration curve, quantitation proves to be very challenging since the results are displayed as a colour gradient with a percentage scale bar.

The latest study on PFAS-concrete interactions examined the distribution of PFAS in a concrete pad in an FTA in Australia.⁸⁴ The authors performed depth profiling on the core extracted from the pad and again found that PFOS and PFHxS were the dominant PFAS present, suggesting the historical use of ECF-based foams. Spatial sampling from the surface of the core revealed the highest concentrations near the FTA structure and the drain pipe, while these concentrations decreased on the outer perimeter of the site. Some variation in the depth distribution of PFAS was observed between cores, but no consistent trend was identified. A TOP assay was also conducted on a few samples, yielding a 30% increase in total PFAS post-TOP, indicating the presence of precursors. Finally, PFAS levels in cement and aggregate components of concrete were compared as a function of depth. The general trend was that the cement contained anywhere from 1-15 times more PFAS than the aggregate. However, this is unsurprising as aggregates are impermeable to even water, while the cement matrix has many

functional voids. It is interesting to note how this task was accomplished since it is very difficult to separate aggregate from concrete without cross-contamination.

Recently, a method for extracting PFAS from contaminated asphalt was proposed, and the use of six different extraction solutions, as well as a clean-up step, was examined.⁸⁵ The extraction solutions tested were all methanol-based solutions with either ammonia, hydrochloric acid, ammonium acetate, or a mix, except the last solution was acetonitrile and acetone with ammonia. A total of 22 target PFAS (carboxylic acids, sulfonic acids, and fluorotelomers) were tested for their extraction efficiency, and it was found that methanol with 1% ammonia performed the best, with the most precise recovery of the added extraction standard for the test. Even though concrete and asphalt use different binders and are made from very different ingredients, results from this study may be helpful as a starting point for method development for extraction from concrete samples.

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85. Srivastava P, Williams M, Du J, Navarro D, Kookana R, Douglas G, et al. 2022. Method for extraction and analysis of per- and poly-fluoroalkyl substances in contaminated asphalt. Anal Methods-Uk 14(17), 1678-89. **CHAPTER 3:** Uptake of per- and polyfluoroalkyl substances into concrete from aqueous film-forming foams: Experimental investigations and comparison to field-impacted samples

To be submitted to *Environmental Science & Technology*

Abstract

The widespread use of aqueous film-forming foams (AFFF) in firefighting activities has led to significant environmental contamination with per- and polyfluoroalkyl substances (PFAS), particularly at military bases, airports, and firefighter training areas. While research has focused on the environmental fate of PFAS in soil and groundwater, limited attention has been given to the interaction between PFAS and building materials, such as concrete. The goal of the research is to understand the initial phase of the contamination and delineate the factors that impact the magnitude of PFAS retention by and penetration into concrete. Laboratory experiments were conducted first to assess the uptake kinetics of various PFAS compounds in concrete. The yearlong uptake experiments show that summed PFAS concentrations in the solutions pooling on the concrete surface remain stable over 365 days, suggesting limited PFAS lost into the concrete matrix initially. However, extraction of concrete cores reveals PFAS throughout the entire depth, indicating penetration beyond surface levels, but the total mass in the concrete core is relatively small compared to the total PFAS applied to the solution. Varying concentration profiles for PFAS suggest complex diffusion behaviors influenced by surface characteristics, PFAS chain length and chemistry, and wetting drying cycles. A comparison of PFAS diffusion from an AFFF solution and a PFAS mixture highlights distinct mobility patterns, with AFFF-derived PFAS exhibiting slower diffusion into concrete cores. Estimated diffusion coefficients suggest PFAS penetrates concrete faster when surfaces are chipped or damaged, and intermittent wetting and drying cycles potentially accelerate PFAS penetration. Additionally, field-impacted concrete samples from a Canadian military base were characterized. The field samples demonstrate similar diffusion trends, with shorter-chain PFAS exhibiting greater mobility in the concrete matrix. Overall, these findings enhance the understanding of how concrete interacts with PFAS by identifying specific factors affecting uptake and demonstrating differences between field- and laboratory-contaminated cores.

Keywords: PFAS, AFFF, concrete, diffusion, uptake, surface

3.1 Introduction

The use of aqueous film-forming foams (AFFF) at military bases, airports, and other firefighter training areas has caused contamination of the surrounding environment due to the high persistence of per- and polyfluoroalkyl substances (PFAS) present in these foams.^{1, 2} Historically, AFFFs produced by electrochemical fluorination (ECF) made up the majority (~75%) of foams used at these sites due to their superior firefighting performance in fighting hydrocarbon or class B fires.³ Since the initial attention to PFAS contamination from sites that use AFFF, and more broadly, AFFF use in general,⁴ there have been many studies investigating the environmental fate of PFAS in soil, groundwater, and surface water from resulting AFFF contamination at impacted sites.⁵⁻⁸

Although soils and groundwater make up the majority of the natural environment surrounding these sites for PFAS to contaminate, other materials that make up the built environment, such as construction materials including concrete and asphalt, can also act as an important receptor and source of continual PFAS contamination at these sites. Concrete and asphalt are two commonly used building materials, with runways and some taxiways being built mainly from asphalt, while tarmacs, hangers, and other general surfaces are built from concrete. At airports and military bases with historical use of AFFF dating back to its introduction in the 1960s, training areas for using AFFF were performed on either a slab consisting of concrete, asphalt, or a mix of both,⁹ or it was performed directly on soil or gravel.¹⁰ Design standards from the US Federal Aviation Administration (FAA) on the construction of firefighter training facilities note that the training burn area may be either made from concrete or a series of highdensity membrane liners. The area surrounding the burn area, known as the apron, must be made of concrete to support the weight of aircraft rescue and firefighting vehicles, with the burn area and apron having adequate drainage installed.¹¹ With these guidelines being published in 1992, it is assumed that many training areas built after this time conformed to this design standard, with at least minimal covering of the training area with concrete or asphalt.

Studies on the presence of PFAS in concrete and interactions of PFAS or AFFF with concrete are very limited. Confirmation of the presence of PFAS in concrete was first published by Baduel et al. (2015) which documented contamination of dominant PFAS, including perfluorooctanesulfonic acid (PFOS), perfluorooctanoic acid (PFOA), and 6:2 fluorotelomer sulfonate (FTSA) in a concrete pad at a firefighter training area in Australia. The study showed

that as proximity to the drain increased, the concentrations of PFOS and PFOA in concrete sampled from multiple points increased, recording maximum concentrations of 224 and 1.26 g/g, respectively. Interestingly, high concentrations of long-chain perfluorocarboxylic acids (PFCAs) from PFNA to PFTriA were reported, and a high chain length-low mobility relationship was presented, consistent with the expected mobility behaviors of these compounds in porous media. Experiments on the kinetics of desorption of PFAS from cores extracted from the site demonstrated the fast initial leaching of PFAS from the concrete, but concentrations quickly plateaued after ~6 and ~25 hours for PFOS and PFOA, respectively.

Later work further assessed the leaching potential of PFAS from concrete. Before sealants were applied to concrete, consistently high amounts of PFOS leached out after repetitive rainfall simulations one day or 130 days apart. A performative assessment of candidate sealants to limit leaching from concrete was done with moderate success of sealants being achieved, but their feasibility of application for existing AFFF-impacted concrete remains uncertain.^{13, 14} An additional study on the quantification of PFAS through an impacted concrete pad at was done, where improvements were made in assessing the spatial variability of four dominant PFAS at the pad.⁹ TOP assay performed on the concrete extraction samples yielded around a 30% increase in total PFAS measured. These same studies indicate that intermittent wetting and drying cycles of concrete surfaces may increase the rate of penetration of chloride. Cores from the same site were also imaged using a technique known as desorption electrospray ionization mass spectrometry imaging (DESI MSI) to view the profile of penetration of PFOS and PFHxS, revealing the bulk of PFAS is retained in the top 1-2 cm of the cores.¹⁵

So far, the studies that have examined these interactions have focused on assessing desorption rates on field-contaminated concrete from the same site and initial characterization of dominant PFAS present in the cores. However, given the high number of AFFF-impacted sites and potentially large quantities of impacted materials, understanding the initial uptake and contamination of concrete by AFFF, such as the effect of concrete surface type or additives and the AFFF types, would assist the risk assessment and mitigation efforts. The characterization and fundamental mechanisms responsible for concrete contamination by AFFF are poorly understood, as suggested by Douglas et al. (2023). PFAS preferential distribution within concrete, analytical methods and measurement techniques for impacted materials, and environmental factors affecting uptake are a few examples of the knowledge gaps.¹⁶

The purpose of this work is to address some questions pertaining to the initial contamination of concrete by AFFF. A series of experiments are performed in the study to evaluate the uptake of various PFAS present in an ECF-based AFFF and a mix of 12 common PFAS without AFFF additives in concrete cast in-house. We compared the effect of concrete surface type, intermittent wetting and drying cycles, and the influence of PFAS chain length. Additionally, field-impacted concrete samples from a Canadian military base are extracted, analyzed, and compared to the lab cores to determine the variability and elucidate the kinetics and mechanisms of contamination. This is the first study to investigate the factors that impact the uptake of PFAS by concrete from the aqueous phase and compare and contrast results from the characterization of concrete cores obtained from an impacted site.

3.2 Materials and Methods

3.2.1 Chemicals and reagents

Analytical standards from multiple suppliers were used for the analysis of PFAS during the experimentation. Perfluorocarboxylic acids (PFCAs), perfluorosulfonic acids (PFSAs), n:2 fluorotelomer sulfonic acids (FTSAs), perfluoroalkylsulfonamides (FASAs), perfluorooctanesulfonamidoacetic acid (FOSAA), N-methyl-perfluorooctanesulfonamide (MeFOSA), N-ethyl-perfluorooctanesulfonamide (Et-FOSA), N-methyl perfluorooctanesulfonamide acetic acid (Me-FOSAA), N-ethyl perfluorooctanesulfonamide acetic acid (Et-FOSAA), and 6:2 fluorotelomer sulfonamide betaine (6:2 FTAB) were purchased from Wellington Laboratories (Guelph, ON, Canada). Perfluoroalkyl sulfonamide amines (PFSAm), N-trimethylammoniopropyl perfluoroalkanesulfonamides (PFSAmS) and perfluorooctane-amido ammonium salt (PFOAAmS) were custom synthesized by the Beijing Surfactant Institute (Beijing, China). All PFAS solutions used for the uptake experiment were prepared using solid chemicals or liquid solutions (non-analytical standard grade) from Sigma-Aldrich (Oakville, ON, Canada). Standard solutions of fluoride and phosphate, certified for ion chromatography analysis, were purchased from MiliporeSigma (Oakville, ON, Canada). All isotope-labelled internal standards were purchased from Wellington Laboratories. HPLC-grade acetonitrile (ACN), methanol (MeOH), formic acid (FA), isopropanol (IPA), water, and sodium hydroxide were purchased from Fisher Scientific (Ottawa, ON, Canada). AFFFs used in the study were donated by an anonymous supplier. Further information on chemical purity, a full list of isotope-labelled internal standards, and other chemicals used are provided in Appendix A (Table A.1 - A.3).

3.2.2 Concrete casting and core preparation

Concrete was made in a Primo PM10 small batch stand mixer using a modified mix design based on a standard mix from the US Federal Aviation Administration (FAA) used for airport tarmacs and taxiways. The mix used tap water and ordinary Portland Cement (OPC). Mixing was performed in batches of either 1 or 2 kgs, then poured into rectangular moulds of $103 \times 51 \times 29$ mm, and the surface was finished using a small magnesium float. After the initial set of concrete, the surface was further finished by lightly brushing a small broom across the surface to create a non-slip surface. The slabs were moist-cured with a damp cloth left on the surface for 48 hours, with water added to the cloth every 12-18 hours to ensure adequate moisture remained on the surface, allowing continuous hydration of the cement.

Table 3.1 Concrete mix design used for PFAS & AFFF contamination experi
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Aggregates	Cement	Water	Aggregate Grading	w/c Ratio
65%	24.2%	10.8%	1-4.75mm diameter	0.446

After the 48-hour moist curing period, the slabs were removed from the moulds and allowed to cure for 30 days at ambient room temperature and humidity. Core samples were taken from the slabs by fixing slabs into a vice upside down and coring with a Cleereman 511 drill press supplied with cutting water with a 19.05 mm masonry drill bit. The cores used in the experiment were ~19 mm in diameter and ~29 mm in height. After drilling, half of the cores were left with a finished surface while the other half had their surface chipped with a hammer and chisel, giving a rough chipped surface to partially expose aggregates to replicate the mechanical wear of concrete in real FTAs due to harsh environmental conditions and training exercises.

Aggregates from a size of 1-4.75 mm in diameter were used rather than normal-sized aggregates found in regular mix designs for two reasons. Firstly, ASTM C31 procedures for making concrete test specimens restrict the maximum aggregate size to one-third of the cylinder mould or core size.¹⁷ Secondly and more importantly, the mix was designed to be a scaled-down

version of a standard concrete mix to allow the analysis of the concrete by instruments that do not allow for analysis of very large samples, such as SEM-EDS and DESI-MSI. Using a much smaller aggregate size makes it possible to observe the interfacial transition zone (ITZ) in the concrete, as well as the general interface between the cement matrix and the aggregates. Additionally, during the extraction of concrete cores, it allows for a representative sample to be taken from the core that is not overwhelmingly comprised of aggregates alone but a mix of particles that come from the crushed aggregate and cement matrix. A complete sieve analysis of aggregates used is presented in Appendix A (Table A.4 & Figure A.1). Concrete density, percent absorption, and percent permeable voids were calculated by performing the ASTM C642 test standard.¹⁸ Full-scale cylinders measuring 102 mm in diameter and 193 mm in height were cast and tested for their compressive strength as per ASTM C39.¹⁹ The results from ASTM C6429 and C39 tests are available in Appendix A (Table A.5 and A.6).

Before analysis via DESI-MSI, concrete core samples were dried at room temperature for five days after the uptake experiment. Samples were then cut in half down the length of the core using an Allied High Tech (Cerritos, CA, USA) TechCut 4 Low-Speed Saw with a 0.02-inch diamond plated blade at a slow cutting speed of 400 RPM. Due to the small size of the cores, the saw blade and sample reached a maximum temperature of 30 °C even without water cooling, which is otherwise required for concrete cutting.

3.2.3 Experimental setups and sampling

A custom sample setup (Figure A.3) was built to hold each concrete core, which was sealed at the sides, left open to the atmosphere at the bottom, and enclosed on the top surface where PFAS or AFFF solution was pooled and left to potentially diffuse into the concrete. In each setup, the concrete core (as described in Section 3.2.2) was placed into a rubber tubing and sealed with hose clamps to ensure watertight. A long tube of acrylic measuring 23 cm in height was then placed on top of the core inside the rubber ring, where another hose clamp was used to secure the acrylic tube to the top of the core. Finally, the acrylic tube was capped with a rubber cap to prevent evaporation of the pooled solution. The acrylic tube formed a chamber where a solution could be contained to be pooled on the surface of the concrete without major losses to evaporation or leaks. Each setup was tested by filling the full 45 mL chamber with water and leaving it for 24 hours to observe if any leaks had formed, which was indicated by a loss of water in the chamber or water appearing externally on the setup.

A total of 30 setups were divided into two groups: static uptake setups and wet/dry uptake setups. Two sets of solutions were used for the setups depending on the tested experimental condition. The first solution comprised of a mix of 12 PFAS each at 10 mg/L in tap water; the PFAS included were PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFBS, PFHxS, PFOS, 6:2 FTSA, and 8:2 FTSA. The second solution was a 3M Light Water AFFF diluted to 3% in tap water. This AFFF was previously characterized by Liu et al. (2024).²⁰ Table 3.2 summarizes the experimental setups and the number of sample replicates used. Each of the setups had one thin sample similar to the concrete cores used in other setups, but it was only 1 cm in height, allowing it to fit in the chamber of an SEM-EDS.

Experiment:	Static Uptake				Wet/Dry Uptake	
Solution:	A mix of 12 PFAS		AFFF 3%			
Surface Type:	Flat	Chipped	Flat	Chipped	Flat	Chipped
Replicates:	3	3	3	3	3	3
Controls:	3		3		N/A	
Thin Samples:	1	1	1	1	1	1

 Table 3.2 Summary of sample replicates

After ensuring there were no leaks in the constructed setups, 40 mL of the 12 PFAS mix solution or AFFF solution was pooled onto the surface of the concrete in the acrylic chamber and then the chamber was capped, marking the beginning of the experiment.

For the first five days of the experiment, sampling was conducted every day, then every week until day 49, and then every 14 to 90 days until day 365 (full sampling schedule in Table A.7). Prior to sampling, each setup was gently mixed three times, after which the top cap was removed, and 180 uL of the sample was taken and diluted into 1620 uL of methanol. An additional 20 uL of sample was used to take pH measurements for one of the three replicates in each setup using pH papers with a reference scale of 6.5-13 in 0.5-unit increments. Sometime between days 119 and 231, AFFF control setups 1 and 3 broke, leaking the contents into the container they were placed in, leaving only one AFFF control for the last four sampling points of the experiment. Samples from the setups were stored in the freezer at -20 °C for chemical

analysis. Setups from the wet/dry uptake experiment were dosed with 200 μ L of AFFF at 3% at weekly intervals for 24 weeks. Setups were left uncapped at room temperature to allow the AFFF to evaporate. Since no aqueous samples pooled on the surface of these setups, aqueous samples were not collected, and therefore, these concrete cores were only analyzed for PFAS after concrete powder extraction.

3.2.4 Concrete core powder collection and extraction

On day 365, one year after the uptake experiment began, a final sample was taken, and the pooled solution of either PFAS or AFFF was transferred to a container. The cores were then removed from the setups and left to dry at room temperature for five days. Two of the three replicates from each experimental condition tested were then subject to powder collection and extraction. The remaining replicate was used for DESI-MSI analysis.

Powder from each core was collected by drilling into the top surface of the core secured in a rubber housing placed in a vice using a Victoria drill press at a speed of 1250 rpm with a 3/16-inch masonry bit attached, with powder being collected at the following depths: 0.25, 0.5, 1, 1.5, 2, and 2.5 cm. The drill bit was cleaned three times with methanol in between each collection. The powder was collected from the hole drilled through the core by brushing powder that had accumulated on the core surface from the screwing action of the drill bit. Drilling and powder collection were performed starting on the top surface of the core and drilling downwards; drilling radially on the side was not feasible because of the small sample size. Due to the cores only being around 29 mm in height, as the drill approached the bottom of the core, pieces of the core could fragment, leading to unsuccessful collection of the last measurement at a depth of 2.5 cm. Similarly, as the chipped samples were slightly shorter than the flat samples, powder collection at the 2.5 cm depth was often tricky and impossible beyond the 1 cm depth in the wet/dry uptake setups. Powder samples were stored in glass vials at room temperature until extraction. A depth profile of cores from a Canadian FTA was also constructed by taking powder samples at 1 cm intervals of the cores. As the cores came from a real slab, they were of adequate size where radial drilling was acceptable for the structural integrity of the core to collect powdered samples. Images of both lab-contaminated cores with setups and the field-collected cores are available in Figures A.2 - A.5.

Concrete powder extraction was performed using the previously validated method. Powder samples were weighed and then transferred to 15 mL centrifuge tubes where 5 mL of methanol was added. Samples were then vortexed for 30 seconds, sonicated for 10 minutes, and then centrifuged at 5000 rpm for five minutes. The supernatant was then transferred to a new vial, and the powder was subjected to the extraction cycle an additional two times. The resulting ~14 mL of supernatant containing the PFAS extracted from the cores was then concentrated by blowing nitrogen and heating at 45 °C until the final volume was 2 mL. Samples were then transferred to microcentrifuge vials and centrifuged at 21,000 g to separate any particles that did not settle during the extraction. Samples were then stored at -20 °C until analysis.

3.2.5 Instrumental analysis and quality control

Samples were analyzed on a Vanquish ultra-high performance liquid chromatography (UHPLC) coupled to a high-resolution Orbitrap mass spectrometer (HRMS) (ThermoFisher Scientific, Waltham, MA, USA). Samples were run in full scan MS mode with polarity switching from 50-1000 m/z. Select samples were run using targeted MS/MS (t-MS²) mode in both positive and negative polarity modes at normalized collision energies of 20, 35, and 50% to confirm structures observed in full scan mode. Full details on the instrumental analysis, including the UHPLC method and Orbitrap scan parameters, can be found in Table A.8. A range of dilutions of the samples were conducted (2-16,000 ×) in order to ensure that all analytes would fall into the calibration range. Mass-labelled internal standards were added to all samples, including calibration standards and check standards at a final concentration of 3 ng/mL except MPFOS, which was added to a final concentration of 100 ng/mL to accurately quantify PFOS, which represents a disproportionately high composition PFAS in ECF-based AFFFs, while simultaneously being able to quantify less abundant PFAS. Procedural blanks and check standards recovered satisfactorily, and no PFAS were detected in procedural blanks by the method.

Total fluoride (TF) measurement samples were analyzed using a Mitsubishi AQF-2100H combustion system comprised of an ABC-210 sample introducer, HF-210 furnace, and GA-210 absorption unit. Samples were injected into quartz sample boats and run through the combustion system, where organic fluorine is converted into fluoride. Post-combustion samples were then analyzed for fluoride concentration on a ThermoFisher Dionex ICS-5000⁺ using conductivity. Samples were not tested for their inorganic fluorine contents as the amounts of inorganic fluoride

from background sources are expected to be very low compared to AFFF solutions. Further, cement does not contain fluoride-containing minerals. Full information on the instrument methods used in the AQF-2100H and ICS-5000⁺ are presented in Tables A.9 and A.10.

3.3 Results and Discussion

3.3.1 Potential PFAS uptake into cores by measurement of solution

The concentration of 10 PFAS in the solution containing the mix of 12 PFAS (except 6:2 FTSA and 8:2 FTSA as discussed below) remained steady and ranged 70-130% of the initial concentrations in each of the three setups: flat surface, chipped surface, and control for 365 days (Figure 3.1 a-f). The relatively steady aqueous concentration for each of the triplicates in both flat and chipped surfaces indicated that either no significant amount of PFAS had diffused into the concrete through the top surface or the amount diffused into the concrete was too small to quantify relative to the mass remaining in the solution. As discussed later, PFAS were detected by LC-HRMS analysis throughout the entire depth of the cores after extraction of the powder samples, indicating that PFAS have diffused into the concrete matrix (Figure 3.3). Although 8:2 FTSA and 6:2 FTSA were included in the original solution of 12 PFAS pooled onto concrete, a rapid decrease in the concentration of around 40% of 8:2 FTSA in the first three days of the experiment was observed for all replicates in the flat surface, chipped surface, and controls. This result was likely attributed to 8:2 FTSA precipitating out of the solution, probably due to its aqueous solubility below 10 mg/L in the test solution. For 6:2 FTSA, the concentration profile did not indicate any precipitation, but there was a significant increase of around 40% at day 28, after which the concentration remained steady until day 119, after which analysis for these two compounds was stopped. Concentration profiles for 8:2 and 6:2 FTSA can be found in Appendix A (Figure A.6). Based on the literature, PFAS sorption to or diffusion into a solid matrix can occur within a few days of contact, samples were taken daily for the first 5 days of the experiment, but since there was no major change in concentration, these time points were not shown in Figure 3.1. Nevertheless, the concentrations at all sampling points for each PFAS can be found in Appendix A (Figure A.7).

The PFSA concentration profiles in the setups containing AFFF as the pooled solution (Figure 3.1 j-l) showed somewhat similar concentration profiles to the setups containing a mix of 12 PFAS (Figure 3.1 d-f). As both sets of samples from the two solutions pooled onto the surfaces showed no decrease in PFSA concentrations, no conclusion could be reached on solely

this outcome on the effects that additives or PFAS precursors in the foam have on the diffusion of these PFAAs into concrete. However, comparing the extraction of powders from cores from the two solutions in the two solutions reveals very different results, which are discussed further in Section 3.3.2. On the other hand, the PFCAs in the AFFF solution (Figure 3.1 g-i) increased from 1.36 times the initial concentration for PFOA to 1.87 times for PFBA, with the increase occurring between days 28 and 119. This was later found to be caused by the generation of PFCAs from the abiotic transformation of a class of precursors in the foam known as PFAAAm or AmPrFAAd. The complete characterization profile of the AFFF used was previously reported by Liu et al. (2024). Concentration profiles for precursors are presented and discussed further in Chapter 4.



Figure 3.1 Concentration of PFAAs from pooled solutions on concrete cores contaminated with a mix of 12 PFAS (a-f) and AFFF 3% (g-l) by surface type.

TF content of the pooled solutions in both setups was determined via CIC analysis. According to Figure 3.2, TF in both setups, with the mix of 12 PFAS and the diluted AFFF, show acceptable recovery (70-130%) of the starting day 0 concentrations. Despite the relatively large data variations, the results confirm that the majority of PFAS, if not all, remained in the solution phase after 365 days. Therefore, the increase in PFCA concentrations shown in Figure 3.2 g,h must be accompanied by a decrease in other precursor compounds.

Although the TF displays no significant decrease of PFAS from the pooled solution, suggesting limited diffusion, there may be possible precursor classes with preferential diffusion or absorption into the cement matrix. As these individual precursors can make up a small portion of TF in ECF foams, care should be taken when examining CIC data of AFFF solutions. Instead, CIC should serve as a complementary technique to the MS data of the precursor being examined in addition to screening for possible transformation products. Attempting to complement the concentration profiles from the pooled solutions with results of PFAS extracted from the powder of concrete cores can also prove difficult as some precursors abiotically transform after initial contact with the concrete and during the extraction process. This is explored in depth in Chapter 4. Generally, the total fluorine results indicate that diffusion is not significant for the total PFAS measured, but care should be taken when comparing CIC data to individual PFAS present in the foam other than the dominant PFSAs.



Figure 3.2 Average TF content of the 12-PFAS mix solution and the AFFF solution pooled onto concrete surfaces, as measured by CIC.

3.3.2 Depth profiles of PFAS in concrete cores

After the conclusion of uptake experiments, concrete powder at various depths of the concrete cores was subjected to solvent extraction. As shown in Figure 3.3, PFAS had diffused

into the concrete matrices and penetrated to the last powder collection depth of 2.5 cm, and probably also reached the bottom of the core at a depth of 2.9 cm. PFAS depth profiles of cores pooled with a mixture of 12 PFAS (Figure 3.3a-h) and AFFF solution (Figure 3.3i-p) are plotted in relation to PFAS concentration at depths of 0.25 cm in concrete cores; 0.25 cm represents powders collected between 0 and 0.25 cm, and 0.50 cm represents powders collected between 0 and 0.25 cm, and 0.50 cm represents powders collected between 0 and 0.25 cm, and 0.50 cm represents powders collected between 0 and 0.25 cm, and 0.50 cm represents powders collected between 0 are presented in Figure A.8. Additionally, the two replicates from each setup that were extracted for a PFAS depth profile are plotted separately as there was high variability between replicates when plotting both in absolute concentration and as a function of the concentration at 0.25 cm. Despite samples being cast and finished the same way, the large discrepancy between samples suggests that surface properties such as micro and macropores that are not visible may be causing this difference. Furthermore, the powder extracted may be heterogeneous, and the proportion of aggregate to cement in the powder mix might also contribute to this variability.

Nevertheless, as shown in Figure 3.3, the chain length relationship was clearly visible in the cores with the mix of 12 PFAS pooled on them, both for PFCAs and for PFSAs, and in both flat and chipped surfaces. Shorter chain PFAAs had greater concentrations deeper into the core, which indicates that these compounds had a higher diffusion rate. However, PFOA, PFNA, and PFDA have similar concentration profiles, with little difference in penetration depth, suggesting diminishing effects of low mobility beyond a chain length of eight carbons. PFCAs with a chain length below eight tend to be much more mobile, particularly noticeable in the chipped surface cores where the PFBA concentrations at depths of 2 cm are 3.99 and 12.3 times the concentration at 0.25 cm for cores 1 and 2 (Figure 3.3 - k, 1), respectively. Similar trends are observed for PFSAs, with much higher concentrations found deeper for the chipped surfaces (Figure 3.3 g & h). This is somewhat expected given that finished concrete surfaces such as the flat ones used in this experiment have a dense cement matrix with very little void space in the top millimeters. In contrast, chipped surfaces have the first few millimeters of the cement matrix removed, so the solution pooled on its surface is directly exposed to air-entrained voids, micropores, as well as the interfacial transition zone of exposed aggregates, creating many preferential flow paths for PFAS to follow to reach the core quickly.

The same PFAS in the pooled solution of AFFF follows a very different pattern as compared with compounds in the mix of 12 PFAS. Both PFCAs and PFSAs in the AFFF

solution for the flat concrete surfaces tend to have much lower relative concentrations throughout the whole depth of the core as compared with the same compounds in the mix of 12 PFAS. For PFCAs, this difference may be attributed to the differences in the initial concentrations between the two solutions. The 12 PFAS solution had an initial concentration range for PFCAs of 6.96 to 8.03 mg/L for PFHxA and PFNA, respectively, whereas the AFFF solution had an initial concentration range of only 0.26 to 1.51 mg/L for PFBA and PFNA respectively. For PFSAs, the two solutions have similar magnitudes of PFSAs (except for PFOS), which indicates that the different distribution within the concrete matrix cannot be explained by the initial PFSA concentrations alone. An interesting phenomenon is observed in all four PFSA plots from the AFFF mix (Figure 3.3 m-p): the concentration profile shows that PFSAs with a chain length of six carbons or higher have very limited mobility compared to those with a four or five-carbon chain length. Furthermore, there is no difference in the relative concentrations after six carbon chain lengths. PFHxS has the same relative concentration as other long-chain PFSAs (C7-C12), suggesting equal limited mobility of these compounds diffusing through concrete. This effect was not observed for PFSAs in the 12 PFAS solution, where PFHxS and PFOS still generally followed the chain length dependency of decreasing concentration with increasing chain length. This effect is also not found for PFCAs, where a clear chain length relationship can be observed in the AFFF solution for C4 to C8 chain lengths. It is hypothesized that this effect comes from other components in the AFFF. In addition, the DESI-MSI images (Figure 3.4) of the final core replicate from this set confirm this chain length result and are discussed further below.

A mass balance calculation was carried out by combining the PFAS measured in the pooled solution and the PFAS measured in the core by estimating the total PFAS burden in the entire core, with the day 0 amounts indicating the starting mass spiked into the system. The mass of PFAS in the cores was estimated by taking the concentration at each depth and computing the average mass in each 0.5 cm slice of core based on the density of the concrete calculated using ASTM C642. The mass of PFAS in the pooled solution was calculated using the theoretical amount of liquid remaining after the last sampling day. Recoveries for the solution and cores spiked with the mix of 12 PFAS were from 96.6% to 122% (mean 112%). Recoveries for the AFFF solution PFSAs were from 43.8% to 107% (mean 75.7%), but the recovery for PFCAs could not be determined as there was the transformation of some precursors leading to PFCA

PFAS inside the concrete only makes up a small portion of the total PFAS originally spiked in the setups. The concentration of PFAS in the cores only made up 0.99% to 10.9% (mean 3.8%) of the mass balance in the case of the mix of 12 PFAS. Similarly, in the AFFF solution for PFSAs, this amount was slightly higher, with the cores making up 1.6% to 18.5% (mean 9.40%) of the total mass balance. Full recoveries and mass balance of PFAS recoveries from the cores and pooled solutions are in Figure A.9.



Figure 3.3 Depth profile of PFAAs in concrete cores contaminated with a mix of 12 PFAS (a-h) and AFFF 3% (i-p) by surface type.

Diffusion coefficients inside the concrete matrices were estimated using the absolute concentration profiles and Fick's second law of diffusion Eq. (1). This equation can be simplified using assumptions in ASTM C1556 to Eq. (2).²¹ This equation is in the form where PFAS are assumed to have no lateral transfer during diffusion, and the source concentration is assumed to

be an infinite source. The second condition holds in this experiment as the majority of PFAS mass remained in the solution phase on day 365.

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \qquad (1)$$
$$C(x,t) = C_s - (C_s - C_i) \cdot \operatorname{erf}\left(\frac{x}{\sqrt{4Dt}}\right) \qquad (2)$$

In Eq. (2), *erf* represents the Gaussian error function, C(x, t) is the concentration at a given depth and time in the core, while C_s is the surface concentration, C_i represents the initial concentration of PFAS within the core, x is the depth of extraction of the core, t is the time of exposure, and finally D is the diffusion coefficient. As extractions on clean concrete revealed no background PFAS in the concrete mix, the equation can be further simplified to its final form to Eq. (3).

$$C(x,t) = C_s \left[1 - \operatorname{erf}\left(\frac{x}{\sqrt{4Dt}}\right) \right] \quad (3)$$

Using non-linear regression analysis, the diffusion equation (Eq. (3)) was fit to the absolute concentration profiles from the powder extractions using the method of least squares. Calculation of C_s and D can be performed numerically while t is set as a constant value of 3.15E7 seconds representing the 365-day contact time. For PFAS that follow the same general trend as chloride diffusion into concrete,^{22, 23} it is possible to fit a curve with high R² values. However, compounds such as PFBA, PFPeA, PFBS and PFPeS failed to converge to a solution in the equation, so the diffusion coefficient cannot be calculated using this method. Therefore, diffusion coefficients for PFOA and PFOS in the cores pooled with the mix of 12 PFAS, as well as PFOA for the cores pooled with the AFFF solution, were computed with full diffusion curves available in Figures A.10 and A.11. The calculated diffusion coefficients do not vary by a great degree between PFOS and PFOA, nor between the two sets of values for PFOA from the two different solution types. There were noticeable differences between the flat and chipped surfaces with both PFOA sample sets, with chipped surfaces having diffusion coefficients that were 2.3 and 29 times larger than samples with flat surfaces. The same result did not hold for PFOS due to the fast diffusion in flat core 1.

DESI-MSI scans of the top ~6 mm of a replicate flat surface core sample were collected from the pooled AFFF solution setups (Figure 3.4), with the right side of each image showing the core top surface. The images visually show some chain length relationships with an increase in penetration depth and decreasing chain length, with minor yet notable differences in PFOS, PFHpS, and PFHxS. PFPeS, however, has a much greater penetration depth, with the large pockets of PFPeS still being retained in the top 3 mm, but a very strong signal in the bottom 3 mm indicates its higher mobility or diffusion. These results agree with the HRMS data from the core powder extractions (Figure 3.3m & n), as PFPeS and PFBS are shown to have higher diffusion than the PFSAs with chain lengths of C6 and higher. PFBS was found using DESI, but its ion was in extremely low abundance. With both the aqueous phase MS and surface MS results agreeing, it is clear that this phenomenon is occurring, but it is unclear why PFSAs with chain lengths above C5 have similar depth of penetration profiles and why PFPeS and PFBS diffusion are much quicker. The penetration profiles also show that the bulk of PFAS found is in the cement matrix and not in the aggregates, which is expected as the cement matrix is a porous network of microfissures and pores of different sizes. In contrast, aggregates are relatively impermeable minerals that PFAS do not penetrate.²⁴ The minor PFAS showing up in the aggregate here, especially in the middle aggregate in the center of the core, could come from contamination during the surface polishing.



Figure 3.4 (a) The image of a lab-contaminated concrete core with a flat surface after exposure to 3% AFFF for 365 days, and DESI-MSI of PFOS (b), PFHpS (c), PFHxS (d), PFPeS (e), in the top 6 mm.

The literature consistently shows that having intermittent wetting and drying cycles can accelerate the penetration of chlorides into concrete from chloride ingress studies,²⁵ so a similar effect was hypothesized for organic contaminants such as PFAS. In the flat surface samples extracted from the cores subjected to repeated wetting and drying cycles (Figure 3.5), PFCAs and PFSAs penetrate to very similar depths regardless of chain length, drastically different from the wet cores discussed above. The absolute concentration profiles for the wet/dry cores are presented in Figure A.12. For chipped cores, only three successful extractions (depth of 0.25, 0.5, and 1 cm) were able to be taken before both cores disintegrated into many pieces, and thus those data are not presented. Examining the differences in PFCAs and PFSAs (C4-C8) within replicates yields another difference as PFCAs tended to have a mean $C_{0.5cm}/C_{0.25cm}$ value of 0.39 \pm 0.04, whereas for PFSAs, this value was 0.30 ± 0.03 for flat surface Core #1, suggesting a statistically significant difference between the two sets of compounds (p<0.005). The same trend held for flat surface Core #2 with $C_{0.5cm}/C_{0.25cm}$ values of 0.20 \pm 0.04 and 0.13 \pm 0.02 for PFCAs and PFSAs, respectively, but the significance was not as strong for this core (p<0.008), with PFOA being removed as an outlier (z-score of 3.1) This observation again underscores that

subtle microscopic differences in concrete surfaces and heterogeneity of concrete matrix can greatly affect PFAS transport inside the solid material.

As contamination factors vary widely between the cores with solution pooled on them and the cores subjected to intermittent wetting and drying, it can be difficult to compare extraction results between the two types of cores. Very different amounts of PFAS were available to be diffused into the two different setups and for different periods. Static setups pooled with AFFF solution had a combined PFCA (C4-C8) and PFSA (C4-C12) mass of $16.7 \pm$ 2.6 mg in the solution available to diffuse into the core, whereas the wet/dry setups were only spiked with a total amount of the same PFAS of 4.27 ± 0.65 mg. Despite the pooled setups having ~4 times more PFAS available for diffusion into the cores, the wet/dry setups had comparable PFAS penetrating the bulk of the core. Flat surface cores from the wet/dry setups had a combined PFCA (C4-C8) and PFSA (C4-C12) mass of 2.17 and 2.50 mg for Cores #1 and #2, respectively, whereas the flat surface Cores #1 and #2 from the pooled AFFF setups had 4.06 and 2.24 mg total PFAS respectively. Calculating the mass of PFAS retained in the top 1 cm of the chipped surface cores to allow a direct comparison between wet/dry cores and pooled cores gave similar results to the flat surface cores, with wet/dry cores #1 and #2 having 3.40 and 1.96 mg of combined PFAS respectively. In contrast, the chipped surface cores from the AFFF pooled solution setup had 2.76 and 1.55 mg of combined PFAS, respectively. The results from the PFAAs extracted from the wet/dry cores would suggest that having intermittent wetting and drying cycles like what is experienced at AFFF-impacted sites can moderately increase the depth of penetration of PFAS into concrete, regardless of chain length. Comparing the differences in depth of penetration of different compounds from the pooled solutions and the wet/dry setups, it is likely that two different mechanisms are present here. For the pooled solutions, the chain length vs. depth of penetration relationship would suggest that regular diffusion is the dominant mechanism. However, for the wet/dry setups, the dominant mechanism is more likely from the advective effects of capillary action downward through the pores, with diffusion also likely occurring, but to a much lesser extent than in the pooled solutions.²⁶ In this mechanism, the rate of migration of the AFFF solution is controlled by the rate of water ingress. With every application of AFFF, the liquid is able to move through the dry surface to connect to the inner part of the core, which remains partially saturated even between applications, causing PFAS to migrate deeper into the core.

In this study, we did not test non-PFAS wetting events such as rainfall or washing the concrete's surface with water, so we do not know how they affect surface wetting events. PFAS penetration could be decreased by capillary suction within concrete pores and upward diffusion of PFAS into upper layers and out of the core, as demonstrated by Thai et al. (2022).¹³



Figure 3.5 Depth profile of PFAAs in flat surface concrete cores subject to repetitive wet and dry cycles (a-d).

3.3.3 Depth Profiles of Field-Contaminated Cores

The concrete cores from a firefighter training area (FTA) at a Canadian military base were subject to the same characterization method as the lab-contaminated cores. As shown in Figure 3.6, the four cores showed different PFAS profiles (Figure 3.6), even though they were cut from the same slab. As previously shown in lab-contaminated materials, the heterogeneity of the concrete material is partly responsible for the variations, among many possible factors. However, some similarities can be found among the four cores in terms of chain length relationship, with the shorter chain PFAS being more mobile in general, showing higher relative concentration at the same depth. Absolute concentration profiles for the cores are available in Figure A.13. These data show that the absolute amount of PFAS recovered at each depth in each core was much less than in the lab-contaminated cores. Take PFOS, one of the most abundant PFAS found in the FTA cores, as an example. PFOS in the pooled lab-contaminated cores at a depth of 1 cm ranged from 12.1 to 28.9 μ g/g (mean 19.6 μ g/g), whereas in the FTA cores also at a depth of 1 cm this ranged from 0.03 to 0.11 μ g/g) (mean 0.06 μ g/g), with these values being similar to cores obtained in the site characterized by Williams et al. (2023). Of the PFAAs detected in both the lab-contaminated cores and FTA cores, PFHxS was the only PFAS that was more abundant in the FTA cores, with mean concentrations of 1.16 and 0.81 μ g/g in the FTA and lab-contaminated cores, respectively. The relative concentration of PFHxS to PFOS in the FTA cores was nearly 20, whereas in the lab-contaminated cores pooled with the AFFF solution, this relative concentration was only 0.04. The results for the lab-contaminated cores are expected as PFOS is the most dominant PFAS in the ECF AFFF, with PFHxS being the second most dominant PFAA at a concentration of about 5.5% of PFOS. Therefore, the results from the FTA cores may suggest that there were additional sources of PFHxS, such as many PFHxS precursors, which may transform to generate PFHxS; this is explored further in Chapter 4. Furthermore, the FTA cores were subjected to repeated heating and cooling cycles (during fire training activities) and also natural weathering and leaching processes, which all contribute to distinct PFAS profiles in the concrete.

Interestingly, 6:2 FTSA was the most dominant PFAS in the FTA cores, ranging from 0.29 to $3.34 \ \mu g/g$ (mean 1.69 $\ \mu g/g$). Except for Core #1, 6:2 FTSA quickly dropped to amounts near the detection limit after the 1 cm depth. The high abundance of 6:2 FTSA, combined with the low depth of penetration into the cores, suggest that historical use of AFFF was ECF-based. However, in recent years, a switch to FT-based AFFF was made, aligning with product timelines in North America for ECF vs FT foam demand. The FTA cores also showed a spike in concentrations of PFOS in Cores #2 and #3 at depths of 8 and 5 cm, respectively. PFOS was the only PFAS detected at these depths that spiked to levels two orders of magnitude higher than the concentration at the previous depth, but it is unclear why the spike occurred. At the bottom depth of Core#1, the curved upward profile indicates the possibility of interacting with the soil layer or gravel layer beneath. The wicking effect of repetitive wetting and drying cycles that occur at the bottom of the slab when in contact with a partially saturated soil layer may cause this increase.



Figure 3.6 Depth profile of PFAAs in concrete cores from a Canadian FTA that was contaminated by AFFFs.

3.4 Environmental Implications

As the uptake of PFAS into concrete at controlled rates has not been demonstrated in the literature, this study provides the first investigation into the phenomenon. Although the application of AFFF during training exercises has many factors not examined by this study, the combination of lab and field-based data provides insights into the initial contamination phase of concrete by AFFF and the factors affecting the kinetics of uptake into cement-based matrices. Contrasting uptake conditions were investigated, along with calculated diffusion rates of various PFAAs based on depth profiles. This work shows that PFAS can diffuse through concrete surfaces relatively easily, regardless of the additives in AFFF. However, compared to the original amount in a 3% AFFF or a defined PFAS mixture, PFAS retained in concrete only makes up a few percent of the total PFAS. According to this quantitative information, PFAS-contaminated concrete might not retain a significant amount of the total PFAS present at contaminated sites, depending on the mass of impacted concrete materials.

Our observations show that PFAS distributions within the concrete matrix are highly variable from location to location and even for cores cut from the same slab. Initial PFAS concentrations, solution compositions, wet/dry cycles, concrete surface conditions and concrete matrix heterogeneity all play a role. According to DESI-MSI and LC-MS analysis, after 1-year exposure, most PFAS inside the concrete appear trapped in the top few millimeters of the

surface. However, with hundreds of repeat applications like what occurs at impacted sites over decades, the intermittent wetting and drying periods between applications are expected to greatly accelerate this penetration into concrete, regardless of the chain length of PFAS. Based on this study, and also other publications, it appears that the shallow depths of impacted concrete are still responsible for retaining a large fraction of PFAS mass. In addition, the study has shown that concrete surface type also greatly affects the rate of PFAS contamination, with chipped surfaces with exposed aggregates having faster diffusion rates into the cement matrix. This issue is particularly relevant at many legacy AFFF sites, since the concrete surfaces from these sites directly involved in AFFF training are very likely to be somewhat damaged, with the top layer removed from weathering, mechanical wear, or fires. Damaged surfaces with air-entrained voids, micropores, and the interfacial transition zone of exposed aggregates pose preferential flow paths for PFAS to reach the core quickly.

What has not been elaborated in this Chapter is the role of interconversion among PFAS, especially the transformation of precursors to persistent PFAAs when AFFF are in contact with concrete. The topic will be discussed in depth in Chapter 4. While multiple studies have examined the leaching of AFFF from impacted concrete ¹²⁻¹⁴, many knowledge gaps still exist on the interactions between AFFF and impacted construction materials at impacted sites, including contaminated asphalt, potential for concrete re-use and recycling, and interactions between contaminated concrete and surrounding soil layers.

3.5 Acknowledgement

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CHAPTER 4: Abiotic transformation of per- and polyfluoroalkyl substances in the presence of concrete: Implications for chemical extraction and contamination characterization

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Abstract

The contamination of concrete by per- and polyfluoroalkyl substances (PFAS) at aqueous film-forming foam (AFFF)-impacted sites poses significant challenges for environmental remediation efforts due to the high stability of these compounds. Despite their prevalence at these sites, methods for extracting PFAS from impacted concrete have not been validated, impeding the efforts to assess and mitigate the contamination. In this work, the extraction method is validated for characterizing PFAS from AFFF-impacted concrete through spikerecovery experiments. Seven solvent conditions were tested for their efficacy at extracting perfluoroalkyl acids (PFAAs) and 14 different classes of precursors in electrochemical fluorination (ECF)-based AFFF from concrete powder. Methanol with 100 mM of ammonium acetate was found to be optimal in extracting the widest range of anionic, cationic, and zwitterionic compounds, but other solvent conditions had similar recovery performance for most PFAS classes. The recovery of perfluorocarboxylic acids (PFCAs) and perfluoroalkyl sulfonamides (FASAs) greatly exceeded 100%, suggesting their formation from precursor substances during exposure to concrete. Conversely, perfluoroalkyl amido amines (PFAAAm) almost completely disappeared during concrete exposure. Alkaline hydrolysis was responsible for the breakdown of PFAAAm to form PFCAs, but other unidentified sources also attributed to the significant generation of the latter. Similar abiotic transformation was also observed in the uptake experiments discussed in the previous chapter of the thesis, where PFCAs and FASAs were slowly increasing in the solution phase, with PFAAAm decreasing at the same time. Further experiments on four sulfonamide precursors suggested salting-out effects rather than compound degradation caused their rapid decrease in concentration, suggesting relatively high stability of sulfonamide precursors.

Keywords: PFAS, AFFF, concrete, abiotic transformation, precursor, hydrolysis

4.1 Introduction

The extensive use of aqueous film-forming foams (AFFF) at airports and military bases has caused significant contamination issues by per- and polyfluoroalkyl substances (PFAS) with surrounding environmental matrices, including soil, water, and even construction materials such as concrete.^{1, 2} PFAS in the original formulation of the AFFF may differ from those in environmental samples from AFFF-impacted sites since environmental processes can alter PFAS chemical structures.^{2, 3} Contamination of construction materials by PFAS can occur by application of AFFF directly onto their surface during firefighter training activities, runoff of PFAS-contaminated water into drains, or spills or leaks from AFFF storage facilities.⁴ The scale and severity of the PFAS contamination of concrete are yet to be revealed. There have been numerous studies examining methods for extracting and characterizing PFAS in impacted soil or water, but only one has documented PFAS extraction from construction materials, allowing chemical characterization and risk assessment, as well as assessment of treatment effectiveness.

Different studies have reported that methanol-based solvent extractions with an acidic, basic, or an ion exchange agent (commonly ammonium acetate) are optimal for extracting the wide range of anionic, cationic, and zwitterionic PFAS that are commonly found in AFFF.⁸⁻¹¹ These methods are sufficient for soils, but their applicability to concrete has not been evaluated.¹ Srivastava et al. (2022) presented the first and only effort to assess the efficacy of extraction methods from PFAS-contaminated asphalt. The solvent extraction cycle consisted of vortexing, sonication, and centrifugation steps and concentration in nitrogen. Perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkyl sulfonic acids (PFSAs), and fluorotelomer sulfonates (FTSAs) extracted using the solvent conditions tested did not differ significantly in recovery. However, the solvent combination methanol + methanol/1 % NH3 + methanol/0.4 M HCl had poor PFCA recovery. They also noted that recovery was acceptable for this method regardless of the amount of spiked PFAS, with 2 μ g/kg and 200 μ g/kg (PFAS/asphalt) having comparable recoveries. In the other published works that examined PFAS contamination in concrete, mixtures of methanol with 1-2 % ammonium hydroxide or acetone were used to extract concrete powder, but the efficacy of these methods was not evaluated.^{1, 4, 6}

There is a diverse mix of anionic, cationic, and zwitterionic precursors in AFFF, which are polyfluorinated compounds capable of transforming into perfluoroalkyl acids (PFAAs), each

with varying degrees of stability, and some of them can undergo both biotic and abiotic transformations.¹²⁻¹⁴ Successful treatment of PFAS by hydrothermal alkaline treatment (HALT) has been demonstrated, a treatment technique that causes both precursors and terminal PFAAs to mineralize by a combination of high temperatures (250 - 350 °C), high pressure (3.9 - 25 MPa), and alkaline conditions $(pH \sim 14)$.¹⁵⁻¹⁷ It is unclear what exact purpose the addition of a base such as NaOH serves, but it has been demonstrated that defluorination is not nearly as efficient when the reaction is conducted under neutral pH.¹⁸ As the presence of a strong base was deemed important for PFAS breakdown in AFFF in HALT processes, measurement of parameters such as pH and calcium ion concentration (as an indicator of calcium hydroxide release) in experiments with concrete was important for determining if a similar relationship existed in this work.

This study aimed to develop a suitable method for extracting a wide range of PFAS from AFFF-impacted concrete using a spike-recovery experiment. During the spiking and equilibration phase of clean concrete powder with AFFF, it was determined that perfluoroalkyl amido amine (N-(3-(dimethylamino)propyl)-perfluoroalkylamide) (PFAAAm) compounds, amide-based precursors in the foam, was transforming with subsequent generation of PFCAs. The same PFAAAm compounds were seen to transform with simultaneous generation of PFCAs and FASAs observed in the uptake experiment in Section 3.3.1. In both experiments, perfluoroalkyl sulfonamides (FASAs) were found to be generated along with PFCAs, yet their parent compounds are yet to be identified. In addition, four common electrochemical fluorination (ECF)-based AFFF precursors were tested for their ability to convert into terminal FASAs in the presence of concrete.

4.2 Materials and Methods

4.2.1 Chemicals and reagents

A mixture of analytical standards, as previously described in Section 3.2.1, was used for the analysis of PFAS. Most native and internal standards were purchased from Wellington Laboratories (Guelph, ON, Canada), and the rest of the standards were purchased from Beijing Surfactant Institute (Beijing, China). A comprehensive list of standards and corresponding internal standards used are available in Table A.1. The Calcium standard rated for atomic absorption spectroscopy (AAS) was purchased from MiliporeSigma (Oakville, ON, Canada). Glacial acetic acid, ammonium acetate, ammonium hydroxide (29%), and calcium hydroxide

were all purchased from Fisher Scientific (Oakville, ON, Canada). Nitrogen gas with a purity of 99.998% was from purchased MEGS Inc. (St-Laurent, QC, Canada). pH measurements were conducted with pH papers with a scale from 6.5 to 13 in 0.5-unit increments.

4.2.2 Sample preparation for the spike-recovery extraction test

The spike-recovery extraction experiments were first performed on clean concrete powder spiked with AFFF to assess mass recovery and experimental accuracy. At this stage, concrete powder collected from field-impacted cores was avoided because they contained unknown amounts of PFAS. AFFF-spiked concrete powder samples that were extracted were referred to as spike-before (SB) samples, whereas clean powder that was extracted with solvents first and then spiked with AFFF was referred to as spike-after (SA) samples.

The clean concrete powder was obtained by taking blocks of concrete previously cast from a mix design described in Section 3.2.2, and grinding them into a fine powder. The powder was then passed through a 250- μ m sieve to filter out large particles. The powder was then mixed for 1 or 5 days with an ECF-based AFFF diluted to 1 %. The goal was to achieve a ratio of 1 g of powder per 2 mL of 1 % AFFF solution. After mixing, the contaminated slurry of concrete powder and AFFF was dried at room temperature until the dried weight was within \pm 5% of the original mass of powder. The powder was then homogenized for a minute with a mortar and pestle, and any lumps were broken. The powder was then portioned into 0.3 g per sample, placed into 15 mL centrifuge tubes, and then subjected to an extraction cycle as described below.

Table 4.1 Extraction solutions tested in the spike-recovery experiment.

Additive to methanol:	Pure methanol	CH ₃ COOH	CH ₃ COONH ₄	NH4OH
Extraction Solutions:	1. Methanol	2. 10 mM	3. 10 mM 4. 100 mM 5. 400 mM	6. 0.1 % 7. 1 %

A volume of 4 mL of extraction solution comprised of pure methanol or methanol with acetic acid, ammonium acetate, or ammonium hydroxide at various concentrations was added to the contaminated powder. Table 4.1 shows the types of extraction solutions tested. The mixture was then vortexed for 0.5 minutes, ultrasonicated for 10 minutes, and finally centrifuged at 8600g for 5 minutes, after which the supernatant was transferred to a new tube. This process was repeated two more times. The combined extract from three sequential extractions (~11 mL

summed) was then concentrated to 5 mL using N_2 and mild heating at 40 °C. The extracts collected here represented the SB samples.

The same extraction procedure was undertaken for the SA samples, but the extractions were done with clean, uncontaminated concrete powder. After concentrating to 5 mL, 0.6 mL of the AFFF stock solution was spiked into the 5 mL solvent extract. The extracts collected here represented the SA samples.

In addition to SB and SA samples, non-spike (NS) samples were also designated by completing the extraction procedure described for SA samples, but no AFFF was spiked after extraction. These samples served as a measure for any background PFAS present in the clean concrete or extraction solutions used. The three sample types (SA, SB, and NS) were then spiked with an internal standard mix and analyzed by UHPLC-HRMS for their PFAS profile. The recovery of PFAS was calculated by Eq. (1) to correct for any matrix effects on the HRMS.

$$Recovery(\%) = \frac{SB - NS}{SA - NS} * 100$$
(1)

To determine if the extraction solutions had any effect on the recovery of the PFAS analyzed or if transformation of precursors can occur during the extraction process, an additional extraction experiment was performed as described above with a modified starting condition. In this experiment, the first extraction cycle of three started with of 0.3 g of clean concrete powder, 0.6 mL of AFFF stock solution, and 4 mL of extraction solution. The following two extractions were carried out normally with 4 mL of extraction solution. If any individual compound had a recovery outside the acceptable range (70 – 130 %), it would suggest the either the extraction solutions or the extraction process itself had an effect on the transformation or recovery of the PFAS in the AFFF used.

4.2.3 AFFF precursor degradability test

As briefly discussed in Chapter 3, unexpected abiotic transformation of select PFAS was noted early in the study. To further explore this largely unreported phenomenon, an AFFF precursor degradability test in the presence of the concrete matrix was carried out. Small concrete cylinders were made using a previously developed mix design by casting the concrete in 15 mL centrifuge tubes. After 30-day dry curing, the cores were removed from the tube and cut into smaller cores measuring 1 cm tall and 1.4 cm in diameter. Two separate solutions consisting of PFHxSAm and PFOSAm (each at 1 mg/L) and PFHxSAmS and PFOSAmS (each at 1 mg/L) were prepared in DI water. Each prepared solution was tested and further divided into three setups: concrete, calcium hydroxide, and a control. Sample setups comprised of one of the solutions described above in a small 60 mL polypropylene container with (1) a concrete core, (2) 1 mM calcium hydroxide or (3) nothing else as controls. Solutions were prepared at ratios of 5 mL solution per g of concrete core. Calcium hydroxide and control setups were filled with a flat amount of 15 mL solution. Triplicate conditions were used for each condition, except for the control solutions, which contain PFHxSAm, PFOSAm, PFHxSAmS, and PFOSAmS. A container of concrete in DI water was used as an additional control to test for potential background PFAS leaching from clean concrete.

Test containers were placed in a shaker at 120 rpm and 20 °C for the duration of the experiment. At regular intervals, setups were removed from the shaker, vortexed for 15 seconds, and then subsampled by taking 100 uL of solution and dissolving it in 900 uL of methanol, then storing at -20 °C until analysis. As indicated by the results from the spike-recovery experiment, transformation of certain PFAS was expected to occur rapidly; therefore, a condensed sampling period for the first week was conducted with samples being taken at 2 hours, 8 hours, 1 day, 2 days, 4 days, and 7 days. A final sample was taken on day 26, marking the end of the experiment for determining aqueous concentrations. The entire setup was extracted on Day 56 for mass balance determination, and the procedures are described in Text B.2.

4.2.4 PFAS Uptake Experiments

A parallel study on the uptake of PFAS by concrete was presented in Chapter 3, where PFAS transformation was noted. The relevant data, previously not discussed, are presented here to illustrate the transformative effects of concrete on certain precursors. Detailed information on the data originating from the uptake experiment, including experimental design of aqueous sample setups, concrete mix design and casting, and sample preparation for analysis, can be found in Section 3.2.3.

4.2.5 Instrumental analysis and quality control

Samples were analyzed on a Vanquish ultra-high performance liquid chromatography (UHPLC) coupled to a high-resolution Orbitrap mass spectrometer (HRMS) (ThermoFisher

Scientific, Waltham, MA, USA) as previously described in Section 3.2.5. All samples were analyzed in the full scan MS mode with polarity switching from 50-1000 m/z. Select samples were run using targeted MS/MS (t-MS²) mode in both positive and negative polarity modes at normalized collision energies of 20, 35, and 50% to confirm structures observed in the full scan mode. Full details on the instrumental analysis, including the UHPLC method and Orbitrap scan parameters, can be found in Table A.8. Samples were diluted at different levels (2-5000 ×), so analytes would fall into the range of calibration. Mass-labelled internal standards were added to all samples, including calibration standards and check standards at a final concentration of 3 ng/mg, except for mass-labelled PFOS (MPFOS). MPFOS was added to a final concentration of 100 ng/mL to accurately quantify PFOS, which represents a disproportionately high composition of PFAS in ECF-based AFFFs. Procedural blanks and check standards were run routinely every 10-20 samples to assess instrument drift. There was acceptable recovery of check standards, and no PFAS examined by the method detected in any procedural blanks.

The dissolved Calcium concentrations in test solutions were determined on a ContrAA 800D high-resolution continuum source (HR-CS) AAS (Analytik Jena, Beverly, MA, USA) in flame mode with a short arc xenon lamp. Samples were analyzed for their absorbance at a wavelength of 422.6728 nm. All samples were prepared in ASTM type I deionized water for its non-detect Calcium background. Full details on the instrument method, calibration, and quality control measures are available in Text B.1.

4.3 Results and Discussion

4.3.1 Assessment of PFAS extraction methods from impacted concrete

Extraction recoveries of individual PFAS in the AFFF are graphically presented, separated into three categories, and each displayed in a separate figure. Recoveries for PFSAs are plotted in Figure 4.1. PFCAs and PFAAAm compounds, which both underwent unexpected transformation, are plotted in Figure 4.3. Finally, 6- and 8-carbon chain length precursors from the AFFF are plotted in Figure 4.4. Full details on individual compound structures and recovery for precursors for all solvent conditions are presented in Tables B.3 and B.4.

As shown in Figure 4.1, extraction recoveries of PFSAs with chain lengths of C4-C8 are satisfactory, with an average recovery of 97 ± 4.5 % for the methanol condition. Recovery of longer chain PFSAs starts to decrease after PFOS, with C9, C10, and C12 compounds having a

combined average recovery of 71 ± 31 %, with the most significant drop occurring at C12 (PFDoS). Although long-chain PFAS are present in this AFFF at low amounts when compared to C4-C8 compounds, similar low recoveries were obtained for long-chain PFAS in other studies examining the recovery of PFAAs in soils and animal tissue.^{19, 20} The general low recoveries for these compounds are attributed to their high hydrophobicity. Differences in recoveries between solvent conditions tested were minor for most compounds, with the difference in the average recoveries being within the standard deviations, indicating the similar performance of the extraction solutions. Minor drops in recoveries for the 100- and 400-mM ammonium acetate condition for PFPeS, PFHpS, and PFNS were observed. As these compounds have much lower abundances in AFFF than the even-chain length compounds, their less-than-ideal recoveries have relatively little impact on the summed PFAS concentrations; however, further tests to re-examine the recoveries of these compounds are needed if they appear at high abundance in other types of AFFF foams.





In Figure 4.3, PFCAs (122 - 1576 %) showed exceedingly high recovery beyond 100%, while the opposite was observed for PFAAAm (0 - 6.7 %) with very low recoveries. As the recoveries were at either end of the extreme for acceptable recoveries, the experiment was repeated three more times by varying the concentration of AFFF used, mixing time, and concrete powder. The same trends were consistently observed at all times, except for the magnitude of

recoveries due to the varying amounts of AFFFs and concrete. These results confirm the hypothesis that the generation and degradation of select PFAS occurred. Considering the nearcomplete absence of the PFAAAm class, these precursor compounds exhibit instability when subjected to solvent extraction conditions. PFCA compounds are tentatively confirmed to the terminal products because, among the most classes of PFAS included in the analysis list (PFAA, FASA, MeFASA, EtFASA, MeFASAA, EtFASAA), no other compounds other than PFCA and FASA compounds were observed to have such significant increases. It remained unclear whether this transformation occurred when the clean powder was mixed with AFFF for 1-5 days for the SB condition, if it occurred during the extraction process, or from a mix of both processes. At this point, it was also unclear if the solvent additives had any effect on the recovery of PFAS, particularly for PFAAAm compounds where limited literature is available on this class of precursor.

Leveraging the HRMS data collected, we searched for other transformation products originating from PFAAAm through suspected screening; predicted transformation products were based on known aerobic biodegradation pathways, online prediction software and the literature.²¹ A full list of the potential transformation products screened for is available in Figures B.1 and B.2. However, none of the potential transformation products searched for were successfully identified, except PFCAs. In one of the experimental conditions, complete degradation of C4-C8 PFAAAm occurred within 24 hours. Thus, it is extremely unlikely that this loss is attributed to microbial-facilitated transformation, but abiotic transformation is more plausible. Thus, we hypothesize that the alkaline hydrolysis of the amide group (R-CONH-R'), or the reaction of the amide compounds with water, gave rise to a perfluoroalkyl carboxylic acid (R-COOH, e.g., PFCA) and an amine salt (H₂NR').²² As the reaction may occur quickly with direct cleavage at the C-N group, a one-step reaction is proposed in Figure 4.2. This direct bond cleavage would also explain why no other transformation products were found. Base hydrolysis of an amide (without a perfluoroalkyl chain attached) requires a strong base like NaOH and prolonged heating, and the reaction that we observed was unexpected. Our hypothesis is that the perfluoroalkyl chain alters the electron distribution and electron resonance on the amide group, enhancing the ability of the deprotonated amine to leave. As a result, an amide can be cleaved even without a strong base or significant heat input.



Figure 4.2 Proposed one-step alkaline hydrolysis of an amine compound to form perfluoroalkyl carboxylic acid and an amine salt.

As there were two other classes of precursors with an amide group in the AFFF foam, specifically, TAmPr-FAAd and EtOH-AmPr-FAAd (Appendix B for structures), it is likely that there is partial degradation of these compounds as well, resulting in further generation of terminal PFCAs based on the recovery shown in the precursor recoveries (Figure 4.2). An attempt at a mass balance for conversion of all known amide-containing precursors to PFCAs still cannot explain the significant generation of PFCAs, especially PFBA. It is still unclear why an average of $8.3 \pm 3.7 \times$ the initial starting concentration of PFBA (i.e., the concentration of PFBA in the AFFF foam) was generated, as the most dominant amide or non-amide-containing precursors tend to have either C6 or C8 carbon chain lengths. The excess generation of PFBA, along with PFPeA as the second highest PFCA generated by concentration, could suggest the further transformation of PFCA compounds (e.g., chain shortening) or other unknown precursors in the foam.

In addition to PFCA generation, there was also the generation of FASA, an important class of perfluoroalkyl sulfonamides. On average, their generation was higher than PFCAs; FHxSA was the highest in terms of recovery, $2.9 \pm 0.1 \times$ the starting concentration. In light of the formation of these perfluoroalkyl sulfonamides, it was possible that sulfonamide-based precursors can also be degraded, but probably not through the same pathways as amides, due to the S-N bond stability and retention of the primary amine. Thus, we surmise that the slightly lower-than-average recovery of PFHxSAm and PFOSAm shown in Figure 4.1 could indicate the possible decomposition of these compounds rather than true poor recovery, but further experimentation is needed to confirm this. The recovery of all FASA compounds is presented in Figure B.5.

Previously, nitrifying microorganisms have been suggested to degrade a dominant ECF precursor, PFHxSAm, under the right conditions.²³ The biotransformation of many other

sulfonamide-containing precursors was also summarized in prior works, with FASAs as a common transformation product.²⁴ However, due to the large number of different precursor classes in the foam tested and the many sulfonamide compounds that could potentially degrade, a new experiment was performed to observe if concrete could abiotically transform four sulfonamide precursors commonly found in high concentrations in ECF-based AFFFs. The results from this experiment are summarized in Section 4.3.3.



Figure 4.3 Extraction recoveries of PFCA and PFAAAm compounds from AFFF-contaminated concrete powder in the spike-recovery experiment.

The recoveries of PFSAm and PFSAmS (C6 and C8) showed much more variation between solvent conditions tested, yet no clear trend emerged to allow the selection of the most effective extraction solution (Figure 4.4). Three different solvent conditions had the highest recoveries out of the four compounds tested. PFHxSAm and PFOSAm had average recoveries of 72 ± 16 % and 66 ± 9.8 % respectively, whereas PFHxSAmS and PFOSAmS had recoveries of 93 ± 11 % and 75 ± 12 % respectively. Previously, cationic PFAS such as PFSAm and PFSAmS were found to exhibit highly variable recoveries from soil or sediment. It was hypothesized to be caused by strong ionic interactions between the positively charged PFAS and the negatively charged soil.⁹ Ammonia acetate was found to be an effective solvent additive to allow the effective extraction of these compounds.

The average recovery of all 14 dominant C6 precursors and nine dominant C8 precursors are presented in Figure 4.4, with 12 belonging to the sulfonamide class and two belonging to the amide class. The recovery of many of the *sulfonamide* precursors follows the same trend observed for PFSAs in that, generally, there is little difference in recovery based on the extraction solutions used, with the average recovery being around 80%. As previously noted, the two *amide* precursors had low recoveries of 36 ± 6.9 % and 61 ± 31 % for TAmPr-FAAd and EtOH-AmPr-FAAd, respectively, likely due to their degradation into other PFAS. Three sulfonamide precursors, S-OHPrAmPr-FASAA, SPrAmPr-FASAPrS, SPr-FASA, all displayed much higher recoveries when 100 mM of ammonium acetate was used, with recoveries comparable to other sulfonamides. As there was no difference in the recovery of anionic PFAS extracted with ammonium acetate, a methanol-based ammonium acetate solution may prove very effective in recovering PFAS, including precursors, from AFFF-impacted concrete. If PFAAs are the only PFAS of interest for extraction or HRMS instruments are not available, simple methanol may be used without major changes in the outcomes from extraction.





Figure 4.5 plots the extraction recoveries of PFSA, PFCA, and PFAAAm compounds for the four primary extraction solutions tested. The compound recoveries are well within the acceptable range for recovery, with PFSA, PFCA, and PFAAAm compound classes having recoveries of 113 ± 5.4 %, 112 ± 3 %, and 109 ± 5.2 %, respectively. With no observed loss of PFAAAm compounds or generation of PFCAs, as well as very stable recoveries being achieved, it is very likely that transformation does not occur during the extraction process, nor do the extraction solutions cause transformation. Therefore, transformation must occur during the initial mixing step, where AFFF and clean concrete powder are combined and shaken for 1-5 days. When compared to field-impacted concrete, which is contaminated over several decades from repeat use of AFFF, the transformation process is likely still occurring, albeit slower. Using the extraction method developed above, field-impacted concrete can be successfully characterized without artificial inflation of levels of PFCAs, which will be important when considering the eventual remediation of these sites based on PFAS contamination of concrete.



Figure 4.5 Extraction recoveries of PFSA, PFCA, and PFAAAm compounds during extraction solution and stability test.

4.3.2 Transformation of PFAS in the PFAS uptake experiment

To understand the kinetics behind the transformation of the PFAAAm, PFCA, and FASA compounds, their aqueous phase concentrations in the experiments (i.e., 3% AFFF solution pooled on the top of concrete materials) presented in Section 3.3.1 are plotted in Figure 4.6. As observed in the spike recovery experiment, there appears to be a similar transformation of these three classes of compounds in the uptake experiment. For PFAAAm (Figure 4.6, a-c), in the first seven days, their concentration remains stable and then begins to decrease rapidly, with

PFBAAm decreasing the fastest and PFOAAm decreasing the slowest. Higher stability was observed for those with longer chain lengths; the least abundant PFHpAAm among the class has the second highest stability. Flat and chipped surfaces have very similar profiles. The concentrations in the controls are largely unchanged, suggesting the stability of the compounds and the lack of mechanisms to remove the compounds from AFFF solutions, in the absence of concrete materials. Simultaneously, as these compounds are degraded, PFCAs are generated and plateau around day 100 (Figure 4.6, d-f). There is a rough chain length dependency, with PFBA showing the largest increase and PFOA the smallest. As previously stated, tracking the generation of PFCAs from PFAAAm compounds by mass balance calculation is difficult due to the possible degradation of other precursors. Thus, the concentration profiles shown in Figure 4.6 are only meant to serve as a rough indication of kinetics.

Similarly, FASAs were also generated in the same pooled solution (Figure 4.6, g-i). The highest increases occurred to PFHxSA and FOSA, and the chain length dependence cannot be identified. Again, it is still unclear which precursor(s) are transforming into these products.



Figure 4.6 Relative concentrations (normalized to Day 0) of PFAAAm (a-c), PFCA (d-f), and FASA (g-i) compounds in the AFFF solutions pooled on flat and chipped concrete surfaces from the uptake experiment discussed in Chapter 3.

In the uptake experiment, calcium concentration and pH in the pooled solutions were measured and shown in Figure 4.7. As the concentration of calcium increases, presumably from the leaching of calcium hydroxide, there is a lagging but similar increase in pH, which also corresponds with the kinetics of degradation and generation of the three transformation compounds. The results from the uptake experiment support the previously proposed mechanism that the degradation of amide-containing precursors is due to alkaline hydrolysis from leaching of calcium hydroxide from the concrete. Slightly faster generation of PFCAs and FASAs can be seen in the flat surface concrete samples as well as a corresponding higher calcium concentration and pH at the same time points, suggesting that finished concrete surfaces can transform compounds faster due to the higher amount of calcium available for leaching, against chipped surfaces which contain more exposed aggregate per the same surface area. Although the conditions were only slightly basic at pHs of 7.5 and 8.5 at day 100 for the chipped and flat surface, respectively, the already complete transformation of PFCA, PFAAAm, and FASA compounds at this point would that the reactions primarily occur at the concrete-water interface because of high localized pH.

The current experimental setups were not sterile, but we did not expect to have significant microbial biomass because of the lack of nutrients, carbon sources and the initial microbial inoculums from the tap water and concrete materials. To rule out the microbial-facilitated degradation, an ATP measurement was conducted on day 290. Additionally, agar plates were prepared on days 246 and 365 to gauge microbiological activity. Full details on the methodology are available in Appendix B. The very low ATP amounts in the pooled solution would suggest limited microbial activities, ruling out the presence of biodegradation of precursors. Additionally, agar plates only had minor colony formation on the lowest dilution prepared, further suggesting there was limited biomass present.



Figure 4.7 Calcium concentration (a) and solution pH (b) in the AFFF solutions pooled on flat and chipped concrete surfaces from the uptake experiment discussed in Chapter 3.

4.3.3 PFSAm and PFSAmS transformation analysis

Results obtained in both the uptake and spike-recovery extraction experiments indicated the transformation of amide-based precursors in ECF-AFFF solutions when exposed to concrete, whether a surface of a low specific surface area or concrete powders with a large specific area. These experiments also showed the generation of FASA compounds from sulfonamide precursor(s), which were yet to be identified in the AFFF foam. Figure 4.4 shows the consistently acceptable (or marginally acceptable) recoveries of various classes of sulfonamide compounds hovering around 60~90%, which, however, cannot be used to indicate their chemical stability in solutions exposed to concrete. Therefore, another experiment, as described in Section 4.2.3, on two classes of dominant sulfonamide precursors commonly found in ECF-AFFFs, was carried out to examine their stability. Using concrete cores and constant solution shaking, the experiment was designed to aim for transformation kinetics somewhat faster than those in the uptake experiment (concrete core, no shaking), but slower than the 1-day reaction in the spike-recovery experiments (concrete powder, shaking).

Examining the PFSAm and PFSAmS concentration in Figure 4.8 a-c shows that the concentration of the two C8 compounds, PFOSAm and PFOSAmS, drop off very quickly in the presence of concrete surfaces within 8 hours. A less rapid drop-off followed for the same compounds in 1 mM calcium hydroxide (equivalent to 40 mg/L Ca²⁺) solution. The corresponding C6 compounds, PFHxSAm and PFHxSAmS, did not have any drop in concentration in the solution of these four compounds for both the setups with concrete and calcium hydroxide. This would suggest that neither of these C8 compounds was abiotically degrading through alkaline hydrolysis, but rather may be precipitating through the salting-out effect. The salting-out effect due to calcium ions is expected to affect long-chain PFAS more than short-chain in soils, but this has not been evaluated in aqueous phases.²⁵



Figure 4.8 Concentration of PFSAm and PFSAmS C6 and C8 compounds from non-analytical grade standards with (a) concrete, (b) 1 mM calcium hydroxide, (c) and control.

A recovery test was done after the last sample was taken on day 26 to determine if the lost C8 compounds could be recovered. Information on the method of the recovery test performed is available in text B.2. Despite the somewhat aggressive extraction condition, only

minor amounts of PFOSAm and PFOSAmS were able to be recovered at 35 % and 41 %, respectively, compared to the amount recovered from the day 26 sample of 14 % and 12 % for PFOSAm and PFOSAmS respectively which did not have any aggressive extraction. Recovery rates obtained in the extraction experiment were much higher at 66 ± 9.8 % and 75 ± 12 % for PFOSAm and PFOSAmS, respectively. It is unclear why the amount extracted after day 26 was so low, given that there would have been much more calcium in the spike-recovery test and, therefore, a stronger salting-out effect than in the precursor degradation test. Results from the recovery test are available in Figure B.3.

4.4 Environmental Implications

Although previous work on PFAS breakdown from the HALT process has been shown, degradation of amide-based precursors with calcium hydroxide from concrete has not been demonstrated. The hydrolysis reaction in alkaline conditions of these precursors facilitated by calcium hydroxide release from concrete to form terminal PFCAs is presented as a major abiotic degradation pathway. It remains unclear which precursor(s) are also degraded by concrete to form terminal FASAs or if degradation of amide-based PFAS can form sulfonamides during the transformation process.

Recovery of anionic PFSAs is shown not to be affected by the addition of a solvent aid and therefore, a simple methanol-based extraction procedure is expected to be sufficient for acceptable recoveries (70 - 130 %). Recovery of some sulfonamide precursors in AFFF is affected by the solvent additive. It was shown that 100 mM of ammonium acetate in methanol had much higher extraction efficiency than pure methanol for three different sulfonamide-based precursors. Assessing the recovery of amide-containing precursors in AFFF-impacted concrete is difficult due to their vulnerability to transformation when calcium hydroxide is released during initial and subsequent aqueous contamination events. However, the recovery of PFCAs and PFAAAm compounds was shown to not be affected by the extraction process nor the extraction solutions used, allowing successful characterization of these two classes of compounds in fieldimpacted concrete. Opportunities for future studies could include assessing the transformation of PFAAAm compounds when exposed to concrete and determining if a pure solution of these compounds can be commercially or custom synthesized to confirm that PFCAs are the only terminal product.

The concentration profile from the uptake experiment shows the rapid leaching of calcium hydroxide from concrete, which directly correlates to the subsequent drop in the concentration of PFAAAm compounds and a corresponding rise in PFCA concentrations. This further reinforces the idea that the mechanism responsible for transformation is calcium hydroxide-based. Further experimentation testing four dominant sulfonamide-based precursors, PFHxSAm, PFOSAm, PFHxSAmS, and PFOSAmS, for their potential to transformation into FASAs, did not show any significant breakdown but did show the hypothesized salting out effect that concrete can cause, something to consider when investigating contaminated sites.

Overall, this work provides a robust method for extracting a wide range of anionic, cation, and zwitterionic PFAS from AFFF-impacted concrete, as well as documents the transformation of an amide-based precursor into PFCAs. High concentrations of terminal PFAS such as PFCAs, FASAs, and even possibly PFSAs found in concrete at AFFF-impacted sites should not be ruled as original AFFF components, but can also be from transformation of precursors given the long residence time of these compounds in concrete and the demonstrated transformations that can occur.

4.5 Acknowledgement

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CHAPTER 5: Summary and Future Work

5.1 Summary

This work aimed to close existing knowledge gaps on interactions between AFFF and concrete, particularly under conditions relevant to impacted sites. The two Chapters presented elucidate some of the kinetics and physical and chemical processes that are involved with the uptake of AFFF and PFAS into concrete, as well as methods for extracting PFAS from AFFF-impacted concrete and possible abiotic transformations that can occur. Finally, these results from lab-based experiments are compared to field-impacted concrete from a real impacted site in Canada.

In Chapter 3, the extent of PFAS uptake by flat and chipped concrete surfaces is compared by pooling two solutions consisting of a mix of 12 PFAS and an ECF AFFF onto concrete surfaces. The impact of intermittent wetting and drying cycles on AFFF uptake into concrete was also compared to static pooled solutions. Concrete cores from the uptake experiment were then extracted at various depths to observe the profile of various PFAS. Finally, concrete cores from an impacted site in Canada were also extracted and compared to labcontaminated cores to observe differences in trends. While the summed concentration of PFAS pooled onto concrete surfaces remained constant throughout the 365-day experiment, PFAS was detected at all depths in the core to a final depth of 2.5 cm, exhibiting that PFAS can migrate through the cement matrix at variable rates. Unsurprisingly, chipped surfaces had much faster diffusion for all PFAS due to direct exposure to the pore network. There was a variation in the migration rate, which occurred with longer chain PFAS in the AFFF solutions above C6, having the same rate of diffusion of C7-C12 compounds. PFCAs and PFSAs from the mix of 12 PFAS tended to be more mobile than in the AFFF solution. Extraction of the core subject to wetting and drying cycles revealed equal rates of diffusion of all PFAS present, suggesting a more accurate depiction of what may occur at impacted sites due to the rates of AFFF application. However, results from the extraction of the real impacted cores displayed a somewhat similar trend to those from the uptake experiment, with longer chain PFAS having less mobility throughout the cores. Finally, a mixture of 6:2 FTSA and PFOS was the most dominant PFAS in the field-impacted cores, suggesting a mix of ECF and FT foams were used.

Chapter 4 presented a method for extracting a wide range of anionic, cationic, and zwitterionic PFAS from AFFF with 14 distinct classes of precursors being examined. From the seven extraction solutions tested, methanol with ammonium acetate was the most efficient in

achieving acceptable recoveries (70-130%) for the PFAS screened for in the AFFF. No major differences in extraction efficiency were observed for the anionic PFAS such as PFSA, PFSAm, and PFSAmS compounds between different extraction solutions tested. It was discovered very quickly during the first iteration of the spike-recovery extraction test that some amide-based precursors could be transformed during extraction to PFCAs. The proposed mechanism for this transformation was alkaline hydrolysis from the release of calcium hydroxide from the concrete. This mechanism indicated a fast reaction with PFCAs predicted as the only terminal fluorinated products as no intermediates screened for were found. However, this transformation of amidebased precursors does not explain the generation of FASA compounds; thus, more work is needed to determine their formation pathway. Experimentation on the potential transformation of PFSAm and PFSAmS compounds showed a significant decrease in C8 compounds, which was determined to likely be coming from the salting out effect inducted from the release of salts from the concrete.

5.2 Future work

Many unanswered questions remain on the environmental fate of PFAS in AFFFimpacted construction materials, including concrete and asphalt, at contaminated sites. Specifically, it is unknown what effect contaminated concrete may have on other important environmental matrices, such as soil and water, due to their proximity to each other at these sites. This thesis investigated the uptake or contamination phase of concrete with an ECF-based AFFF, developed an extraction method, and identified the abiotic transformation process of a precursor class that may occur in concrete. Future studies can benefit from the experimental data in the thesis to allow the development of a mathematical model to simulate PFAS transport within a concrete matrix. For instance, the migration of a few compounds in the static exposure experiments can be satisfactorily simulated using Fick's First Law of Diffusion, but not the others and also not in the experiments with repeated wetting and drying. Mathematical simulation may resolve the processes by considering capillary action and possibly transformation in a concrete matrix. Such simulation may also be used to simulate PFAS leaching out of concrete.

Although ECF-based AFFFs were among the most used foams in military bases, FTbased foams have been widely used in recent years in both military and non-military facilities. The applicability of our extraction method to these foams needs to be further assessed. In

addition, fluorotelomers generally show lower stability than ECF-based compounds, and therefore, their interactions with concrete might also lead to significant breakdown of some compounds, posing challenges in accurately assessing the extent of the contamination. FT-based foams also contain few PFCAs or PFSAs, and most of the components are zwitterionic and anionic surfactants. Most of these polyfluorinated surfactants are not even routinely monitored, but they are hidden sources of PFCAs and must be considered in risk assessment and future remediation efforts.

Further, there will eventually be a need to dispose of or remediate the contaminated concrete at impacted sites such as military bases and airports, just as contaminated water and soils are being dealt with now. It will be essential to develop feasible remediation strategies to meet the future challenge of dealing with contaminated construction materials at contaminated sites when eventual regulations become enforced.

Appendix A: Supplemental Information for Chapter 3

Text A.1 DESI MSI instrument method and sample preparation

Concrete cores cut in half were polished using an industrial grade polisher with mode medium grit and fine grit polishing plate, where roughly 1-2 mm of the concrete surface was removed in the process. The polished concrete core was loaded onto the DESI-XS (Waters, MA) two-dimensional stage, equipped with a high-performance cartridge-based sprayer and heat transfer line (Waters Corporation; Wilmslow, UK). The DESI-XS source was operated at a capillary voltage 0.7 kV, a cone voltage 40 V, source temperature of 100 °C, a gas pressure of 0.09Mpa and a heated transfer line temperature of 350 °C. The DESI-XS sprayer had a spray angle of 85° and a distance of 1-2 mm from sample surface. The solvent system consisted of 95:5 MeOH/Water with 0.1% formic acid and 200 pg/uL leucine enkephalin by a U3000 UHPLC pump (ThermoFisher) at a rate of 8 μ L/min. The DESI-XS source was connected to a Waters Multi-Reflecting time of flight (MRTOF) mass spectrometer, which was operated with default instrument settings apart from MS profile conditions where a manual profile was used to optimise signal at lower m/z's (See table below).

The DESI experiments were conducted at a 200 μ m x 200 μ m pixel size with a scan time of 1 second per pixel. All experiments were conducted with a continuous lock mass correction using leucine enkephalin (*m*/*z* 554.26202 [M-H]⁻) present within the mobile phase. This correction was performed post-acquisition. The lockmass corrected data was then imported into SCILS Lab (Bruker) using default settings from the Waters MRT, except using a 10mDa bin size when processing the data. The data was processed with no normalisation and images were produced using a gradient colour scale (flexImaging).

Methanol (LC-MS/MS grade) and Water (MilliQ) was purchased from Merck (Millipore) and used with no further modification.

Analyte	Name	Ion Formula	Theoretical	Observed	Error	RT	Sources of
			m/z	m/z	(ppm)	(min)	standards
PFBA	Perfluorobutanoic acid	$[C_4F_7O_2]^-$	212.9792	212.9791	-0.6	2.99	
PFPeA	Perfluoropentanoic acid	$[C_5F_9O_2]^-$	262.9760	262.9756	-1.6	4.12	
PFHxA	Perfluorohexanoic acid	$[C_6F_{11}O_2]^-$	312.9728	312.9724	-1.27	4.93	
PFHpA	Perfluoroheptanoic acid	$[C_7F_{13}O_2]^-$	362.9696	362.9689	-1.9	5.62	
PFOA	Perfluorooctanoic acid	[C ₈ F ₁₅ O ₂] ⁻	412.9664	412.9660	-1.1	6.24	
PFNA	Perfluorononanoic acid	[C ₉ F ₁₇ O ₂] ⁻	462.9632	462.9629	-0.7	6.86	
PFDA	Perfluorodecanoic acid	$[C_{10}F_{19}O_2]^-$	512.9600	512.9601	0.2	7.48	
PFUnA	Perfluoroundecanoic acid	[C ₁₁ F ₂₁ O ₂] ⁻	562.9568	562.9572	0.6	8.11	Wellington
PFDoA	Perfluorododecanoic acid	[C ₁₂ F ₂₃ O ₂] ⁻	612.9537	612.9539	0.4	8.74	Laboratories
PFTrDA	Perfluorotridecanoic acid	[C ₁₃ F ₂₅ O ₂] ⁻	662.9505	662.9504	0.03	9.32	Canada)
PFTeDA	Perfluorotetradecanoic acid	[C ₁₄ F ₂₇ O ₂] ⁻	712.9473	712.9471	-0.2	9.79	
PFHxDA	Perfluorohexadecanoic acid	$[C_{16}F_{31}O_2]^-$	812.9409	812.9412	0.4	10.74	
PFOAcDA	Perfluorooctadecanoic acid	[C ₁₈ F ₃₅ O ₂] ⁻	912.9345	912.9352	0.8	12.03	
PFBS	Perfluorobutane sulfonate	$[C_4F_9SO_3]^-$	298.9430	298.9422	-2.7	4.99	
PFPeS	Perfluoropentane sulfonate	[C ₅ F ₁₁ SO ₃] ⁻	348.9398	348.9388	-2.9	5.75	
PFHxS	Perfluorohexane sulfonate	[C ₆ F ₁₃ SO ₃] ⁻	398.9366	398.9358	-1.9	6.40	
PFHpS	Perfluoroheptane sulfonate	[C ₇ F ₁₅ SO ₃] ⁻	448.9334	448.9329	-1.2	7.03	

Table A.1 Full list of native analytes with available analytical standards.

PFOS	Perfluorooctane sulfonate	$[C_8F_{17}SO_3]^-$	498.9302	498.9302	-0.5	7.64
PFNS	Perfluorononane sulfonate	$[C_9F_{19}SO_3]^-$	548.9270	548.9269	-0.1	8.24
PFDS	Perfluorodecane sulfonate	[C ₁₀ F ₂₁ SO ₃] ⁻	598.9238	598.9237	-0.2	8.81
PFDoS	Perfluorododecane sulfonate	[C ₁₂ F ₂₅ SO ₃] ⁻	698.9174	698.9164	-1.5	9.63
FBSA	Perfluorobutane sulfonamide	[C ₄ F ₉ SO ₂ NH] ⁻	297.9590	297.9583	-2.3	5.93
FHxSA	Perfluorohexane sulfonamide	[C ₆ F ₁₃ SO ₂ NH] ⁻	397.9526	397.9519	-1.7	7.12
FOSA	Perfluorooctane sulfonamide	[C ₈ F ₁₇ SO ₂ NH] ⁻	497.9462	497.9463	0.2	8.07
MeFOSA	N-methyl-perfluorooctane sulfonamide	[C ₉ F ₁₇ SO ₂ NH ₃] ⁻	511.9619	511.9619	0.0	8.68
EtFOSA	N-ethyl-perfluorooctane sulfonamide	$[C_{10}F_{17}SO_2NH_5]^{-1}$	525.9775	525.9774	-0.3	8.90
FOSAA	Perfluorooctane sulfonamidoacetic acid	$[C_{10}F_{17}SO_4NH_3]^-$	555.9517	555.9518	0.2	7.98
MeFOSAA	N-methyl-perfluorooctane sulfonamidoacetic acid	$[C_{11}F_{17}SO_4NH_5]^{-1}$	569.9673	569.9677	0.7	8.48
EtFOSAA	N-ethyl-perfluorooctane sulfonamidoacetic acid	$[C_{12}F_{17}SO_4NH_7]^{-1}$	583.9830	583.9834	0.7	8.70
6:2 FTSA	6:2 fluorotelomer sulfonate	$[C_8F_{13}H_4SO_3]^-$	426.9679	426.9670	-2.2	5.84
8:2 FTSA	8:2 fluorotelomer sulfonate	$[C_{10}F_{17}H_4SO_3]^-$	526.9615	526.9608	-1.3	6.99
PFHxSAm (AmPr- FHxSA)	Perfluorohexane sulfonamidoalkyl amine	$[C_{11}H_{14}F_{13}N_2O_2S]^+$	485.0563	485.0550	-2.7	5.82

PFOSAm (AmPr-	Perfluorooctane	$[C_{13}H_{14}F_{17}N_2O_2S]^+$	585.0499	585.0482	-2.9	6.69	Beijing Surfactant
FOSA)	sulfonamidoalkyl amine						Institute (Beijing,
							$C(1, 1, \dots, n)$
PFHxSAmS	Perfluorohexane	$[C_{12}H_{16}F_{13}N_2O_2S]^+$	499.0719	499.0704	-3.1	5.87	China)
(NTAmP-FHxSA)	sulfonamidoalkyl ammonium						
PFOSAmS (NTAmP-	Perfluorooctane	$[C_{14}H_{16}F_{17}N_2O_2S]^+$	599.0656	599.0635	-3.4	6.76	-
FOSA)	sulfonamidoalkyl ammonium						

 Table A.2 Full list of internal analytical standards.

Analyte	Acronym	Name	Ion Formula	Theoretical	Observed	Error	RT	Sources of
				m/z	m/z	(ppm)	(min)	standards
¹³ C ₄ -PFBA	MPFBA	Perfluoro-n-(¹³ C ₄) butanoic acid	[¹³ C ₄ F ₇ O ₂] ⁻	216.9926	216.9925	-0.6	2.99	
¹³ C ₅ -PFPeA	M5PFPeA	Perfluoro-n-(¹³ C ₅) pentanoic acid	[¹³ C ₅ F ₉ O ₂] ⁻	267.9928	267.9924	-1.3	4.12	Wellington
¹³ C ₅ -PFHxA	M5PFHxA	Perfluoro-n-(1,2,3,4,6- ¹³ C ₅) hexanoic acid	[¹³ C ₅ F ₁₁ O ₂] ⁻	317.9896	317.9893	-1.0	4.93	Laboratories (Guelph, ON,
¹³ C ₄ -PFHpA	M4PFHpA	Perfluoro-n-(1,2,3,4- ¹³ C ₄) heptanoic acid	$[^{13}C_4F_{13}O_2]^-$	366.9830	366.9825	-1.5	5.62	Canada)
¹³ C ₈ -PFOA	M8PFOA	Perfluoro-n-(¹³ C ₈) octanoic acid	$[^{13}C_8F_{15}O_2]^{-1}$	420.9933	420.9930	-0.5	6.24	

¹³ C ₉ -PFNA	M9PFNA	Perfluoro-n-(¹³ C ₉) nonanoic acid	[¹³ C ₉ F ₁₇ O ₂] ⁻	471.9934	471.9933	-0.3	6.86	
¹³ C ₆ -PFDA	M6PFDA	Perfluoro-n-(1,2,3,4,5,6- ¹³ C ₆) decanoic acid	$[^{13}C_6C_4F_{15}O_2]^-$	518.9802	518.9805	0.7	7.48	
¹³ C ₇ -PFUnA	M7PFUdA	Perfluoro-n-(1,2,3,4,5,6,7- ¹³ C ₇) undecanoic acid	$[^{13}C_7C_4F_{21}O_2]^-$	569.9803	569.9809	1.0	8.11	
¹³ C ₂ -PFDoA	MPFDoA	Perfluoro-n-(1,2- ¹³ C ₂) dodecanoic acid	[¹³ C ₂ C ₁₀ F ₂₃ O ₂] ⁻	614.9604	614.9609	0.8	8.74	
¹³ C ₂ -PFTeDA	M2PFTeDA	Perfluoro-n-(1,2- ¹³ C ₂) tetradecanoic acid	$[^{13}C_2C_{12}F_{27}O_2]^{-1}$	714.9540	714.9540	0.1	9.79	
¹³ C ₃ -PFBS	M3PFBS	Perfluoro-1-(2,3,4- ¹³ C ₃) butanesulfonate	[¹³ C ₃ C ₁ F ₉ SO ₃] ⁻	301.9531	301.9524	-2.2	4.99	
¹³ C ₃ -PFHxS	M3PFHxS	Perfluoro-1-(1,2,3- ¹³ C ₃) hexanesulfonate	[¹³ C ₃ C ₃ F ₁₃ SO ₃] ⁻	401.9467	401.9463	-1.0	6.40	
¹³ C ₈ -PFOS	M8PFOS	Sodium perfluoro-1-(¹³ C ₈) octanesulfonate	$[^{13}C_8F_{17}SO_3]^-$	506.9571	506.9568	-0.5	7.64	
¹³ C ₄ -PFOS	MPFOS	Sodium perfluoro-1- (1,2,3,4- ¹³ C ₄) octanesulfonate	[¹³ C ₄ C ₄ F ₁₇ SO ₃] ⁻	502.9436	502.9427	-1.7	7.64	
¹³ C ₈ -FOSA	M8FOSA-I	Perfluoro-1-(¹³ C ₈) octanesulfonamide	[¹³ C ₈ F ₁₇ NHSO ₂] ⁻	505.9730	505.9734	0.6	8.09	
d ₃ -N- MeFOSA	d-N-MeFOSA	N-methyl-d3 -perfluoro- 1-octanesulfonamide	[C ₉ F ₁₇ NSO ₂ D ₃] ⁻	514.9807	514.9823	3.4	8.67	
d ₅ -N-EtFOSA	d-EtFOSA	N-ethyl-d5 -perfluoro-1- octanesulfonamide	$[C_{10}F_{17}NSO_2D_5]^{-1}$	531.0089	531.0104	2.8	8.89	
--	-------------	---	---------------------------------	----------	----------	------	------	---
d ₃ -N-	d3-N-	N-methyl-d3 -perfluoro-	$[C_{11}F_{17}NSO_4D_5H_2]^-$	514.9807	514.9823	3.1	8.67	-
MeFOSAA	MeFOSAA	1- octanesulfonamidoacetic acid						
¹³ C ₂ -6:2 FTSA	M2-6:2 FTSA	1H,1H,2H,2H-perfluoro (1,2- ¹³ C ₂) octanesulfonate	$[^{13}C_2C_6F_{13}H_4SO_2]^-$	428.9746	428.9757	2.6	5.84	
¹³ C ₂ -8:2 FTSA	M2-8:2 FTSA	1H,1H,2H,2H-perfluoro (1,2 $^{-13}C_2$) decanesulfonate	$[^{13}C_2C_8F_{17}H_4SO_2]^-$	528.9682	528.9672	-1.9	6.99	
6:2 FTAB	M6:2 FTAB	6:2 fluorotelomer betaine	$[C_{15}F_{13}H_{20}N_2SO_4]^+$	571.0931	571.0923	-1.4	5.89	
PFOAAmS	MPFOAAmS	Perfluorooctane amidoalkyl ammonium salt	$[C_{14}H_{16}F_{15}N_2O]^+$	513.1018	513.1006	-2.2	5.90	Beijing Surfactant Institute (Beijing, China)

Native analyte	Corresponding internal standard
PFBA	MPFBA
PFPeA	M5PFPeA
PFHxA	M5PFHxA
PFHpA	M4PFHpA
PFOA	M8PFOA
PFNA	M9PFNA
PFDA	M6PFDA
PFUnA	M7PFUdA
PFDoA	MPFDoA
PFTrDA	M2PFTeDA
PFTeDA	M2PFTeDA
PFHxDA	M2PFTeDA
PFOAcDA	M2PFTeDA
PFBS	M3PFBS
PFPeS	M3PFHxS
PFHxS	M3PFHxS
PFHpS	M8PFOS
PFOS	M8PFOS or MPFOS
PFNS	M8PFOS
PFDS	M8PFOS
PFDoS	M8PFOS
FBSA	M8FOSA-I
FHxSA	M8FOSA-I
FOSA	M8FOSA-I
MeFOSA	d-N-MeFOSA
EtFOSA	d-EtFOSA

Table A.3 List of native standards and corresponding internal standards.

FOSAA	d3-N-MeFOSAA
MeFOSAA	d3-N-MeFOSAA
EtFOSAA	d3-N-MeFOSAA
6:2 FTSA	M2-6:2 FTSA
8:2 FTSA	M2-8:2 FTSA
PFHxSAm (AmPr-FHxSA)	M6:2 FTAB or MPFOAAmS
PFOSAm (AmPr-FOSA)	M6:2 FTAB or MPFOAAmS
PFHxSAmS (NTAmP-FHxSA)	M6:2 FTAB or MPFOAAmS
PFOSAmS (NTAmP-FOSA)	M6:2 FTAB or MPFOAAmS

 Table A.4 Sieve analysis of aggregates used in the concrete mix design.

Sieve #	Sieve	Sieve (g)	Sieve +	Aggregates	Percent	Cumulative	Percent
	Opening		Aggregates	(g)	Retained	Percent	Passing
	(mm)		(g)			Retained	
4	4.75	590.24	591.11	0.87	0.1	0.1	99.9
8	2.38	431.45	693.97	262.52	15.5	15.5	84.5
10	2	428.09	554.69	126.6	7.5	23.0	77.0
12	1.68	475.26	610.91	135.65	8.0	31.0	69.0
14	1.4	450.31	576.24	125.93	7.4	38.4	61.6
16	1.18	614.73	750.12	135.39	8.0	46.3	53.7
18	1	465.17	613.77	148.6	8.8	55.1	44.9
20	0.85	433.61	463.99	30.38	1.8	56.9	43.1
40	0.42	403.49	467.65	64.16	3.8	60.7	39.3
Pan		331.63	989.63	658	38.8	99.4	0.6

	1	2	3
Mass of oven-dry sample in air (g)	17.70	17.86	16.78
Mass of surface dry sample in air after immersion (g)	19.03	19.19	17.99
Mass of surface dry sample in air after immersion and boiling (g)	19.12	19.23	18.09
Height (mm)	29.60	28.96	28.63
Diameter (mm)	18.90	18.92	18.75
Volume (cm ³)	8.30	8.14	7.91
Apparent mass of sample in water after immersion and boiling (g)	10.81	11.09	10.18
Dry bulk density (g/cm ³)	2.13	2.19	2.12
Apparent density	2.57	2.64	2.54
Volume of permeable voids, %	20.63	20.31	19.79

Table A.5 Bulk density and volume of permeable voids in lab cast concrete as per ASTM C642.

Table A.6 Compression strength of full-sized cast cores as per ASTM C39.

Core	1	2	3
Diameter (mm)	102.5	102.7	101.7
Height (mm)	193	190.5	193.5
Surface area (mm)	8252	8284	8123
Ultimate Load (kN)	322.2	284.3	323.1
Ultimate Compressive Strength (MPa)	39.05	34.32	39.77

Day						
0	0.25	1	2	3	5	7
14	21	28	35	42	49	72
91	105	119	231	280	322	365

Table A.7 Sampling schedule for PFAS uptake experiment.

Table A.8 UHPLC-HRMS instrument method parameters

Instrument	ThermoFisher Var	ThermoFisher Vanquish UHPLC coupled to a ThermoFisher Orbitrap				
	Exploris 120					
Ionization	Positive and negative electrospray					
Acquisition mode	Full scan MS mod	e				
	t-MS ² mode					
Analytical column	ThermoFisher Hyp	persil GOLD C18 1.9 μm, 100 x 2.1 mm				
Delay column	Kintex 5 µm EVO	C18				
Column temperature	40 °C					
Ion transfer tube temperature	325 °C					
	350 °C	50 °C				
Mobile phases	A: HPLC water with 0.1% formic acid					
	B: Acetonitrile wit	h 0.1% formic acid				
Gradient profile at 0.45 mL/min	Time (min)	Percentage B				
flow rate	0.1	10.0				
	7.0	72.5				
	8.5	100.0				
	12.5	100.0				
	12.6	10.0				
	17.5	End				
Injection volume	10 uL					
Orbitrap parameters	Sheath gas flow ra	te: 40 (a.u.)				
	Auxiliary gas flow	rate: 5 (a.u.)				
	Sweep gas flow rate: 1 (a.u.)					

	Ion transfer tube temperature: 325 °C
	Vaporizer temperature: 350 °C
	Spray voltage: +3500 V or -2500 V
Full scan mode parameters	Resolution: 60,000
	Scan range: m/z 100-1000
t-MS ² mode parameters	Normalized collision energy: 20, 35, 50%

Table A.9 Ion chromatography instrument method parameters

Instrument	ThermoFisher Dionex ICS-5000 ⁺				
Detection	Conductivity detector				
Analytical column	Dionex IonPac AS18-Fast-4µm 2 x 150 mm				
Guard column	Dionex IonPac AG18-Fast-4µm 2 x 30 mm				
Column temperature	30 °C				
Flow rate	0.25 mL/min				
Eluent	Sodium hydroxide				
Eluent gradient	<u>Time (min)</u> S	Sodium hydroxide (mM)			
	0.0	1.0			
	20.0	6.20			
	20.0	End			
Suppressor	4 mA				
Injection volume	10 uL				

Table A.10 Combustion unit instrument method parameters

Instrument	AQF-2100H
Inlet temperature	1000 °C
Outlet temperature	900 °C
Argon flow rate	200 mL/min
Oxygen flow rate	400 mL/min

Boat program	<u>1st</u>			<u>2nd</u>				
	Position	Time	Speed	End Time	Cool Time	Home Time	Ar Time	O ₂ Time
	180	60	20	240	60	60	60	300
Injection volume	100 uL							
Absorption solution	5 mL							
volume								



Figure A.1 Sieve analysis of aggregates used in concrete mix design.



Figure A.2 (a) Flat (left) and chipped (right) surface type in lab-cast concrete cores, (b) full profile of flat core.



Figure A.3 (a) Pooled concrete core setups with triplicates and extra thin sample for SEM imaging, (b) thin sample setup for SEM imaging (left) and uptake setup with pooled solutions (right), (c) wet and dry setup (cores not visible in setups).



Figure A.4 Side profile of FTA cores.



Figure A.5 The view of the top surface of FTA cores starting with Core #1 on the top left going clockwise to Core #4 on the bottom left.



Figure A.6 6:2 and 8:2 FTSA relative concentration plots from the uptake experiment used 1 mix of 12 PFAS





Figure A.7 Absolute concentration plots of all sample points for uptake experiment for (a-f) setups pooled with mix of 12 PFAS, and (g-l) setups pooled with AFFF solution.



Figure A.8 Absolute concentrations of PFASof lab-contaminated cores from (a-h) mix of 12 PFAS and (i-p) 3% AFFF solution.



Figure A.9 Recovery of PFAS from pooled solution and core extractions after 365 days for (a,b) cores pooled with a mix of 12 PFAS and (c,d) cores pooled with 3% AFFF solution.





Figure A.10 Diffusion curves for PFOS and PFOA from cores with a solution of 12 PFAS pooled on the surface. D and Cs represent the computed diffusion coefficient and surface concentration, respectively.



Figure A.11 Diffusion curves for PFOS and PFOA from cores with the AFFF solution pooled on the surface. D and Cs represent the computed diffusion coefficient and surface concentration, respectively.



Figure A.12 Absolute concentrations of PFAAs in flat surface wet and dry cores in the setup exposed to a mix of 12 PFAS.



Figure A.13 Absolute concentrations of PFAAs and 6:2 FTSA in the FTA cores.

Appendix B: Supplemental Information for Chapter 4

Text B.1 AAS instrument method and quality control measures

As mentioned in Section 4.2.5, calcium concentration in solutions was determined using ContrAA 800D high-resolution continuum source (HR-CS) AAS (Analytik Jena, Beverly, MA, USA) in flame mode with a short arc xenon lamp. The flame was supplied with an acetylene-air mix at 80 L/h and the flame height was 6 mm. Samples were analyzed for their absorbance at a wavelength of 422.6728 nm. The sequence began with five deionized water blanks, followed by the calibration curve and samples. A check standard was run every 20 samples to ensure no significant instrument drift. Additionally, a second calibration curve was run at the end of the sequence. All samples were injected into the flame three times, and an average was taken, giving the final measurement. The calculated standard deviations from these instrument triplicate measurements are not presented in Figure 4.7a but rather the standard deviation from the replicate samples. The sample measurement was rejected and re-run if the standard deviation was over 20 %.

Text B.2 Extraction procedure on post-day 26 samples from the AFFF precursor degradation test

Although the experiment ended on day 26, the sample setups were left in the shaker in case the experiment needed to be continued. The data showed a very quick plateau of all compounds after day 18, so the day 55 samples were expected to have a very similar concentration profile to the day 26 sample. On day 55 of the experiment, a final sample was taken, and the entire setup was solvent extracted in an attempt to recover the remaining PFAS mass.

The extraction procedure began with emptying the containers in the setups into a 50 mL centrifuge tube. Afterward, 5 mL of methanol was added to the container and vortexed for one minute with the concrete piece still inside the container (in the case of setups 1-9). After vortexing, the liquid was added to the original amount and poured into the 50 mL centrifuge tube. An additional 1 mL of 1 M HCl in methanol was added to the container and vortexed for 1 minute, after which the liquid was added to the 50 mL centrifuge. The weight of the liquid was measured to determine the amount that the solution was diluted to accurately calculate PFAS recovery. The full extraction solution of around 18 mL was then vortexed for one minute and then centrifuged at 5000 rpm for 5 minutes. A subsample from this extraction solution was taken and internal standard was added at 3 ng/mL and analysis was performed on the UHPLC-HRMS as described in Section 4.2.5.

Text B.3 Microbiological controls for uptake experiment

Two separate microbiological tests were done for the uptake experiment to rule out any biotic degradation of PFAS precursors. An ATP measurement was done on day 290 by taking 500 uL of sample from the setup and analyzing it on a luminometer where a rough estimate of ATP was given. Different agar mediums of R2A, nutrient-rich, TSB, and LB were prepared and solution pooled from the uptake experiment was added to the plates at dilutions of 1000 x, 100 x, 10 x, and no dilution. The plates were then incubated for 16 hours at 30 °C to observe if any colonies formed. On day 365, mediums were prepared again, and a swab was taken from inside the pooling chamber and spread on the surface of the medium, then incubated at 30 °C to observe if any colonies had formed. Results from ATP measurement and agar plates are presented in Table B.2 and Figure B.4. Only agar plates that had colony growth (3 plates out of 30) are shown, while all others (27 out of 30) did not have any growth.

Analyte	Name	Ion Formula	Theoretical	RT
			m/z	(min)
Am-OHPr-FBSAPrA		$[C_{12}H_{18}F_9N_2O_5S]^{-1}$	473.0787	4.61
Am-OHPr-FHxSAPrA-		$[C_{14}H_{18}F_{13}N_2O_5S]^{-1}$	573.0723	5.59
Am-OHPr-FPeSAPrA		$[C_{13}H_{18}F_{11}N_2O_5S]^-$	523.0755	5.12
AmPr-FBSAPrS	N-dimethyl ammonio propyl perfluorobutane sulfonamido Propyl Sulfonate	$C_{12}H_{19}O_5S_2N_2F_9]^+$	507.0664	4.74
AmPr-FPeSAPrS	N-dimethyl ammonio propyl perfluoropentane sulfonamido Propyl Sulfonate	$C_{13}H_{19}O_5S_2N_2F_{11}]^+$	557.0633	5.24

Table B.1 List of analytes without analytical or non-analytical grade standards.

AmPr-FHxSAPrS	N-dimethyl ammonio propyl perfluorohexane sulfonamido	$C_{14}H_{19}O_5S_2N_2F_{13}]^+$	607.0601	5.77
	Propyl Sulfonate			
AmPr-FHpSAPrS	N-dimethyl ammonio propyl	$C_{15}H_{19}O_5S_2N_2F_{15}]^+$	657.0569	6.23
	perfluoroheptane sulfonamido			
	Propyl Sulfonate			
AmPr-FOSAPrS	N-dimethyl ammonio propyl	$C_{16}H_{19}O_5S_2N_2F_{17}]^+$	707.0537	6.69
	perfluorooctane sulfonamido Propyl			
	Sulfonate			
EtOH-Am-OHPr-FBSA		$[C_{11}H_{17}O_4SN_2F_9]^-$	443.0693	4.82
EtOH-Am-OHPr-		$[C_{12}H_{17}O_4SN_2F_{11}]^{-1}$	493.0661	5.32
FPeSA				
EtOH-Am-OHPr-		$[C_{13}H_{17}O_4SN_2F_{13}]^-$	543.0629	5.82
FHxSA				
EtOH-AmPr-FPrSA	N-	$[C_{10}H_{17}O_3SN_2F_7]^+$	379.0921	4.07
	hydroxyethyldimethylammonioprop			
	yl perfluoropropanesulfonamide			
EtOH-AmPr-FBSA	N-	$[C_{11}H_{17}O_3SN_2F_9]^+$	429.0889	4.73
	hydroxyethyldimethylammonioprop			
	yl perfluorobutanesulfonamide			
EtOH-AmPr-FPeSA	N-	$[C_{12}H_{17}O_3SN_2F_{11}]^+$	479.0857	5.29
	hydroxyethyldimethylammonioprop			
	yl perfluoropentanesulfonamide			
EtOH-AmPr-FHxSA	N-	$\left[C_{13}H_{17}O_{3}SN_{2}F_{13}\right]^{+}$	529.0825	5.73
	hydroxyethyldimethylammonioprop			
	yl perfluorohexanesulfonamide			
EtOH-AmPr-FHpSA	N-	$[C_{14}H_{17}O_3SN_2F_{15}]^+$	579.0793	6.17
	hydroxyethyldimethylammonioprop			
	yl perfluoroheptanesulfonamide			
EtOH-AmPr-FOSA	N-	$[C_{15}H_{17}O_3SN_2F_{17}]^+$	629.0761	6.60
	hydroxyethyldimethylammonioprop			
	yl perfluorooctanesulfonamide			

EtOH-AmPr-FPrSA-	N-hydroxyethyl dimethylAmmonio	$[C_{12}H_{21}O_4SN_2F_7]^+$	423.1183	4.10
EtOH	Propyl perfluoropropane			
	SulfonamidoEthanol			
EtOH-AmPr-FBSA-	N-hydroxyethyl dimethylAmmonio	$[C_{13}H_{21}O_4SN_2F_9]^+$	473.1151	4.71
EtOH	Propyl perfluorobutane			
	SulfonamidoEthanol			
EtOH-AmPr-FPeSA-	N-hydroxyethyl dimethylAmmonio	$\left[C_{14}H_{21}O_4SN_2F_{11}\right]^+$	523.1119	5.23
EtOH	Propyl perfluoropentane			
	SulfonamidoEthanol			
EtOH-AmPr-FHxSA-	N-hydroxyethyl dimethylAmmonio	$[C_{15}H_{21}O_4SN_2F_{13}]^+$	573.1087	5.70
EtOH	Propyl perfluorohexane			
	SulfonamidoEthanol			
EtOH-AmPr-FHpSA-	N-hydroxyethyl dimethylAmmonio	[C16H21O4SN2F15] ⁺	623,1055	6.14
EtOH	Propyl perfluoroheptane		02011000	0.11
	SulfonamidoEthanol			
	SunonannuoLunanoi			
EtOH-AmPr-FOSA-	N-hydroxyethyl dimethylAmmonio	$\left[C_{17}H_{21}O_4SN_2F_{17}\right]^+$	673.1023	6.55
EtOH	Propyl perfluorooctane			
	SulfonamidoEthanol			
EtOH_AmPr_EPrSAPrS	N-Hydroxyethyl dimethyl Ammonio	[CuHarOcSaNaEa]+	501.0050	4.12
	Propyl		501.0959	4.12
	n orflygn and soulfor or ide			
	Prograficate			
	PropyiSullonate			
EtOH-AmPr-FBSAPrS	N-Hydroxyethyl dimethylAmmonio	$\left[C_{14}H_{24}O_{6}S_{2}N_{2}F_{9}\right]^{+}$	551.0927	4.73
	Propyl perfluorobutaneSulfonamido			
	PropylSulfonate			
EtOH-AmPr-FPeSAPrS	N-Hydroxyethyl dimethylAmmonio	$[C_{15}H_{24}O_6S_2N_2F_{11}]^+$	601.0895	5.23
	Propyl			
	perfluoropentaneSulfonamido			
	PropylSulfonate			
	NT TL. d		(51.09/2	5 (9
EtOH-AmPr-	N-Hydroxyethyl dimethylAmmonio	$[C_{16}H_{24}O_6S_2N_2F_{13}]'$	651.0863	5.68
FHXSAPrS	Propyl pertluorohexaneSulfonamido			
	PropylSultonate			

EtOH-AmPr-	N-Hydroxyethyl dimethylAmmonio	$[C_{17}H_{24}O_6S_2N_2F_{15}]^+$	701.0831	6.12
FHpSAPrS	Propyl			
	perfluoroheptaneSulfonamido			
	PropylSulfonate			
EtOH_AmPr_FOSAPrS	N_Hydroxyethyl dimethyl Ammonio	$[C_{10}H_{24}O_{2}S_{2}N_{2}F_{12}]^{+}$	751 0804	6.60
LIOIT-AIII I-I OSAI IS	Propyl perfluorooctaneSulfonamido		751.0004	0.00
	Propyl Sulfonate			
	riopyisuitonate			
EtOH-AmPr-FHxAd	N-	$[C_{13}H_{18}F_{11}N_2O_2]^+$	443.1187	4.73
	hydroxyethyldimethylammonioprop			
	yl perfluorohexaneamide			
EtOH-AmPr-FOAd	N-	$[C_{15}H_{18}F_{15}N_2O_2]^+$	543.1123	5.61
	hydroxyethyldimethylammonioprop			
	vl perfluorooctaneamide			
EtOH-AmPr-N-		$[C_{11}H_{20}F_7N_2O_3S]^+$	393.1077	4.19
MeFPrSA				
EtOH-AmPr-N-		[C12H20F0N2O3S]+	443.1045	4.81
MeFBSA		[- 1220-)- 2 - 5]		
EtOH-AmPr-N- MeEPes A		$[C_{13}H_{20}F_{11}N_2O_3S]^+$	493.1014	5.30
Merresa				
EtOH-AmPr-N-		$[C_{14}H_{20}F_{13}N_2O_3S]^+$	543 0982	5 72
MeFHxSA			5 15.0902	5.72
EtOH-AmPr-N-		$[C_{15}H_{20}F_{15}N_2O_3S]^+$	593.095	6.27
MeFHpSA		[- 15-20-15-2 - 5-]		
EtOH-AmPr-N-		$[C_{16}H_{20}F_{17}N_2O_3S]^+$	643.0918	6.65
MeFOSA				
PFBAAm	N-(3- (dimethylamino)propyl)-	$[C_9H_{14}ON_2F_7]^+$	299.0989	3.20
	Perfluorobutylamide)			
			240.0057	4.10
PFPeAAm	N-(3- (dimethylamino)propyl)-	$[C_{10}H_{14}ON_2F_9]^{+}$	349.0957	4.10
	Perfluoropropylamide)			
PFHxAAm	N-(3- (dimethylamino)propyl)-	$[C_{11}H_{14}ON_2F_{11}]^+$	399.0925	4.73
	Perfluoropentylamide)			
PFHnAAm	N-(3- (dimethylamino)propyl)-	$[C_{12}H_{14}ON_{2}F_{12}]^{+}$	449 0893	5.26
	Perfluorohevylamide)		119.0095	5.20
	r emuoronexylamide)			

PFOAAm	N-(3- (dimethylamino)propyl)- Perfluorooctylamide)	$[C_{13}H_{14}ON_2F_{15}]^+$	499.0861	5.76
PFPrSAm	perfluoropropane sulfonamido propyl amine	$[C_8F_7H_{12}N_2O_2S]^+$	333.0513	4.12
PFBSAm	perfluorobutane sulfonamido propyl amine	$[C_8F_7H_{12}N_2O_2S]^+$	383.0481	4.66
PFPeSAm	perfluoropentane sulfonamido propyl amine	$[C_8F_7H_{12}N_2O_2S]^+$	433.0449	5.31
PFBSAmS	N-trimethylammoniopropyl Perfluorobutanesulfonamide	$[C_{10}H_{16}O_2SN_2F_9]^+$	399.0783	4.82
S-OHPrAmPr-FPeSAA	N-SulfohydroxyPropyl dimethyl AmmonioPropyl perfluoropentaneSulfonamido Acetic Acid	$[C_{15}H_{21}O_8S_2N_2F_{11}]^+$	631.0636	4.26
S-OHPrAmPr- FHxSAA	N-SulfohydroxyPropyl dimethyl AmmonioPropyl perfluorohexaneSulfonamido Acetic Acid	$[C_{16}H_{21}O_8S_2N_2F_{13}]^+$	681.0605	4.73
S-OHPrAmPr- FHpSAA	N-SulfohydroxyPropyl dimethyl AmmonioPropyl perfluoroheptaneSulfonamido Acetic Acid	$[C_{17}H_{21}O_8S_2N_2F_{15}]^+$	731.0573	5.21
SPrAmPr-FPrSAPrS	N- SulfoPropyldimethylAmmonioProp yl perfluoropropaneSulfonAmidoProp ylSulfonate	$[C_{14}H_{26}F_7N_2O_8S_3]^+$	579.0734	3.66
SPrAmPr-FBSAPrS	N- SulfoPropyldimethylAmmonioProp yl	$[C_{15}H_{26}F_9N_2O_8S_3]^+$	629.0702	4.26

	perfluorobutaneSulfonAmidoPropyl			
	Sulfonate			
SPrAmPr-FPeSAPrS	N- SulfoPropyldimethylAmmonioProp yl perfluoropentaneSulfonAmidoPropy lSulfonate	$[C_{16}H_{26}F_{11}N_2O_8S_3]^+$	679.067	4.78
SPrAmPr-FHxSAPrS	N- SulfoPropyldimethylAmmonioProp yl perfluorohexaneSulfonAmidoPropyl Sulfonate	$[C_{17}H_{26}F_{13}N_2O_8S_3]^+$	729.0638	5.26
SPr-An-OHPr-FHpAd		$\left[C_{14}H_{16}F_{15}N_{2}O_{5}S\right]^{+}$	609.0535	5.69
SPr-FHxSA		$[C_9H_8O_5S_2NF_{13}]^-$	519.9564	6.11
TAm-OHPr-FHxSA	N-TrimethylAmmonio- hydroxyPropyl perfluorohexane SulfonAmide	$[C_{12}H_{16}F_{13}N_2O_3S]^+$	515.0669	5.69
TAmPr-FPeAd	N-TrimethylAmmonioPropyl perfluoropentaneAmide	$[C_{11}H_{15}F_9N_2O]^+$	363.1113	4.09
TAmPr-FHxAd	N-TrimethylAmmonioPropyl perfluorohexaneAmide	$[C_{12}H_{15}F_{11}N_2O]^+$	413.1082	4.81
TAmPr-FHpAd	N-TrimethylAmmonioPropyl perfluoroheptaneAmide	$[C_{13}H_{15}F_{13}N_2O]^+$	463.1050	5.33

Table B.2 ATP measurements from pooled AFFF solution on the concrete surface from uptakeexperiment described in Section 3.3.1.

Sample type:	AFFF pooled on flat concrete	AFFF control
ATP amount:	527 pg/mL	405 pg/mL

Structure	Acronym	Full name	Other acronym used
	PFCA	Perfluoroalkyl carboxylic acid	
$ F = \begin{bmatrix} F \\ H \\ S \\ F \end{bmatrix}_{n} O^{-} $	PFSA	Perfluoroalkane sulfonate	
$F = \begin{bmatrix} F \\ F \\ F \end{bmatrix}_{n}^{0} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}$	n:2 FTS	X:2 fluorotelomer sulfonate	n:2 FTSA
$ \begin{bmatrix} F \\ O \\ S \\ F \\ F \\ F \\ NH_2 \\ NH_2 $	FASA	PerFluoroalkane sulfonamide	
$F \begin{bmatrix} F \\ H \\ F \end{bmatrix}_{n}^{O} N H H H$	AmPr-FAAd	N-dimethyl ammonio propyl perfluoroalkane amide	PFAAAm
$F = \begin{bmatrix} F \\ G \\ F \\ F \\ F \\ N \\ O \\ H \\ H$	AmPr-FASA	N-dimethyl ammonio propyl perfluoroalkane sulfonamide	PFSAm

Table B.3 Full PFAS list with chemical structure and names.

[F] Q	TAmPr-FASA	N-trimethylammoniopropyl	PFSAmS
F F N N N N N N N N N N N N N N N N N N		perfluoroalkanesulfonamide	
0 " 0H	AmPr-FASAPrS	N-dimethyl ammonio propyl	
		perfluoralkane sulfonamido propyl	
$ F = \begin{bmatrix} I \\ F \end{bmatrix}_{n} \begin{bmatrix} I \\ O \end{bmatrix}_{N} \xrightarrow{N} \xrightarrow{N} \xrightarrow{N} \xrightarrow{N} \xrightarrow{N} \xrightarrow{N} \xrightarrow{N} \xrightarrow$		sulfonate	
	EtOH-AmPr-FASA	N-hydroxyethyldimethylammonio	
F T S NH N ⁺ OH		propyl perfluoroalkanesulfonamide	
но	EtOH-AmPr-FASA-	N-hydroxyethyl dimethylammonio	
	EtOH	propyl perfluoroalkane	
		sulfonamidoethanol	
O ", OH	EtOH-AmPr-	N-Hydroxyethyl dimethylammonio	
	FASAPrS	propyl perfluoroalkanesulfonamido	
		propylsulfonate	
	EtOH-AmPr-FAAd	N-	
		hydroxyethyldimethylammoniopropyl	
		perFluoroAlkaneamide	
	1	1	

0 	S-OHPrAmPr-	N-sulfohydroxypropyl dimethyl	
	FASAA	ammoniopropyl	
		perfluoroalkanesulfonamido acetic acid	
0			
	SPrAmPr-FASAA	N-Hydroxyethyl dimethylammonio	
		propyl perfluoroalkanesulfonamido	
		hydroxy propyl sulfonate	
0	SPrAmPr-FASAPrS	N-sulfopropyldimethylammoniopropyl	
S-OH		perfluoroalkane	
		sulfonamidopropylsulfonate	
	SPr-FASA	N-sulfo popyl	
$ \begin{bmatrix} F + F \\ F \end{bmatrix}_{n}^{H} \begin{bmatrix} S \\ H \\ H \end{bmatrix}_{n}^{H} \\ H \end{bmatrix}_{n}^{H} \begin{bmatrix} S \\ H \\ H \end{bmatrix}_{n}^{H} \begin{bmatrix} S \\ H \\ H \end{bmatrix}_{n}^{H} \\ H \end{bmatrix}_{n}^{H} \begin{bmatrix} S \\ H \\ H \\ H \end{bmatrix}_{n}^{H} \\ H \\ H \end{bmatrix}_{n}^{H} \\ H \\ H \\ H \end{bmatrix}_{n}^{H} \\ H \\$		perfluoroalkanesulfonamide	
	TAm-OHPr-FASA	N-trimethylammonio-hydroxypropyl	
		perfluoroalkane sulfonamide	
[F] C	TAmPr-FAAd	N-trimethylammoniopropyl	
		perfluoroalkaneamide	

Solvent Condition:	MeC	Н	10 m CH ₃ CC	M OOH	100 m CH ₃ COO	nM DNH4	1 % NH	ĺ₄OH
Recovery (%)	Ave	SD	Ave	SD	Ave	SD	Ave	SD
AmPr-FBSAPrS	62	7	64	8	74	4	60	7
AmPr-FPeSAPrS	66	8	67	8	79	5	63	6
AmPr-FHxSAPrS	65	7	68	9	79	5	64	6
AmPr-FHpSAPrS	67	7	69	8	83	4	65	6
AmPr-FOSAPrS	67	7	73	9	80	3	64	8
EtOH-Am-OHPr-FBSA	79	6	71	9	82	6	80	6
EtOH-Am-OHPr-FPeSA	79	5	74	8	83	6	78	6
EtOH-Am-OHPr-FHxSA	81	6	77	10	85	6	81	7
EtOH-AmPr-FPrSA	76	6	70	8	81	5	78	4
EtOH-AmPr-FBSA	71	6	66	9	74	5	71	5
EtOH-AmPr-FPeSA	65	6	63	9	73	5	65	6
EtOH-AmPr-FHxSA	67	6	62	9	72	4	66	6
EtOH-AmPr-FHpSA	58	10	59	10	61	4	57	8
EtOH-AmPr-FOSA	64	6	60	8	69	4	66	5
EtOH-AmPr-FPrSA-EtOH	73	7	69	8	81	7	76	4
EtOH-AmPr-FBSA-EtOH	78	6	73	9	81	4	77	5
EtOH-AmPr-FPeSA-EtOH	77	6	68	11	82	5	79	5
EtOH-AmPr-FHxSA-EtOH	77	7	74	8	85	5	78	6
EtOH-AmPr-FHpSA-EtOH	77	7	74	10	80	2	80	6
EtOH-AmPr-FOSA-EtOH	80	8	78	9	86	5	88	8
EtOH-AmPr-FEtSAPrS	4	23	6	14	7	20	6	18
EtOH-AmPr-FPrSAPrS	67	6	66	8	78	5	67	6
EtOH-AmPr-FBSAPrS	74	7	72	8	82	5	72	6
EtOH-AmPr-FPeSAPrS	77	7	74	8	86	4	77	7
EtOH-AmPr-FHxSAPrS	78	7	76	8	86	4	78	6
EtOH-AmPr-FHpSAPrS	78	5	77	8	83	3	74	7
EtOH-AmPr-FOSAPrS	79	6	78	8	87	4	78	7
EtOH-AmPr-FHxAd	30	6	27	9	30	5	30	5
EtOH-AmPr-FOAd	43	11	38	12	44	5	42	6
S-OHPrAmPr-FPeSAA	33	9	58	6	79	4	28	10
S-OHPrAmPr-FHxSAA	34	6	59	9	78	4	28	9
S-OHPrAmPr-FHpSAA	38	10	65	7	84	4	32	8
SPrAmPr-FBSAA	83	6	75	9	90	4	83	7
SPrAmPr-FPeSAA	84	7	79	8	90	5	82	7
SPrAmPr-FHxSAA	86	6	81	9	92	5	84	4
SPrAmPr-FPrSAPrS	30	7	51	8	74	5	27	7

Table B.4 Average extraction recoveries of AFFF precursors from the spike-recovery test.

SPrAmPr-FBSAPrS	33	10	57	6	80	4	29	6
SPrAmPr-FPeSAPrS	35	10	60	8	82	4	30	7
SPrAmPr-FHxSAPrS	42	6	65	7	85	4	34	7
SPr-An-OHPr-FHpAd	65	10	68	10	78	7	64	11
SPr-FHxSA	25	6	74	13	123	4	20	7
TAm-OHPr-FHxSA	60	7	50	10	65	5	60	9
TAmPr-FPeAd	29	7	26	9	28	6	30	6
TAmPr-FHxAd	57	10	49	9	56	10	56	6
TAmPr-FHpAd	99	6	92	9	101	6	109	8

Ave = Average SD = Standard deviation



Figure B.1 Degradation products screened for PFAAAm compounds. The 8-carbon compound, PFOAAm, is shown as an example. Only PFOA (and other PFCAs) were identified in samples.



Figure B.2 Degradation products screened for PFSAm and PFSAmS compounds. The 8-carbon compounds, PFOSAm and PFOSAmS, are shown as an example. Note: The order of compounds does not represent the breakdown pathway. None of the above degradation products were identified in the samples.



Figure B.3 Recovery of PFSAm and PFSAmS compounds and in AFFF precursor degradation test. The day 26 sample represents the recovery of the compound on day 26 relative to the starting concentration measured while the extraction samples represent the amount recovered post-day 26 after an extraction procedure relative to the starting concentration measured.



Figure B.4 Agar plates with colony growth during uptake experiment described in Section 3.3.1. Left to right: Tryptic Soy Agar (200 CFU/mL), Luria-Bertani agar (600 CFU/mL), Nutrient agar (2,200 CFU/mL).



Figure B.5 Average extraction recoveries of perfluoroalkyl sulfonamides from the spike-recovery test.