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HEALTH GOALS FOR PERFLUORINATED ALKYL
SUBSTANCES (PFAS): A REVIEW OF BRANCHED
ISOMERS, THE ROLE OF INDUSTRIAL SOURCES, AND
THE IMPLICATIONS OF PFAS IN BIOSOLIDS ON END-
OF-LIFE DISPOSAL METHODS

by

Katarina Schulz

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ABSTRACT

HEALTH GOALS FOR PERFLUORINATED ALKYL SUBSTANCES (PFAS): A REVIEW OF BRANCHED ISOMERS, THE ROLE OF INDUSTRIAL SOURCES, AND THE IMPLICATIONS OF PFAS IN BIOSOLIDS ON END-OF-LIFE DISPOSAL METHODS

by

Katarina Schulz

The University of Wisconsin-Milwaukee, 2021
Under the Supervision of Professor Rebecca Klaper

Per- and polyfluorinated alkyl substances, or PFAS, have been used for over half a century, but have become an emerging contaminant of significant concern due to their newly found widespread occurrence and recalcitrance in the environment, their tendency to bioaccumulate, and the health effects now associated with a very low level of exposure. Many gaps in knowledge remain about the fate of these chemicals in the environment and the extent of their impacts on biota. This thesis aims to fill some of the recognized gaps in knowledge: differences between linear and branched isomers of PFAS, predicting the presence of PFAS contamination in wells, and the implications of PFAS in municipal biosolids.

TABLE OF CONTENTS

Abstract	ii
List of Figures.....	vi
List of Tables	viii
List of Abbreviations	x
Acknowledgements	xii
 Chapter 1: Introduction.....	 1
 Chapter 2: Branched isomers of perfluoroalkyl substances (PFAS): A review of recent literature	 9
2.1 Introduction	9
2.2 Variation in PFAS Isomer Profiles in The Environment	12
2.2.1 Surface water and sediments	15
2.2.2 Soil and groundwater.....	17
2.2.3 Other environmental media: biosolids and seawater	18
2.3 Distribution Patterns in Plants	19
2.3.1 Isomer ratios in different plant structures.....	19
2.4 Distribution Patterns of Linear versus Branched PFAS in Animals	20
2.4.1 Isomer distribution patterns in wildlife	21
2.4.2 Geographical differences in wildlife isomer profiles	23
2.5 Unique Sources and Exposure Routes	25
2.5.1 Previously unidentified sources of branched PFOS isomers	25
2.5.2 Isomer profiles of indoor exposure	26
2.6 Regional Differences in Human Exposure and Accumulation	26
2.6.1 Geographic differences of isomer loads in humans.....	26
2.6.2 Other factors affecting isomer profiles in humans.....	32
2.7 Isomer-specific Associations with Health Outcomes	33
2.7.1 Health studies in adults.....	34
2.7.2 Health studies in pregnant women	36

2.7.3	Health studies in prenatal exposure and children	37
2.8	Analysis and Remediation.....	38
2.8.1	Novel analysis methods for branched isomers	38
2.8.2	Removal abilities for branched isomers	39
2.9	Conclusions and Future Research Needs.....	40
Chapter 3: Linking industrial point sources to PFAS contamination in wells: Michigan case study		42
3.1	Introduction	42
3.2	Methods	44
3.2.1	Michigan well and industry data.....	44
3.2.2	Linking industrial sites to PFAS contamination	47
3.2.3	Probit Models.....	48
3.2.4	Cluster analysis	53
3.3	Results and Discussion	54
3.3.1	Industrial and well sites.....	54
3.3.2	Linking industrial sites to PFAS contamination	57
3.3.3	Probit models, 1 km	59
3.3.4	Probit models, 0.5 km	60
3.3.5	Cluster analysis	61
3.4	Conclusions.....	63
Chapter 4: Implications for PFAS Contamination in Biosolids End of Life Disposal		65
4.1	Introduction	65
4.2	Methods	66
4.2.1	Biosolids Sampling and Preparation	66
4.2.2	Centrifuge Tests	68
4.2.3	Batch Desorption Experiment	69
4.2.4	Calculation of Sorption Constants and Retardation Factors	70
4.2.5	Incineration Experiment	71
4.3	Results	73
4.3.1	Batch Desorption Experiment	73

4.3.2	Calculation of Sorption Constants and Retardation Factors	77
4.3.3	Incineration Experiment	78
4.4	Discussion	80
4.4.1	Batch Experiment	80
4.4.2	Calculation of Sorption Constants and Retardation Factors	80
4.4.3	Incineration Experiment	82
Chapter 5: Conclusions and Future Research		84
References		88
Appendices		103
Appendix A: Nationwide PFAS use survey.....		103
Appendix B: Raw results from biosolids batch experiment.....		107

LIST OF FIGURES

Figure 2.1: Graphical abstract highlighting findings from review of branched versus linear PFAS isomers.	12
Figure 3.1: (a) Total groundwater wells per county, indicated by the numerical value on each county, and percentage of wells with PFAS in each county as shown by color scale. (b) Number of PFAS industry sites in Michigan by county.	57
Figure 3.2: Local Moran's I for PFAS clusters in Michigan (detected wells only).	63
Figure 4.1: Photos of (a) Experimental setup with air pump, CORBO sampler, and funnel (respectively from left to right) outlined in red; (b) a closer view of the funnel, after adjusting slightly higher to prevent melting.	72
Figure 4.2: Photo of air pump and CORBO attached to calibration device, to achieve a flow rate of 10 mL/min. The pump was calibrated before both the blank and the sample run.	72
Figure 4.3: PFHxA concentration versus time in S1, S2, and S3.	74
Figure 4.4: PFHpA concentration versus time in S1, S2, and S3.	75
Figure 4.5: PFOA concentration versus time in S1, S2, and S3.	75
Figure 4.6: PFHxS concentration versus time in S1, S2, and S3.	76
Figure 4.7: PFOS concentration versus time in S1, S2, and S3.	76
Figure 4.8: (a) Dried biosolids in crucible prior to incineration: mass 12.04 g; (b) remaining ash of biosolids sample after incineration: mass 3.66 g.	79
Figure 4.9: Calculated K_{oc} value versus chain length within each family of PFAS studied (PFCAs, PFSA, and precursors), along with trend lines. Precursors in this figure include N-MeFOSAA and N-EtFOSAA.	81
Figure B1: Results from the test batch, also used as R1 for S1. All compounds shown in (a), (b), and (d) were not present in R2 and R3 due to dilution of samples or, in the case of PFBA, due to flawed methodology that was later modified. In (c), PFPeA and PFBS were not seen in remaining replicates, but PFHxA and 6:2 FTSA were and are also shown in Figure 4.3 (c) and (f), respectively.	113
Figure B2: Concentration of 6:2 FTSA versus time in S1.	115
Figure B3: Concentration of PFNA versus time in S2.	115
Figure B4: Concentration of 6:2 FTSA versus time in S3.	116
Figure B5: Concentration of N-MeFOSAA versus time in S3.	116
Figure B6: Concentration of N-EtFOSAA versus time in S3.	117

Figure B7: Concentration of PFDA versus time in S3.....	117
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LIST OF TABLES

Table 2.1: Branched and linear PFAS in the abiotic environment.	13
Table 2.2: Branched and linear PFAS in biota. Concentrations are in ppb.	23
Table 2.3: Branched and linear PFAS in human blood serum. Concentrations are in ppb. If sum not given in paper, it is estimated from adding concentrations of linear and branched.	27
Table 3.1: Industry groups included in the spatial analysis, the associated NAICS codes for specific industries within those groups, and the sources that led to the inclusion of those industries.	46
Table 3.2: Summary statistics of variables used in Probit regression analysis – 0.5 km and 1 km buffers (N= 1081).	49
Table 3.3: Michigan Industries within defined buffer sizes (0.1,0.5,1.0 km) of drinking water wells with detected PFAS concentrations. For total number of identified industrial sites in Michigan, n = 2,696 ⁿ	54
Table 3.4: Probit regression analysis results for 1 km buffers (n = 1081).	58
Table 3.5: Probit regression analysis results for 0.5 km buffers (n = 1081).	58
Table 3.6: Significant clusters and outliers identified using Local Moran's I for PFAS clusters in Michigan (detected wells only).	62
Table 4.1: Information about the wastewater treatment facilities that provided biosolids for this project. Facilities wish to remain anonymous so names are withheld.	67
Table 4.2: Initial concentrations of PFAS in the three facilities' biosolids, in ppb based on dry weight. Concentrations were reported as wet weight for S3, so the S3 values in this table have been corrected based on the calculated percent moisture of the S3 solids (94.7%).	67
Table 4.3: Results of first test to determine appropriate centrifuge time and rpm for batch experiment water samples. "Slow" indicates a rpm of 3,000 for 15 minutes and fast indicates a rpm of 10,000 for 2 minutes. Biosolids were shaken at 150 rpm in DI water prior to centrifugation to mimic batch experiment conditions. Each test was done in triplicate.	69
Table 4.4: Turbidity and particle sizes following centrifugation at 10,000 rpm for one hour. Test done in triplicate.	69
Table 4.5: Average Log K _{oc} values calculated from batch results.	77
Table 4.6: Calculation of retardation factors (R _f s) for each PFAS compound in different soil scenarios.	77

Table 4.7: PFAS concentrations found in the biosolids used in the incineration experiment and in the furnace exhaust from the blank run and the biosolids run. The units of concentration are ng/g, which is equivalent to ppb.	79
Table 4.8: Comparison of K_{oc} values calculated in this study to prior studies on PFAS sorption.	80
Table A1: Industries included in nationwide PFAS use survey and their associated NAICS codes.....	103
Table A2: Breakdown of response subset from internet survey aimed at PFAS-using industries (n=1081).....	106
Table B1: Batch results from solids S1. Concentrations are in ppb. Yellow highlight indicates that results were flagged for interference, transition ion ratio failure, or failure to meet QA/QC standards. Blue highlight indicates that results were between LOD and LOQ, so the concentration is an estimate. Yellow highlight with blue outline indicates that both the aforementioned qualities apply.....	107
Table B2: Batch results from solids S2. Concentrations are in ppb. Yellow highlight indicates that results were flagged for interference, transition ion ratio failure, or failure to meet QA/QC standards. Blue highlight indicates that results were between LOD and LOQ, so the concentration is an estimate. Yellow highlight with blue outline indicates that both the aforementioned qualities apply.....	109
Table B3: Batch results from solids S3. Concentrations are in ppb. Yellow highlight indicates that results were flagged for interference, transition ion ratio failure, or failure to meet QA/QC standards. Blue highlight indicates that results were between LOD and LOQ, so the concentration is an estimate.....	111

LIST OF ABBREVIATIONS

AFFF	Aqueous film-forming foams
APFO	Ammonium perfluorooctanoate
DI	Deionized
ECF	Electrochemical fluorination
ECHO	Enforcement and Compliance History Online
EGLE	Department of Environment, Great Lakes, and Energy
FOIA	Freedom of Information Act
FOSA	Perfluorooctane sulfonamide
FTSA	Fluorotelomer sulfonate
GAC	Granular activated carbon
GIS	Geographic information system
HDPE	High-density polyethylene
IX	Ion exchange
NAICS	North American Industry Classification System
ND	Not detected
N-EtFOSAA	N-Ethyl perfluorooctane sulfonamidoacetic acid
N-EtFOSE	N-ethyl perfluorooctane sulfonamidoethanol
N-MeFOSAA	N-Methyl perfluorooctane sulfonamidoacetic acid
N-MeFOSE	N-methyl perfluorooctane sulfonamidoethanol
PFAS	Per- and polyfluorinated alkyl substances
PFBA	Perfluorobutanoic acid
PFBS	Perfluorobutane sulfonate
PFCA	Per- and polyfluorinated carboxylic acids
PFDA	Perfluorodecanoic acid
PFDoA	Perfluorododecanoic acid
PFDS	Perfluorodecanesulfonic acid
PFECHS	Perfluoroethylcyclohexanesulfonate
PFHxA	Perfluorohexanoic acid

PFHxDA	Perfluorohexadecanoic acid
PFHxS	Perfluorohexane sulfonic acid (or sulfonate)
PFNA	Perfluorononanoic acid
PFNS	Perfluorononansulfonic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonic acid (or sulfonate)
PFOSA	Perfluorooctane sulfonamide
PFPeA	Pefluoropentanoic acid
PFSA	Per- and polyfluorinated sulfonic acids
PFTeDA	Perfluorotetradecanoic acid
PFTTrDA	Perfluorotridecanoic acid
PFUnA	Perfluoroundecanoic acid
POP	Persistent organic pollutant
POSF	Perfluorooctane sulfonyl fluoride
ppb	Parts per billion
ppt	Parts per trillion
RO	Reverse osmosis
SWAN	Study of Women's Health Across the Nation
TMF	Trophic magnification factor
UCMR3	Third Unregulated Contaminant Monitoring Rule
USEPA	United States Environmental Protection Agency
VOC	Volatile organic compound
WISLH	Wisconsin State Lab of Hygiene
WSSN	Water Supply Serial Number
WWTP	Wastewater treatment plant

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Chapter 1: Introduction

Per- and polyfluorinated alkyl substances, or PFAS, are contaminants of emerging concern due to their widespread occurrence and recalcitrance in the environment, their tendency to bioaccumulate, and the wide variety of health effects associated with exposure (Lindstrom et al., 2011b). The original use of PFAS was in fluoropolymer production for nonstick coatings, but since their inception in the mid-1900s they have been used in a wide variety of industries ranging from industrial lubricants to semiconductors (Kissa, 2001).

Perfluorinated alkyl substances are synthesized by two methods. The more common method, electrochemical fluorination (ECF), reacts straight-chain hydrocarbons with hydrofluoric acid to create perfluorooctane sulfonyl fluoride (POSF) which can then go through various reactions to add different functional groups to create perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA) and other PFAS. All compounds produced from POSF are considered PFOS equivalents due to their potential to break down into PFOS. This process yields only about ~70% desired linear product, with the majority of the remainder being comprised of branched compounds as well as some ring isomers. The second method is telomerization, in which perfluoroethylene and perfluoroethyl iodide react to make straight chain perfluorinated iodides, which can then be converted to perfluorinated carboxylic acids (such as PFOA) and fluorotelomer alcohols and olefins. This process yields almost exclusively the desired straight chain product (Lindstrom et al., 2011b; Vyas et al., 2007). Because ECF was the primary method of manufacturing PFAS prior to 2000 and is still in use today, a significant portion of PFAS in the environment are branched isomers; however, the differences

between branched and linear isomers are not well explored, and thus was investigated in Chapter 2 of this thesis.

Estimates of global production place manufacture of POSF in the thousands of tonnes per year from the mid-1970s until 2000, when their main manufacturer 3M voluntarily began their phase-out of long-chain PFAS production (Paul et al., 2009; Wang et al., 2014). Since 2000, many major chemical producers in North America and Europe have also phased out production of long-chain PFAS but continue to produce short-chain compounds and other alternatives, including GenX chemicals, in their place (Ateia et al., 2019; Xiao, 2017). GenX chemicals are similar to PFOA but contain an oxygen atom in the carbon chain as well as a branched chain (EPA, 2018). Structures of select PFAS and GenX can be found in the appendix. Eight-carbon compounds, such as PFOA and PFOS, have been primarily produced in China since the mid-2000s, but at much lower levels (up to 400 t annually PFOS and PFOA combined) than the past (Liu et al., 2017). Uncertainty about how much newer alternatives and different isomers contribute to PFAS contamination remains a gap in knowledge and helps formulate the first research question addressed in this thesis, addressed in Chapter 2.

Because they are both hydrophilic and lipophilic, PFAS are used in both water- and oil-proof coatings and treatment, including nonstick coatings (Kotthoff et al., 2015). They are also used in aqueous film-forming foams (AFFFs) for putting out fires. PFOA and other PFAS are used in chemical manufacture as surfactants and leveling agents, as well as in fluoropolymer production (including products such as Teflon) (Lindstrom et al., 2011b). Some pesticides use perfluorinated chemicals as their active ingredient (Lo et al., 2015).

Once manufactured, PFAS are transported in the environment via a variety of both industrial and domestic means. Industrially, exhaust is released into the air. Some of the air emissions can also be deposited in surface water and soil via precipitation (Armitage et al., 2009). Industrial emissions from PFAS production have also been released as wastewater into surface water, both directly and after moving through treatment facilities where they move into solids as well. These solids as well as those from manufacturers may be placed into landfills. Landfill leachate can end up in soil and groundwater, and surface water sources can also end up in soil and groundwater (Hamid et al., 2018; Liu et al., 2017; Oliaei et al., 2013). It has been recognized that municipal biosolids serve as a “sink” for PFAS due to their sorption to solids and have concentrations in the parts per billion (ppb) range (Higgins et al., 2005). While this may mean reduced contamination in water leaving the treatment plants, it does present concern regarding end-of-life disposal methods of biosolids. A handful of studies examine soil contamination resulting from land application of municipal biosolids, and find that increased loading rates of biosolids lead to increased PFAS concentrations in the soils where biosolids are applied (Sepulvado et al., 2011; Zhang et al., 2018). Sepulvado et al (2011) noted the possibility of transport in affected soil leading to contaminated groundwater, and noted that soil screening standards for PFAS do not account for the protection of groundwater. The alternative process for disposal of biosolids is incineration, and no study has yet examined whether this process leads to volatilization of PFAS or their destruction. Chapter four of this thesis investigates the environmental implications of biosolids end-of-life disposal in relation to PFAS contamination.

Other emissions include runoff of AFFFs into both soil and surface water, as well as domestic disposal of PFAS-coated products and materials. Household use also contributes to PFAS contamination in wastewater. There is no evidence of either aerobic or anaerobic biodegradation of PFAS in wastewater sludge/biosolids by microorganisms, but no indication of respiration inhibition either (Beecher et al., 2018; Ochoa-Herrera et al., 2016). They are a cause for environmental concern due to their ability to bioaccumulate and their persistence; they do not break down in the environment by any known process (Ahrens, 2011; Scheringer et al., 2014).

The main routes of human exposure to PFAS are air, household dust, food, and drinking water. More volatile compounds such as the fluorotelomer alcohols are present in the air at higher concentrations. Indoor air tends to have higher concentrations than outdoor air. Household dust contains PFAS that come mostly from coated/treated fabrics and carpets. Studies estimating exposure from food tend to focus on fish, but studies show that eggs, especially from poultry production near contaminated areas, can contain heavy loads of PFAS. Agricultural crops have been shown to uptake PFAS, but how much this contributes to human exposure is not known. Food packaging is often also PFAS coated for repellency and the contact of these packaging materials transfers these compounds to food. Drinking water is also a significant source as few treatment facilities have filters meant to remove PFAS. Drinking water can become contaminated by sourcing from contaminated surface and groundwater. Intake from water can be estimated using the concentration of the water and body weight/water intake estimates for each age group (Fromme et al., 2009). How these intake rates relate to blood serum levels is not yet quantified, but likely much of the load is taken in

due to the tendency of these chemicals to bind to proteins because of their lack of affinity for water or fat. Drinking water can become contaminated by sourcing from contaminated surface and groundwater. There is uncertainty as to how contamination can be predicted and tied to sources of contamination, which forms the basis of the second research question investigated in this thesis, addressed in Chapter 3.

Epidemiological studies about the health effects of PFAS are uncommon for a number of reasons. The general concern about these chemicals comes from long-term exposure as they are not acutely toxic in amounts that humans could feasibly be exposed to. The half-lives of PFAS are much longer in humans than common lab animals such as rats and mice, making it difficult to apply findings in these studies to humans (Zhang et al., 2013). Humans also appear to have a higher affinity for accumulation of branched isomers, which is untrue for animals (Pellizzaro et al., 2018). Many human studies focus on exposed workers, which do not necessarily represent the general populations demographically or in terms of exposure level. Additional epidemiological studies tend to study pregnant women, and it has been found that PFAS can cross the placental barrier (Inoue et al., 2004; Negri et al., 2017). Despite these difficulties, associations have been made between PFAS exposure and pregnancy-induced hypertension, high cholesterol, thyroid disease, ulcerative colitis, decreased immune response, and decreased fertility (Agency for Toxic Substances and Disease Registry (ATSDR), 2018; Kim et al., 2018; Olsen et al., 2009; Z. Zeng et al., 2019). Both human and animal studies have shown hepatic effects, lower birth weight, and various types of cancer (Agency for Toxic Substances and Disease Registry (ATSDR), 2018; W. Liu et al., 2019; Loveless et al., 2006; Sharpe et al., 2010). It should be noted that

the vast majority of studies focus exclusively on PFOS and PFOA, and little to nothing is known about the possible health effects of their precursors, byproducts, and newer alternatives (including short-chain PFAS and GenX chemicals) (Ateia et al., 2019). Additional studies in animals have showed signs of neurotoxicity, which could result in population-level effects (Hallgren et al., 2015). More studies are needed to strengthen these associations, determine at what level of exposure the effects become likely, and learn about how PFAS beyond PFOS and PFOA can impact human health. Due to the lack of robust information and a standardized method of determining risk, the United States Environmental Protection Agency (USEPA) and a number of states that have determined their own health advisory levels differ widely on what constitutes a safe level. Table 1 in the appendix compares recommended maximum levels. Homes near contaminated sites, including landfills from manufacturers that use(d) PFAS and sites where AFFFs have been used, have been found to have concentrations in their water of up to 1000 times higher than the USEPA's health advisory limit of 70 ppt (Matheny, 2019). It is important to understand and quantify exposure from different sources of PFAS contamination, including industrial sources and the extent of contamination from municipal biosolids more fully.

There are three removal technologies for PFAS that are most commonly used: granular activated carbon (GAC) filters, ion exchange resins (IX), and reverse osmosis (RO). All these methods work well at removing longer chain PFAS such as PFOA and PFOS from water (McCleaf et al., 2017). The efficiency of removal, however, decreases sharply with chain length of compounds, especially for GAC filters and IX resins (McCleaf et al., 2017; Zaggia et al., 2016). There are reports of RO having some

success with short-chain PFAS removal, though few papers found had numerical data of RO removal efficiencies with short-chain compounds (Appleman et al., 2014). Little information exists on the performance of any of these technologies on PFAS apart from carboxylic acids (PFCAs) and sulfonic acids (PFSAs). One focus of continued research is the destruction of PFAS rather than simply removal, a difficult process due to the strength of the carbon-fluorine bond. Upcoming technologies in PFAS destruction include *Acidimicrobium* bacteria, sonolysis, chemical oxidation and reduction, nanomaterials, electrochemical oxidation, ozone fractionation, electron beams, and plasma reactors (Cameron et al., 2018; Huang and Jaffé, 2019; Kucharzyk et al., 2017; Ross et al., 2018; Sahu et al., 2018; Saleh et al., 2019). The difficulty of removing and destroying PFAS highlights the need to further understand their presence in the environment.

This thesis will cover three main objectives. First, it will explore the differences between linear and branched isomers of PFOS, PFOA, and perfluorohexane sulfonate (PFHxS) (Chapter 2), discussing how isomers contribute to the overall load of PFAS in the environment, how branched isomers' behavior differs from linear isomers in environmental media as well as organisms, and the evidence of distinct health effects between linear and branched isomers. Second, it will investigate how industrial facilities that use PFAS in their products and/or processes contribute to drinking water contamination (Chapter 3) by identifying which industries use PFAS, mapping their locations, and using Michigan's robust PFAS testing efforts to spatially link industrial sites to contaminated wells. This chapter will also explore other environmental factors that may affect a well's likelihood of contamination. Lastly, this thesis will address the

implications of PFAS contamination in biosolids (Chapter 4), particularly as a result of their end-of-life disposal processes. This was achieved by performing a batch desorption experiment with biosolids as well as through a first-look incineration experiment to determine the extent of PFAS volatilization during biosolids incineration. Each chapter is self-contained, with a general summary and conclusions in Chapter 5.

Chapter 2: Branched isomers of perfluoroalkyl substances (PFAS): A review of recent literature

As published in Science of the Total Environment:

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2.1 Introduction

Per- and polyfluoroalkyl substances (PFAS) are a class of fluorinated organic compounds whose surfactant properties and dual water and oil repellency make them common in a wide variety of both consumer goods and industrial chemical processes (Kissa, 2001). The two most widely studied PFASs, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), have been in production since the 1940s, and although in many countries such as the United States they have been replaced in the last decade by alternative chemicals, these two “legacy” PFAS compounds are still produced in smaller quantities primarily in China and India (Liu et al., 2017). These chemicals have gained notoriety in recent years due to their persistence in the environment and ties to adverse health effects including certain types of cancers, cardiovascular problems, birth defects, and more, and the Stockholm Convention on Persistent Organic Pollutants (POPs) added PFOS and PFOA to their list of industrial POPs in 2009 and 2019, respectively (Stockholm Convention, 2019, 2008). Part of the concern about this class of chemicals comes from the vast number of different compounds (estimates of more than 4,000 variations based on chain length and functional group) and the lack of definitive levels of concern for human health (Nakayama et al., 2019). In addition, these compounds have a long half-life. For

example, PFOA and PFOS have long half-lives in humans of 3.8 and 5.4 years, respectively (Zhang et al., 2013). Historical production of PFAS was done using electrochemical fluorination (ECF), which yields only 70-80% desired linear form for PFOS, 80-85% for PFOA and ~95% for PFHxS, versus more recently production via telomerization which yields nearly 100% desired linear form (Benskin et al., 2010; Lindstrom et al., 2011b; Sundström et al., 2012). The remaining product is comprised mostly of branched isomers of the desired compounds. Because of the differences in production methods over time and location, the ratios of branched and linear isomers found in both the biotic and abiotic environment can vary widely (Buck et al., 2011).

In addition to varying production methods, some of the differences are due their behavior in the environment and in organisms. For example, human serum has shown slight preferential accumulation of branched PFOS isomers, with the linear form contributing to 58-70% of the total PFAS load in human serum as opposed to 70% or more that makes up typical ECF product, with significant regional differences in the isomer composition found in serum (Kärman et al., 2007). While these percentages are close in value, there is generally a slightly lower percentage of linear PFOS found in human serum than in ECF product. Interestingly, animal studies show the opposite as animals seem to preferentially accumulate the linear forms of PFOS and PFOA, which have been shown to have stronger bonding affinities to serum albumin than branched forms (Beesoon and Martin, 2015; Benskin et al., 2009a; De Silva et al., 2009; Greaves and Letcher, 2013; O'Brien et al., 2011; Sharpe et al., 2010). This could lead to different health outcomes for humans and wildlife when exposed to mixtures. Because of the high levels of branched isomers present in human tissues, it is important to determine if

these forms have different health effects than the linear isomers. Until recently, however, mixtures of branched and linear PFAS isomers were looked at as a sum and assumed to have identical health risks. As researchers begin to look for health associations of branched and linear isomers of PFAS separately, they find that different isomers do not always have the same effects (Loveless et al., 2006). It was shown by Loveless et al. (2006) that linear, branched, and linear/branched mixtures of ammonium perfluorooctanoate (APFO, a precursor to PFOA) differ in their toxicity values in rats and mice. In this case, it was found that the branched isomers caused similar but milder reductions in body weight and food consumption/efficiency as compared to linear alone and mixed linear and branched. However, O'Brien et al. (2011) found that the mixed linear and branched PFOS caused changes in more transcripts in chickens than linear alone. It is important to identify and understand the differing behaviors of branched and linear isomers of PFOS due to their abundance in biota and the environment.

This chapter aims to summarize the findings of recent literature regarding the branched isomers of PFAS, compare these results to past studies, and identify future research needs based on gaps in existing knowledge. Specifically, we address trends in occurrence of the linear and branched PFAS isomers, their differences in distribution, sorption to soils and sediments, the evidence of unique health associations, and priorities for future research on PFAS isomers. While there is a larger focus in this paper on branched isomers of PFOS as they are the most widely studied, information on branched isomers of PFOA and PFHxS are also included where available. Preference for linear or branched PFOS isomers will be judged in this paper based on comparison to typical ECF product that is 70% linear and 30% branched; matrices or organisms with

more than 70% linear isomers will be described as preferentially accumulating the linear isomer, and matrices or organisms where the linear isomer makes up less than 70% of the total load will be described as preferentially accumulating the branched isomers. A summary of findings can be found in Figure 2.1.

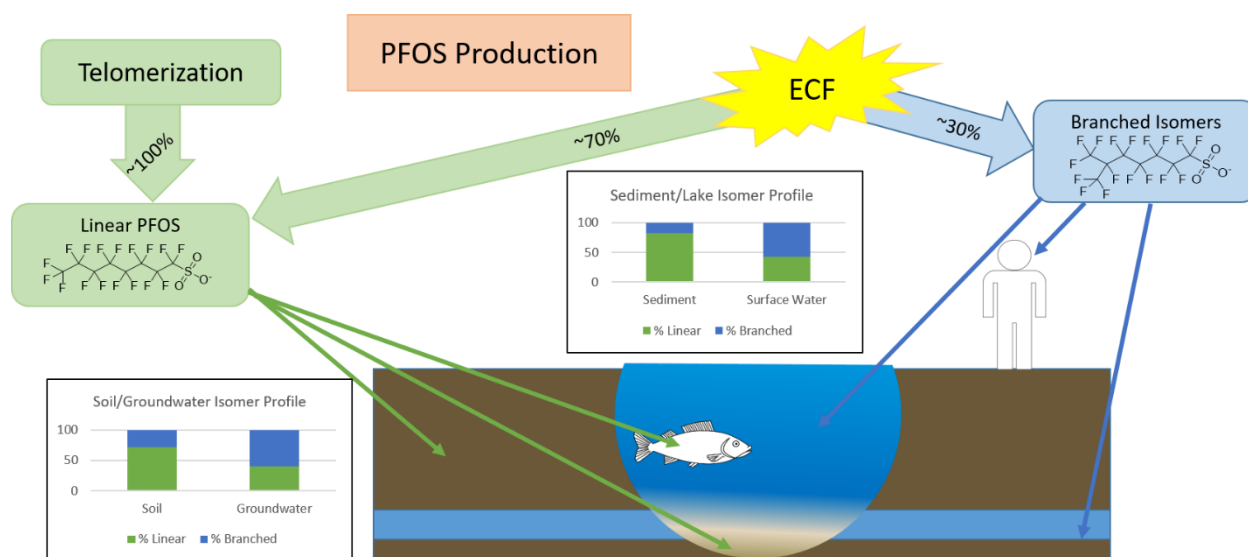


Figure 2.1: Graphical abstract highlighting findings from review of branched versus linear PFAS isomers.

2.2 Variation in PFAS Isomer Profiles in The Environment

It has been well established that PFOS and other PFASs have been found in surface waters worldwide (Paul et al., 2009). Studies of surface water in countries throughout the world have found concentrations to vary widely; in countries such as Brazil, Kenya, and Sri Lanka, where there is minimal if any production of PFASs, measured background levels of PFOS in rivers and lakes range from <1.0-1.52 parts per trillion (ppt), <1.0 to 8.88 ppt, and <1-44 ppt respectively (though 44 ppt was an outlier for concentrations in Sri Lanka and the next highest found was 5.2 ppt) (Zareitalabad et al.,

2013). For example, though PFASs are used in Brazil mostly in the form of the sulfluramid pesticide to combat leaf-cutting ants, there is little to no production of PFASs in Brazil and surface water concentrations in rivers were found to be a maximum of 8.39 ppt (Nascimento et al., 2018). However, continued use of sulfluramid in Brazil is a cause for future concern. Surface waters in the United States, Canada, China, and Europe, where PFAS production occurs, have higher concentrations in surface waters. PFOS levels averaged at 60 ppt in the US, 88 ppt in Canada, and 5.5 ppt in China, but range from non-detects up to 5900 ppt (Canada), and in many cases, exceed state and U.S. federal recommendations for safe levels in drinking water (Zareitalabad et al., 2013). PFASs including PFOS have been detected in areas as remote as the Arctic, and both transport of volatile precursors that then transform as well as sea and aerosol transport of PFCAs and PFSAAs themselves could be contributing reasons for their widespread occurrence (Stock et al., 2007). Large variations exist in branched and linear PFAS concentrations in the environment (Table 2.1). Though few studies have investigated sorption differences between linear and branched PFAS isomers, the little research that has been done indicates that there is indeed variation in how branched and linear isomers of PFOS move through, surface water, sediments soil, and groundwater.

Table 2.1: Branched and linear PFAS in the abiotic environment.

Study	Media	Compound	Sum PFAS	Linear PFAS	Branched PFAS	% Linear	% Branched	Unit	Notes
Gobelius 2018	Surface water in Sweden	PFOS				80.50 %	19.50 %		estimated from figure in SI
Gobelius 2018	Surface water in Sweden	PFOS				92.20 %	7.80%		estimated from figure in SI

Ahrens 2018	River water in Norway	PFO S	3.8	2.0	1.8	52.6%	47.4%	ppb	Norrstrom River, October 2016
Ahrens 2018	River water in Norway	PFO S	4.6	2.6	2.0	56.5%	43.5%	ppb	Ronnean River, October 2016
Ahrens 2018	River water in Norway	PFO S	3.3	1.6	1.7	48.5%	51.5%	ppb	Norrstrom River, January 2017
Ahrens 2018	River water in Norway	PFO S	5.1	2.6	2.5	51.0%	49.0%	ppb	Ronnean River, January 2017
Ahrens 2018	River water in Norway	PFO S	2.0	<0.49	1.5	24.6%	75.4%	ppb	Norrstrom River, April 2017
Ahrens 2018	River water in Norway	PFO S	3.7	2.2	1.5	59.5%	40.5%	ppb	Ronnean River, April 2017
Ahrens 2018	River water in Norway	PFO S	3.7	1.8	1.9	48.6%	51.4%	ppb	Norrstrom River, July 2017
Ahrens 2018	River water in Norway	PFO S	6.4	3.1	3.3	48.4%	51.6%	ppb	Ronnean River, July 2017
Chen 2018	Lake sediment	PFO S				82.8%	17.2%		Lake Taihu, China
Chen 2018	Lake water	PFO S				42.0%	58.0%		Lake Taihu, China
Ma 2018	Lake water	PFO S				48.7%	51.3%		Lake Taihu, China
Ma 2018	River water	PFO S				59.2%	40.8%		Lake Taihu, China
Johansson 2019	Bulk ocean water	PFO S				72.0%	28.0%		Artificial sea spray
Johansson 2019	Ocean surface microlayer	PFO S				82.0%	18.0%		Artificial sea spray
Shi 2018	Lake water	PFO S				78.8%	21.2%		Tangxun Lake, China
Shi 2018	River water	PFO S				89.5%	10.5%		Xiaoqing River, China
Gao 2019	Soil	PFO S	23.1	16.7	6.4	72.3%	27.7%	ppb	Near manufacturing plant in China
Gao 2019	Groundwater	PFO S	35.35	14.1	21.25	39.9%	60.1%	ppt	Near manufacturing plant in China
Chen 2018	Lake water	PFO A				87.1%	12.9%		Taihu Lake, China
Chen 2019	Lake sediment	PFO A				94.9%	5.1%		Taihu Lake, China
Shi 2018	Lake water	PFO A				85.0%	15.0%		Tangxun Lake, China
Shi 2018	River water	PFO A				83.6%	16.4%		Xiaoqing River, China
Gao 2019	Soil	PFO A	1.54	1.35	0.19	87.7%	12.3%	ppb	Near manufacturing plant in China
Gao 2019	Groundwater	PFO A	8.04	4.03	4.01	50.10%	49.90%	ppt	Near manufacturing plant in China
Chen 2018	Lake water	PFH xS				89.1%	11.0%		Taihu Lake, China

Gobelius 2018	Surface water	PFHxS				93.0%	7.0%		Sweden
Gobelius 2018	Groundwater	PFHxS				95.0%	5.0%		Sweden
Ahrens 2018	River water in Norway	PFHxS	2.92	2.30	0.62	78.8%	21.2%	ppt	Ronnean River, October 2016
Ahrens 2018	River water in Norway	PFHxS	3.02	2.30	0.72	76.2%	23.8%	ppt	Ronnean River, January 2017
Ahrens 2018	River water in Norway	PFHxS	3.41	2.75	0.66	80.6%	19.4%	ppt	Ronnean River, July 2017
Ma 2018	Mean lake and river water	PFHxS				89.0%	11.0%		Taihu Lake, China (lake and its riverine inputs)
Gao 2019	Soil	PFHxS	2.33	1.89	0.39	81.1%	16.7%	ppb	Near manufacturing plant in China
Gao 2019	Groundwater	PFHxS	33.5	21.2	12.3	63.3%	36.7%	ppt	Near manufacturing plant in China

2.2.1 Surface water and sediments

Linear PFAS isomers sorb preferentially to sediment compared to branched isomers, which is in accordance with research on PFAS isomer behavior in soil and groundwater. For example, in a study by Yu et al. (2013), isomer profiles in surface water in a water basin near a fluorochemical manufacturing plant in China had a higher percentage of branched PFOS (48.1-62.5%) than typical of ECF product (~30%), indicating more of the linear product was bound to the sediment (Yu et al., 2013). Linear forms of PFOA and PFHxS also dominate in surface waters, found to contribute to 87.1-95.0% of total loads of each compound in China's Lake Taihu (Chen et al., 2018). Preferential sediment absorption of linear PFOS may also contribute to the phenomenon of lakes having lower percentages of linear PFOS than rivers, as currents in rivers may reduce the opportunity for sorption to sediments and lead to linear PFOS remaining in the water at higher ratios compared to lakes. Ma et al (2018) found water in Taihu Lake to contain 51.3% branched PFOS and a river that feeds into Taihu Lake

to have 40.8% branched PFOS (Ma et al., 2018). Lower percentages of linear PFOS in lake fish compared to river fish has similarly been observed (Shi et al., 2018). The same study did not see a distinction between lake and river isomer profiles for PFOA, at 85.0% and 83.6% linear, respectively. It should be noted that preferential degradation of branched precursors, in addition to preferential sorption of branched isomers to soil, may influence the percentage of branched versus linear PFAS content of sediments (J. Liu et al., 2019). Ma et al (2018) also examined isomers of PFOA and PFHxS, and found the percentage of the linear isomer of PFHxS, 89%, represented a lower concentration than the standard ECF product manufactured nearby (96% linear), but the same was not true for PFOA where the lake percentage of 87.1% linear was higher than the ECF product (82% linear) (Benskin et al., 2010; Ma et al., 2018; Sundström et al., 2012). The authors suggested this discrepancy may be due to contributions from an additional source of PFOA or its precursors.

Although the mechanisms for the wide variation in isomer composition are not fully known, branched compounds can make up a significant portion of the total PFAS load in the environment. For example, study of five river sites downstream of industrial areas of varying sizes—including one site approximately 40 meters downstream of a fluoropolymer manufacturing site—in southeastern France found branched PFOS isomers in at least 80% of samples from each site, at higher concentrations in some cases than the linear form (Simmonet-Laprade et al., 2019). Similarly, an analysis of PFOS isomers in Swedish rivers found that in cases where both linear and branched PFOS were detected, concentrations were nearly the same. Overall, branched PFOS accounted for a higher percentage of the total PFAS load in rivers (8.9%) than linear

(4.0%), further displaying the importance of studying the effects of branched compounds (Ahrens et al., 2018). The same conclusions cannot be drawn from this study for PFHxS, which was found to contribute more than 1% of total PFAS at just two sites, only one of which also had branched isomers. More research on the isomer profiles of PFHxS in surface water is needed to understand trends in distribution.

2.2.2 Soil and groundwater

Similar to sediments, linear isomers of PFASs tend to sorb more readily to soil than branched isomers, likely due to the reduced hydrophobicity and greater polarity of the branched compounds (Benskin et al., 2007; Gao et al., 2019). Studies of soil have also determined that the sorption of branched PFOS is dependent on pH, with sorption decreasing with increasing pH (Gao et al., 2019; Uwayezu et al., 2019; Zhou et al., 2019). Linear PFOS and PFOA are known to show the same pH dependence for sorption, and also show a related trend of increasing with increasing zeta potential (Campos Pereira et al., 2018; Ferrey et al., 2012).

Isomer profiles in groundwater vary widely across studies and regions, though it is unclear the cause of such variation. Gobelius et al. (2018) found branched isomers to make up only 8% of the PFOS load and 5% of the PFHxS load in Swedish groundwater (Gobelius et al., 2018). A study of contaminated groundwater in Italy's Veneto region, however, found the overall percentage of branched isomers for PFOS and PFOA to be 22-25% of the total concentrations (Pellizzaro et al., 2018). Even further variation is seen in a study by Gao et al. (2019) near a PFAS manufacturing facility in China that found the linear isomer to account for only 39.9% of total PFOS in groundwater, with branched then making up about 60% (Gao et al., 2019). The same study looked at

branched isomers of PFOA and PFHxS, and while both showed higher percentages of linear in groundwater (88.1% and 77.9% linear, respectively), the percentages in groundwater were lower than those in soil (~100% and 81.1%, respectively), indicating that linear PFOA and PFHxS also sorb preferentially to soil compared to their branched isomers.

These studies show a wide range of groundwater isomer composition across different regions. Future research could look for trends in contamination compared with production volumes of different methods in the region, or could analyze soil and water properties to identify the main factors that determine the isomer profiles of contaminated areas.

2.2.3 Other environmental media: biosolids and seawater

It has been established that PFAS accumulate in sewage sludge; a study in San Francisco showed sludge concentrations of PFOS to range from 14.4 parts per billion (ppb) to 2610 ppb, which are up to six orders of magnitude higher than concentrations commonly found in water (Higgins et al., 2005). However, there appears to be a lack of studies regarding the isomer composition of PFOS in biosolids. One study found branched isomers to make up 19.5% of the total, with one monosubstituted isomer contributing to far more than any others (Zhang et al., 2018). The same study found that only the linear PFOA isomer contributed significantly to the total (97.1%), but linear PFHxS made up 86.3% of the total, a lower percentage than that found in typical PFHxS manufactured using ECF (~96%). Further investigations would be required to confirm these findings and determine the extent to which isomer composition tends to vary in biosolids.

Only one study could be found that looked at PFOS isomers in the oceans. In this case, the contribution of sea spray aerosols to atmospheric PFOS was investigated; it was found that branched isomers made up a larger percentage of total PFOS in bulk water at 28% than the surface microlayer at 18% (Johansson et al., 2019). This significant difference may be due to a reduction in surface activity resulting from branching.

2.3 Distribution Patterns in Plants

There is evidence of PFAS accumulation in plants, and PFOS has been found at low concentrations in cereal seeds and potatoes. According to a review by Ghisi et al. (2019), there is a direct correlation between the concentration of PFASs in soils and the amount taken into plants, though short-chain PFASs tend to accumulate more than the larger compounds such as PFOA and PFOS—in the studies examined, only maize roots appeared to bioaccumulate PFOS with a factor greater than one (8.82) (Ghisi et al., 2019). Soil can become contaminated and therefore impact plants due to contaminated water, land application of contaminated biosolids, and use of PFAS-containing firefighting foams (Houtz et al., 2013; Sepulvado et al., 2011). Though information of PFASs in plants is limited overall, some research has begun on isomeric distribution differences in plants.

2.3.1 Isomer ratios in different plant structures

Based on the limited studies available on plants, it seems that plant uptake also favors linear isomers over branched isomers (Felizeter et al., 2014, 2012; Gobelius et al., 2017). Zhang et al. (2018), who examined isomer patterns in biosolids, also looked at accumulation in maize plants. Overall, both leaves and straws had low levels of total

PFOS (average 0.67-1.74 and 1.82-4.88 ppb, respectively), and in roots only linear and one monosubstituted isomer contributed significantly to the total load, with 80.3% and 13.8%, and 83.2% and 9.6% of total PFOS at each plot respectively (Zhang et al., 2018). Notably, however, the percentage branched isomers changed significantly in different parts of the plant. While the roots at each plot were comprised of 80-83% linear, the straws' PFOS loads ranged from 60-63% linear, indicating a higher translocation potential for branched isomers. It was suggested that this may be due to reduced lipophilicity of branched PFOS. The percentage of linear isomers increased in leaves, however, at 78-85% linear. Overall there is a significant need for additional research on isomer-specific distribution of PFASs in plants.

Source ratios and distance from the source may also play a role in accumulation in plants. For example, isomer profiles of PFOS and PFOA in tree bark near a manufacturing plant in China match that of 3M's ECF product, but a lack of standards prevented similar conclusions from being drawn for PFHxS (Jin et al., 2018). This suggests that tree bark and other plants may be used as possible indicators of the occurrence, isomer pattern, and transport of airborne PFASs.

2.4 Distribution Patterns of Linear versus Branched PFAS in Animals

There is a global distribution of PFASs in wildlife based on studies of a variety of species including fish, birds, and mammals. In a review done by Giesy and Kannan (2001), PFOS concentrations in aquatic mammal tissues were found to range from 3 ppb in ringed seals from the Canadian Arctic to 3680 ppb in mink from the Midwestern USA, and in birds ranged from 1 ppb in polar skua from Antarctica to 2570 ppb in bald eagles from the Midwestern USA (Giesy and Kannan, 2001). The main tissues looked

at in the studies reviewed by this paper were blood plasma, eggs, livers, and muscles because of the tendency of PFASs to bind to proteins. It has been shown from food-chain analysis that PFOS bioaccumulates in the aquatic environment, with proposed bioaccumulation factors ranging from 10-20 in higher-level predators such as mink and bald eagles to 1000 for benthic invertebrates (Kannan et al., 2005).

2.4.1 Isomer distribution patterns in wildlife

Overall there are few studies that have measured the distribution of branched PFAS isomers in wildlife or other animals and creating generalizations from PFOA and PFOS are difficult as the different forms may behave differently. The few studies that exist seem to indicate preferential accumulation of linear isomers. Two recent studies focused on accumulation of PFASs in chickens. In a study of the developmental toxicity of PFOS and a similar replacement chemical, the authors found a preferential accumulation of the linear PFOS isomer in livers, with 75% of liver PFOS being linear as compared to the standard PFOS solution which was 63% linear (Briels et al., 2018). This is in agreement with the findings of an older study of chickens that also found an increase in the proportion of linear PFOS in the livers of chicken embryos (~84% linear) compared to the standard injected into the eggs (~63% linear) (O'Brien et al., 2011). In another recent study of chickens, near a fluorochemical manufacturing facility in China, accumulation of linear PFAS in yolk 91.8%, 98.3%, and 93.5% linear for PFOS, PFOA, and PFHxS, respectively (F. Wang et al., 2019). The same holds true for wildlife, where nestlings of white-tailed eagles in Norway found branched PFOS isomers ranged from 0.29-11.70 ppb of wet weight, while linear PFOS ranged 2.34-31.85 ppb (Løseth et al., 2019). Based on median concentrations, this data shows branched isomers contributing

to only 7.1% and 8.7% of the total at one site, and 16.9% and 16.6% at a second site in 2015 and 2016, respectively.

Similar trends have been found in fish. In the study of French rivers mentioned previously carp were found to preferentially accumulate the linear PFOS isomer, which accounted for 72.9% of the total load in the whole fish, but not the linear PFHxS isomer which was present in similar percentages (92.9%) to typical ECF PFHxS (Zhong et al., 2019). Overall, Zhong et al (2019) found linear PFOS to have a higher bioconcentration factor than its other isomers, and a higher percentage of linear was found in feces than elimination water; the opposite was true of branched isomers, which is in accordance with the reduced hydrophobicity of branched compounds shown from studies of environmental media. In the same study, however, linear and branched PFHxS showed the opposite elimination patterns, with higher percentages of branched compounds found in the feces than the elimination water. It is possible that this is due to differences in hydrophobicity playing a lesser role in distribution of PFASs with slightly shorter carbon chains, but a mechanistic explanation has not yet been confirmed. The study by Simmonet-Laprade et al. (2019) that looked at detection frequencies of PFOS isomers in French rivers also calculated trophic magnification factors (TMFs) for different isomers. Although TMFs were higher for linear PFOS at three river sites which agrees with the findings of Zhong et al. (2019), the TMFs for branched PFOS, ranging from 1.4-8.3, were greater than those of linear PFOS at two out of five of the sites (Simmonet-Laprade et al., 2019). This study shows the potential variability of TMFs in rivers, but was unable to identify factors that may lead to this variation. Additional research in this area could help elucidate the causes of variability and confirm these findings.

2.4.2 Geographical differences in wildlife isomer profiles

Significant geographic variation also exists in wildlife isomer profiles (Table 2.2). For example, in the study of chicken eggs done by Wang et al. (2019), the ratio of linear to branched isomers decreased with increasing distance from the plant. If the primary source of exposure is ground and/or surface water, this could be explained by the possible preferential adsorption of the linear isomer to soil and sediment, removing the linear form from this exposure route. Loseth et al. (2019) also showed geographical differences in barnacle geese, as the nestlings at one site had about double the percentage of branched compounds as those at the other site, regardless of diet and age. A study that sampled eggs from Arctic Barnacle Geese had different results, in that branched PFOS had a significantly higher mean concentration in eggs (2.114 ppb) as compared to linear (0.314 ppb) (Hitchcock et al., 2019). However, it should be noted that branched compounds were only detected in 7% of sampled as compared to 63% of samples for linear also indicating some environmental factors that could lead to differing ratios of isomers.

Table 2.2: Branched and linear PFAS in biota. Concentrations are in ppb.

Study	Animal	Tissue	Compound	Sum PFAS	Linear PFAS	Branched PFAS	% Linear	% Branched	Location
Hitchcock 2019	Barnacle geese	eggs	PFOS	3.125	0.93	2.195	29.8%	70.2%	UK, Norway
Loseth 2019	White-tailed eagle nestlings	serum	PFOS	16.35	14.12	2.23	86.4%	13.6%	Smola, Norway 2015

Loseth 2019	White-tailed eagle nestlings	serum	PFOS	5.9	5.25	0.65	89.0%	11.0%	Smola, Norway 2016
Loseth 2019	White-tailed eagle nestlings	serum	PFOS	21.93	16.55	5.38	75.5%	24.5%	Steigen, Norway 2015
Loseth 2019	White-tailed eagle nestlings	serum	PFOS	9.13	7.01	2.12	76.8%	23.2%	Steigen, Norway 2016
Chen 2018	"organisms"		PFOS				85.5%	14.5%	Taihu Lake, China
Wang 2018	Chickens	egg yolk	PFOS				92.0%	8.0%	Hubei Province, China
Wang 2019	Chickens	egg albumin	PFOS				87.0%	13.0%	Hubei Province, China
Zhong 2019	Carp		PFOS				72.9%	27.1%	Carp purchased from Tianjin farmer's market
Chen 2018	aquatic organisms		PFOA				95.0%	5.00%	Taihu Lake, China
Wang 2019	chickens	egg yolk	PFOA				98.30%	1.70%	Hubei Province, China
Chen 2018	Aquatic organisms		PFHxS				95.9%	4.10%	Taihu Lake, China
Wang 2019	Chickens	egg yolk	PFHxS				93.50%	6.50%	Hubei Province, China

Zhong 2019	Carp	whole fish	PFHxS				92.90 %	7.10%	Carp purchased from Tianjin farmers' market
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2.5 Unique Sources and Exposure Routes

2.5.1 Previously unidentified sources of branched PFOS isomers

Novel sources of branched PFOS isomers have been identified beyond the generally known source from the impure results of manufacture via ECF (Lehmeler, 2005). While studying the different isomers of perfluoroethylcyclohexanesulfonate (PFECHS), commonly used in aircrafts to inhibit the erosive properties of hydraulic fluid, Stefanac et al. (2018) found two PFOS isomers to be present in the PFECHS mixture (Stefanac et al., 2018). It was hypothesized that these isomers, perfluoro-6-dimethylhexane-3-sulfonate and perfluoro-5,5-dimethylhexane-2-sulfonate, formed as a result of the PFECHS ring opening during synthesis; linear PFOS was found in the mixture as well. This shows that while ECF production of PFOS is most likely the main contributor to its branched isomers, these compounds may also arise from the manufacture of other PFASs. Additional isomer analysis of perfluorinated alkyl substances beyond PFOS itself can help shed more light on the sources of branched PFOS. Branched, but not linear, PFOS was also identified in a study examining the release of endocrine-disrupting hormones from various medical devices where both infusion tubes and silicone catheters released a PFOS isomer that was unable to be identified (Gosetti et al., 2018).

2.5.2 Isomer profiles of indoor exposure

Isomer ratios from ECF appear to be retained in the indoor environment. House dust is a known exposure route for PFASs, and studies of household dust in both the full house and specifically children's bedrooms show isomer breakdowns of about 70% linear and 30% branched, matching closely with ECF product (Beesoon et al., 2011; Fromme et al., 2009; Winkens et al., 2018).

2.6 Regional Differences in Human Exposure and Accumulation

It has been established that the main exposure routes of PFASs for humans are indoor air, ambient air, food, drinking water, and house dust (Fromme et al., 2009). Based on the review by Fromme et al. (2009), the average level of daily PFOS intake for the general Western population is 1.6 ppt (concentration based on body weight), with an upper daily intake estimate of 8.8 ppt. Estimates of the total average load of PFOS in human serum vary from around 5-13 ppb depending on location—countries that either currently or historically produced PFOS, such as the United States and Denmark, tend to fall on the higher range of average serum concentration (Gebbink et al., 2015). In general, concentrations of PFOS in blood serum tend to increase with age due to longer term exposure and increased consumption of contaminated food and water (Jian et al., 2018).

2.6.1 Geographic differences of isomer loads in humans

Similar to trends in surface waters and animals, geographic location appears to impact isomer profiles in human serum. Table 2.3 shows the serum levels of linear and branched PFOS, PFOA, and PFHxS observed in studies. Comparing populations of pregnant women in the United States and Puerto Rico shows that women in the US

tend to have higher overall levels of PFOS in their serum (2.05 ppb in Puerto Rico, 2.90 ppb in US), but a lower percentage of the total is comprised of branched compounds at 26.8% in Puerto Rico and 20.7% in the US (Watkins et al., 2019). Both these studies show slight preferential accumulation of the linear isomer, which is contradictory to the majority of human studies. One possible explanation for this is that branched isomers of PFOS and PFOA show a higher trans-placental transfer efficiency than the linear isomer, causing the linear isomers to be retained in the mothers' serum and leading to higher ratios of linear (Beesoon and Martin, 2015). Higher serum levels in the US may be due to the long-term production of PFOS and PFOA in America. In China, where PFOS is still produced, pregnant women show even higher levels of PFOS in serum (4.16 ppb), though the percentage of branched PFOS varies, ranging from 24.8-31.3% (X. Liu et al., 2019; Wang et al., 2018). Samples from the Study of Women's Health Across the Nation (SWAN) in 1999-2000 showed that both linear and branched PFOS and PFOA had associations with ethnicity, geographic region, and country of birth (United States versus a different country), also showing the impact of geographical location (Park et al., 2019). It may be that differences in production methods and volumes can account for regional differences in the isomer profiles of human serum, but additional research would be necessary to confirm this possibility.

Table 2.3: Branched and linear PFAS in human blood serum. Concentrations are in ppb. If sum not given in paper, it is estimated from adding concentrations of linear and branched.

Study	Sample	Compound	Sum PFAS	Linear PFAS	Branched PFAS	% Linear	% Branched	Findings
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Liu 2018	Adults	PFOS	5.28	3.70	1.39	70.1 %	26.3 %	Higher branched concentration associated with enhanced beta-cell function and decreased serum globulin
Zeng 2019	Maternal Cord Blood	PFOS	2.91	2.20	0.71	75.6 %	24.4 %	Lowered Hand, Foot, and Mouth Disease antibody count, higher OR of falling under clinical level of protection
Hu 2019	Adult Women	PFOS	27.8 5	15.8 6	11.9 9	56.9 %	43.1 %	Tap water accounts for very low percentage of PFAS exposure
Park 2019	Middle Aged Women	PFOS	25.4 4	17.8 5	7.23	70.2 %	28.4 %	Levels vary by geographic region, smoking status, diet, menstrual bleeding, parity, country of birth (US vs. outside US), and race; education and dairy consumption associated with linear but not branched; fish, pizza, and fries consumption associated with branched but not linear
Wang 2019	Pregnant Women	PFOS	3.93	2.70	1.23	68.7 %	31.3 %	No association found between serum PFOS levels and gestational diabetes mellitus or post-partum glucose levels

Ye 2018	Children Aged 3-11	PFOS	3.74	2.51	1.23	67.1 %	32.9 %	Older children tend to have higher serum PFAS concentrations, as well as non-Hispanics
Gyllenhammar 2018	Infants	PFOS	14.00	8.60	5.00	61.4 %	35.7 %	Breastfed infants have lower branched concentrations but higher overall PFOS concentrations than bottle-fed infants
Gyllenhammar 2018	Mothers	PFOS	20.00	14.00	7.00	70.0 %	35.0 %	
Jain 2018	Children Aged 6-11	PFOS	4.02	2.67	1.35	66.4 %	33.6 %	Higher linear PFOS levels associated with higher overall cholesterol but not true for branched; higher branched levels associated with lower non-HDL cholesterol. Monomethyl branched isomer only one quantified.
Mora 2018		PFOS	6.20	4.40	1.80	71.0 %	29.0 %	No strong associations between prenatal PFAS exposure and lipid or alanine aminotransferase in mid-childhood. Monomethyl branched isomer only one quantified.
Watkins 2019	Pregnant Women in Puerto Rico	PFOS	2.27	1.66	0.61	73.1 %	26.9 %	50th and 95th percentile concentrations lower in Puerto Rican women

								than US women, means not given for US women
Liu 2019	Pregnant Women	PFOS	4.16	3.13	1.03	75.2 %	24.8 %	No significant association between serum PFAS levels and GDM or glucose homeostasis
Reardon 2019	Pregnant Women	PFOS	3.94	2.72	1.22	69.0 %	31.0 %	Branched PFOS isomers positively associated with TSH levels; association is dose-dependent and strongest in 1st trimester
Nian 2019	Adults	PFOS	30.5 5	15.0 4	15.5 1	49.2 %	50.8 %	Branched PFOS isomers positively associated with alanine aminotransferase (ALT) and odds of having abnormal ALT levels
Tian 2019	Adults	PFOS	30.5 5	15.0 4	15.5 1	49.2 %	50.8 %	Higher levels of PFAS in blood associated with higher odds ratio of obesity, but increase is only significant for linear and not branched PFOS. Same sample population as Nian 2019
Wang 2019	Adults	PFOS	30.5 5	15.0 4	15.5 1	49.2 %	50.8 %	Branched isomers negatively associated with kidney function based on

								glomerular filtration rate and chronic kidney disease. Same sample population as Nian 2019
Liu 2018	Adults	PFOA	1.86	1.75	0.08	94.1 %	4.3%	Higher level of branched PFOA was associated with higher total cholesterol and HDL-C
Zeng 2019	Maternal cord blood	PFOA	1.49	1.44		96.6 %	3.4%	Higher level of total PFAS associated with lower antibody count
Park 2019	Middle aged women	PFOA	4.18	4.07	0.11	97.4 %	2.6%	Concentrations varied based on region, country of birth, parity, diet
Ye 2018	Children aged 3-11	PFOA	1.92	1.23	0.69	64.1 %	35.9 %	Older children tend to have higher serum PFAS concentrations, as well as non-Hispanics
Mora 2018	Pregnant women	PFOA	4.3	4.1	0.2	95.3 %	4.7%	No strong associations between prenatal PFAS exposure and lipid or alanine aminotransferase in mid-childhood.
Liu 2019	Pregnant women	PFOA	2.29	2.25	0.03	98.3 %	1.3%	No significant association between serum PFAS levels and GDM or glucose homeostasis. Only one branched

								PFOA isomer quantified
Nian 2019	Adults	PFOA	8.02	7.83	0.19	97.6 %	2.4%	Linear PFOA more strongly associated with higher ALT levels than branched. Only one branched isomer quantified.
Tian 2019	Adults	PFOA	8.02	7.83	0.19	97.6 %	2.4%	Higher levels of PFAS in blood associated with higher odds ratio of obesity. Same sample population as Nian 2019
Wang 2019	Adults	PFOA	8.02	7.83	0.19	97.6 %	2.4%	Linear PFOA significantly associated with lower glomerular filtration rate, but not branched
Gyllenhamar 2018	Infants	PFHxS	2.81	2.6	0.21	93.1 %	6.9%	Isomer ratio appears to be maintained from mother to infant
Gyllenhamar 2018	Mothers	PFHxS	2.34	2.2	0.14	94.3 %	5.7%	

2.6.2 Other factors affecting isomer profiles in humans

In addition to geographical location, there is evidence that diet may be a factor affecting isomer composition in human serum. Samples from the SWAN study also indicated associations between both linear and branched PFOS and smoking status, diet, menstrual bleeding, parity, and race, whereas only branched had associations with fish, pizza, and fries consumption and only linear had associations with dairy

consumption and educational level (Park et al., 2019). This may indicate that diet contributes to differences in the branched and linear ratios between people. It is possible that dietary differences may partially account for geographic variation, but further analysis is needed to identify such a pattern. There has been no such association with drinking water; one study found that linear and branched PFOS in tap water accounted for only 2.2% and 3.0% of total serum load of each compound, respectively (Hu et al., 2019). This indicates that tap water is not the main source of exposure for the overall population, nor is it likely a main contributor to isomer profile differences between populations. Exposure to PFOS precursors such as perfluorooctane sulfonamides (PFOSAs) that preferentially degrade into branched PFOS isomers may contribute significantly to the isomer distribution in humans, with exposure to precursors accounting for up to 40% of the total body load of PFOS (Benskin et al., 2009b; Miralles-Marco and Harrad, 2015)

2.7 Isomer-specific Associations with Health Outcomes

It is established that PFASs are bioaccumulative and have long half-lives in humans of 3.8 and 5.4 years for PFOA and PFOS, respectively (Zhang et al., 2013). This fact, along with the knowledge that nearly all the general population has some level of PFASs in their blood, has led to a recent surge of epidemiological and toxicological studies. Studies show that PFASs can cross the placental barrier, causing exposure to start before birth (Inoue et al., 2004; Negri et al., 2017). Low birth weight in association with elevated PFAS levels in serum have been reported for both animals and humans, though results are less conclusive with humans as some studies do not show an increased odds ratio of low birth weight while others do (Agency for Toxic Substances

and Disease Registry (ATSDR), 2018). Several studies have shown higher blood serum concentrations of PFASs to be associated with a lowered vaccine response in children (Grandjean et al., 2012; Granum et al., 2013; X. W. Zeng et al., 2019a). There have also been links between exposure to PFASs and elevated incidence of certain cancers, consistently testicular and kidney cancer, and in some studies also breast, bladder, and prostate cancer (Agency for Toxic Substances and Disease Registry (ATSDR), 2018; Alexander et al., 2003; Barry et al., 2013; Bonefeld-Jørgensen et al., 2014; Gilliland and Mandel, 1993; Hardell et al., 2014; Lundin et al., 2009; Steenland and Woskie, 2012; Vieira et al., 2013). It is only recently that researchers have begun to look separately at health effects of different PFOS isomers.

2.7.1 Health studies in adults

Studies that have separated isomers of PFAS in regard to health associations have, in some cases, found certain endpoints associated with branched but not linear isomers and vice- versa. Though many PFAS chemicals have been associated with a higher prevalence of hypertension, one study found the odds ratio to be higher for branched PFOS at 1.26 (95% confidence interval [CI] 1.12, 1.42) than for linear PFOS at 1.11 (95% CI 0.97, 1.27) (Bao et al., 2017). Branched, but not linear, PFOS has been associated with enhanced beta-cell function and decreased levels of serum globulin, an increase in alanine aminotransferase (ALT) levels, a 33% increase (95% CI 5.0%, 67.0%) in odds of having abnormal ALT levels, and decreased kidney function based on glomerular filtration rate and chronic kidney disease incidence in adults (H. S. Liu et al., 2018; Nian et al., 2019; J. Wang et al., 2019). A slightly different trend was seen for PFOA, where linear PFOA was associated with a decreased odds ratio of chronic

kidney disease (0.75; 95% CI: 0.59, 0.97), but branched PFOA had no association with any change in odds ratio (J. Wang et al., 2019). Previous studies have looked at the effects of PFASs on kidney function and have found associations between total PFOS and reduced kidney function (Jain and Ducatman, 2019; Kataria et al., 2015; Stanifer et al., 2018). The findings of J. Wang et al. (2019) indicate that branched PFAS may contribute more than the linear isomer to these associations, but additional research on isomer-specific associations with reduced kidney function is needed to confirm these findings.

Conversely, higher serum concentrations of linear PFOS have shown significant associations with a higher odds ratio of being obese at 1.45 (95% CI 1.06, 1.99) than branched PFOS at 1.33 (95% CI 1.00, 1.77) (Tian et al., 2019). The opposite trend and slightly higher odds ratios were seen for linear and branched PFOA at 1.54 (95% CI 1.08, 2.21) and 1.62 (95% CI 1.05, 2.51), respectively. This shows that functional group and branching can both affect health outcomes, which has been observed in additional studies. Zeng et al. (2019) looked at the association between serum PFOS and PFOA levels and serum uric acid, and found that for both PFOA and PFOS the branched isomer had a higher increase in serum uric acid per log unit, but a starker difference was seen between PFOS and PFOA; each log increase of serum PFOS concentration was associated with increases of 0.09 mg/dL and 0.06 mg/dL, respectively, but PFOA saw increases of 0.30 mg/dL for branched and 0.18 mg/dL for linear (X. W. Zeng et al., 2019b). A similar dependence on both functional group and branching has been seen in a study by Zeeshan et al. (2020). In this study, linear PFOS was associated with a higher odds ratio (3.37, 95% CI 2.50, 4.56) of visual impairment than branched PFOS

(2.25, 95% CI 1.72,2.93), and only linear PFOA was associated with a significantly higher odds ratio (1.79, 95% CI 1.36, 2.37) of visual impairment but not branched PFOA (Zeeshan et al., 2020). Based on evidence that *C. elegans* show different transcriptional changes when fed different ratios of linear and branched PFOS, it is possible the health differences in humans are rooted in transcriptional effects as well (Stylianou et al., 2019).

2.7.2 Health studies in pregnant women

Studies of pregnant women have found associations with blood glucose levels in pregnant women, but results are not consistent. Wang et al. (2018) and X. Liu et al. (2019) both found no association between branched or linear PFOS and PFOA and gestational diabetes mellitus, but the studies differed in their findings regarding blood glucose levels; Liu found that the branched PFOS isomers, but not the linear, had significant positive associations with postpartum glucose levels, while Wang found no significant association between linear or PFOS levels and glucose homeostasis in pregnant women (X. Liu et al., 2019; Wang et al., 2018). This discrepancy may be due to the measurement of glucose levels in pregnant women in one study and postpartum levels in another study, but also warrants further investigation into the effects of PFOS and its isomers on glucose levels during and after pregnancy. Significant associations between branched PFOS and increased thyroid-stimulating hormone (TSH) have been observed in pregnant women, where a 1 ppb increase in plasma concentration of sum branched PFOS isomers led to a 0.286 (95% CI 0.017, 0.555) log unit increase in plasma concentration of TSH (Reardon et al., 2019). No significant association between linear PFOS concentration and TSH concentration was observed.

2.7.3 Health studies in prenatal exposure and children

It is yet unclear if isomer ratios are maintained when crossing the placental barrier; while it is known that PFAS overall do cross this barrier, two studies show higher transfer efficiency of branched isomers and another shows the ratios maintained between mother and fetus (Beesoon et al., 2011; Gützkow et al., 2012; Gyllenhammar et al., 2018; Inoue et al., 2004; Midasch et al., 2007; Olsen et al., 2009). Additional research could help clarify if and how isomer ratios change when crossing the placenta. Associations between prenatal exposure to PFASs and reduced birthweight have already been seen, but recently Li et al. (2017) looked for isomeric distinctions in these associations (Agency for Toxic Substances and Disease Registry (ATSDR), 2018). It was shown that per log unit increase in cord serum concentration of branched PFOS there was a 126.3 g (95% CI -195.9, -56.8) decrease in birth weight, and for linear PFOS the associated decrease in birth weight was less than half that of the branched association at a reduction of 57.2 g (95% CI -103.1, -11.3) (Li et al., 2017). This suggests that branched compounds may have a greater effect on infant birth weight than linear isomers, and indicates a need for additional research on prenatal exposure to branched isomers.

Studies in children have similarly shown health effects associated exclusively with either the branched or linear isomers of PFOS. It has been found that higher cholesterol, a commonly seen association with elevated levels of serum PFOS, can be observed for linear but not branched PFOS in children; branched PFOS actually showed a negative association with non-HDL cholesterol, which has not been seen in previous studies of PFOS (Jain and Ducatman, 2018). Both isomers, however, were

shown to be associated with a lowered response to the hand, foot, and mouth disease vaccine (X. W. Zeng et al., 2019a). Though earlier studies have shown similar trends in decreased vaccine antibody counts in children, no other studies found looked at isomers separately (Grandjean et al., 2012; Granum et al., 2013). As additional epidemiological studies search for associations between PFASs and different toxicological and biochemical endpoints, it is important to analyze linear and branched PFOS separately as these isomers have been shown in a variety of studies to have different effects.

2.8 Analysis and Remediation

2.8.1 Novel analysis methods for branched isomers

As continued research reveals the possibility of differing health effects of branched and linear PFOS and shows the need to analyze isomers separately, novel detection methods are beginning to account for this separation. A recent method specifically for seawater uses vortex-assisted liquid-liquid microextraction with liquid chromatography and linear ion trap Orbitrap (LTQ-Orbitrap) high resolution mass spectrometry, and claims high sensitivity and precision along with the ability to detect both linear PFOS and its branched isomers (Concha-Graña et al., 2018). The method was validated by the National Measurement Institute of the Australian government and may be a useful tool for determining PFAS levels in seawater and tracking movement of these compounds in the oceans, and has sensitivities ranging from 0.7 ppt to 6 ppt and 95-105% recovery. High-resolution differential ion mass spectrometry has also been used for PFAS isomer separation, and this method takes less than three minutes as opposed to current methods that can take minutes to hours (Ahmed et al., 2019). These

findings are optimistic, but require more investigation on additional ion-mobility based methods of analysis as some isomers were much more readily distinguished than others using this method.

2.8.2 Removal abilities for branched isomers

There are three main technologies that are commonly available for removal of PFASs from water: granular activated carbon (GAC), ion exchange resins (IX), and reverse osmosis (RO) (Arias Espana et al., 2015; Tang et al., 2006). In general, it is shown that all these technologies are successful at removing long-chain PFASs including PFOA and PFOS. One of the more common methods of PFAS removal from water, GAC filters, have shown lower removal efficiencies for branched PFOS than for the linear isomers (McCleaf et al., 2017). Additionally, the strength of the carbon-fluorine bonds in PFASs render them extremely difficult to break down, and few methods and no biological processes can degrade these compounds (Lindstrom et al., 2011b). Liu et al. (2018), however, found through experimental results and theoretical calculations the possibility of reductive defluorination of branched PFAS compounds using cobalt complexes as catalysts; the slightly lower bond dissociation energy of tertiary branched compounds allows for this initial bond breakage to happen most readily (J. Liu et al., 2018). If this method can be found to work well at scale it may open the possibility of intentionally creating branched compounds in place of linear—no defluorination was observed for linear PFASs—as they could be later broken down. One of the cobalt complexes investigated was biogenic, indicating a need for future research regarding the fate of branched isomers in biological systems that contain this complex.

2.9 Conclusions and Future Research Needs

Though PFOS has historically been studied in terms of the sum total of all isomers, recent research has indicated that the structural differences between linear and branched isomers of PFOS and other PFASs cause differences in how these chemicals behave in the environment and living organisms. One clear difference is the preferential sorption of the linear isomer to soil and sediments over branched isomers due to reduced hydrophobicity in the branched isomers. While it is demonstrated that most animals preferentially accumulate the linear isomer, the opposite may be true for humans. In addition, some studies that have studied associations between PFAS concentration in human blood serum and a variety of negative health effects have found differences between health outcomes associated with linear versus branched PFOS when analyzing isomers separately. Relative contributions of the different isomers of PFASs in plants is not well studied, but there are indications that different parts of the plant have unique isomer profiles.

The studies discussed in this paper indicate a clear need for continued analysis of branched and linear PFAS isomers separately, as they have been shown to accumulate differently across abiotic matrices, biota, humans, and organs and tissues within living organisms. The apparent preferential accumulation of branched isomers in humans, which is in contrast to trends found in all other animals studied, should be investigated further for confirmation and to identify mechanistic explanations for why accumulation seems to favor branched. In several cases, certain toxicological effects and endpoints were observed for linear but not branched PFOS and PFOA, or vice versa. This calls for not only continued studies that differentiate between isomers, but also investigation into

the mechanisms of transport that cause these distinct accumulation patterns and toxic effects. Additionally, the possibility of differing effects of linear and branched PFASs on biosolids is not well studied and is a future research need. Including an isomer breakdown in future surveys such as National Health and Nutrition Examination Survey would assist in identifying additional associations as well as investigating temporal changes in isomer makeup, especially to track the effects of reduced ECF production of PFAS with the switch to production via telomerization.

The majority of research on specific PFAS isomer behavior focuses on isomers of PFOS, though the small body of research on isomers of PFOA and PFHxS also indicate distinct distribution trends and health associations. Future research should consider separation of isomers for PFOA, PFHxS, and other PFAS compounds in order to confirm these findings.

Chapter 3: Linking industrial point sources to PFAS contamination in wells: Michigan case study

As submitted to Environmental Science and Pollution Research for peer review.

3.1 Introduction

PFAS are known to enter the environment from both industrial and non-industrial waste dumping and effluent, airborne deposition via fumes, firefighting foam use, and disposal of PFAS-containing products in landfills where leaching can occur (Liu et al., 2017; Wang et al., 2014). They have been found extensively in both surface and groundwater drinking water sources water at concentrations ranging from non-detectable to hundreds of parts per trillion (ppt) (Boone et al., 2019). Substantial difficulty exists in predicting where high levels of contamination will occur and the causal sources. Identifying PFAS contamination in groundwater is complicated by the wide variety PFAS compounds in use, the lack of transparency and the variability in their use across multiple products, manufacturing processes, and industries. Although they are used in a diverse spectrum of consumer products and industrial processes, PFAS compounds are often only used in small amounts. Finally, lacking government regulation of PFAS chemicals results in limited reporting of use of these persistent chemicals and thus also results in difficulty funding and targeting monitoring PFAS contamination in the environment (KEMI, 2015).

Studies have shown that exposure to PFAS is associated with a variety of adverse health outcomes in humans, including hypertension, low birth weight, liver problems, thyroid problems, decreased vaccine response in children, and higher incidence of several kinds of cancer (Agency for Toxic Substances and Disease Registry (ATSDR),

2018; Grandjean et al., 2012; Granum et al., 2013; Kim et al., 2018; Nian et al., 2019; X. W. Zeng et al., 2019a; Z. Zeng et al., 2019). Although concerns about PFAS chemicals have existed for over a decade, they have only recently become subject to regulation and these regulations are limited in the scope of the types of PFAS they address. In 2009, PFOS was listed as a persistent organic pollutant under the Stockholm Convention, and PFOA was added to the list in 2019 (Stockholm Convention, 2019, 2008). In 2019, USEPA issued interim recommendations for groundwater contaminated with PFOA and PFOS and is in early stage of risk assessment for both compounds in biosolids (USEPA, 2019).

Lack of information on industrial PFAS use results in the inability of groundwater managers and regulators to identify potential contamination sites efficiently or at a landscape scale for testing and monitoring. A few prior studies have looked at contamination sources of PFAS on various scales. Using data from USEPA's Third Unregulated Contaminant Monitoring Rule (UCMR 3), Hu et al (2016) looked for watershed-level correlation between PFAS contamination and the presence of wastewater treatment plants, military fire training areas, and fluoropolymer facilities that participated in the USEPA's stewardship program to phase out PFAS production (Hu et al., 2016). Associations were found between all types of sites and elevated PFAS concentrations in water. Guelfo et al (2018) created risk ranking for groundwater in the Providence, Rhode Island area based on industrial presence and aquifer vulnerability, listing Department of Defense sites, fluoropolymer manufacturers, landfills, and airports among the types of industrial sites contributing the most PFAS risk to water (Guelfo et al., 2018).

In this study we examined whether existing data about the location of industries known to use PFAS compounds can be used to predict future sites for monitoring. This differs from previous studies by incorporating all industry types found in the literature to use PFAS rather than just PFAS manufacturers, and incorporating extensive well testing data to spatially compare PFAS detections to possible point sources. Michigan was chosen as a study case as it began extensive statewide testing of drinking water wells for PFAS in 2018, and continued in 2019 with quarterly testing of wells that had tested at concentrations above 10 ppt the previous year (State of Michigan, 2018). Few states have completed such widespread testing of drinking water sources. Nationwide testing under UCMR 3 has higher detection limits and covers around 5000 drinking water sources nationwide as opposed to over 1000 in Michigan from state-funded testing alone (USEPA, 2012). The goal of this study is to identify characteristics of wells, including proximity to industrial sites, type of bedrock, and well depth, that significantly impact the likelihood of PFAS contamination in order to help focus testing efforts on wells that share these characteristics in other areas. A survey of PFAS-using industries was also completed as part of this study, but a low response rate led to its exclusion from the final manuscript. Details on the survey can be found in Appendix A.

3.2 Methods

3.2.1 Michigan well and industry data

Well testing data in Michigan was gathered from the Department of Environment, Great Lakes, and Energy's (EGLE) report on PFAS testing using a Freedom of Information Act (FOIA) request submitted in February of 2020. This data identified wells based on their Water Supply Serial Number (WSSN) and did not include locations. This well test data

was merged with the spatially explicit well data from Michigan's geographic information system (GIS) portal that also identified wells using WSSNs and could thus be merged with the well testing data (Michigan Dept. of Environment, Great Lakes, 2019). The PFAS testing data from Michigan included 1126 sites, of which 1087 were included in this analysis after removal of surface water sources. The majority of wells were sampled between April and December of 2018, with one well sampled in September 2017 and seven wells sampled from January through September of 2019. Well water was tested using USEPA's Method 537 Revised 1.1, which tests for 18 PFAS compounds. Concentrations were reported as a sum totals of PFOA and PFOS, and of all PFAS found; this study used the concentrations that included all 18 compounds. Among the well sites included in this study, 107 tested positive for PFAS with a range of total PFAS concentrations from 2 ppt to 1828 ppt and an average concentration of 28.794 ppt, whereas 974 sites did not contain PFAS at detectable levels. Notably, the site with a concentration of 1828 ppt was an outlier, as the next highest concentration was 72 ppt. Industries that use or are sources of PFAS were identified in a literature search. Prior studies on point sources as well as studies analyzing products that contain PFAS led to the inclusion of the industry groups listed in Table 3.1 with their relevant North American Industry Classification System (NAICS) codes and studies that indicated their PFAS use. Briefly, PFAS have a wide variety of industrial uses including nonstick coatings, metal finishing, fabric finishing, plastics manufacturing, lubricants, and pesticides (Buck et al., 2011; Glüge et al., 2020; Guelfo et al., 2018; Herzke et al., 2012; Kissa, 2001; Nascimento et al., 2018). Studies have also indicated PFAS use in medical devices, electronics, cleaning products, and photographic film processes (Clara et al., 2008;

Gosetti et al., 2018; Lin et al., 2009; Xie et al., 2013). Studies indicating PFAS contamination at military sites and landfills are also well documented (Guelfo et al., 2018; Hu et al., 2016; Liu et al., 2017; Oliaei et al., 2013). Industrial sites for Michigan were spatially located using the NAICS codes listed in Table 3.1, and the USEPA's Enforcement and Compliance History Online (ECHO) facility search (USEPA, 2018). Sites include both current and historic facilities as of 8 June, 2020. Industrial and well locations were mapped using the GIS ESRI ArcMap version 10.7 (Redlands, CA, USA).

Table 3.1: Industry groups included in this study, the associated NAICS codes for specific industries within those groups, and the sources that led to the inclusion of those industries.

Industry Type	NAICS Codes	Source(s)
Textiles and Carpets	313210, 313310, 313320, 314110, 314999, 316110	Glüge et al. 2020; Guelfo et al. 2018; Herzke et al. 2012; Kotthoff et al. 2015;
Chemical Manufacturing	325199, 325320, 325622, 325612, 424690	Glüge et al. 2020; Guelfo et al. 2018; Hu et al. 2016; Nascimento et al. 2018
Paper Products	322121, 322219, 322220, 323111, 323120,	Glüge et al. 2020; Guelfo et al. 2018; Herzke et al. 2012; Schaidler et al. 2017
Plastics/ Rubber Manufacturing	325211, 326112, 326113,	Glüge et al. 2020; Guelfo et al. 2018; Schaidler et al. 2017
Grease, Oil, and Lubricant-related industries	324110, 324191, 333318, 336310	Glüge et al. 2020; Guelfo et al. 2018;
AFFF Use	488119, 928110	Glüge et al. 2020; Guelfo et al. 2018; Hu et al. 2016; Milley et al. 2018
Electroplating/Metal Finishing	332813, 332999	Glüge et al. 2020; Guelfo et al. 2018;
Dry Cleaners	812310, 812320	Clara et al. 2008; Glüge et al. 2020
Paint and Coating Manufacturing	325510	Glüge et al. 2020; Herzke et al. 2012;
Medical Instruments/Apparatuses	333249	Glüge et al. 2020; Gosetti et al. 2018
Photographic Film/Chemicals	325992	Glüge et al. 2020; Xie et al. 2013

Landfills	562212	Guelfo et al. 2018; Hepburn et al. 2019; Hu et al. 2016; Liu et al. 2017; Oliaei et al. 2013
Electronics	3344 (all)	Glüge et al. 2020; Lin et al. 2009

3.2.2 Linking industrial sites to PFAS contamination

Previous studies have shown that a 0.5 km radius buffer around a groundwater source and potential contaminants is a sufficiently sized area to study significant correlation between land use and contamination. Johnson and Belitz (2009) found that a 500m circle, though a highly simplified model, was sufficient to show correlation between volatile organic compound (VOC) contamination of groundwater and urban land use (Johnson and Belitz, 2009). Lindstrom et al. (2011a) found that 82% of wells within 0.5 km of fields that received contaminated biosolids tested positive for PFAS (Lindstrom et al., 2011a). Finally, impervious surfaces are known to cause rapid runoff that carries heavy loads pollutants into waterways, which can ultimately impact groundwater sources (Frazer, 2005). Use of PFAS at airports and other places where AFFF foams may be used in paved areas could contribute to pollution from such runoff (Awad et al., 2011). One study has linked landfill, military, and PFAS-producing facilities to drinking water contamination on a hydrologic unit basis using UCMR3 testing data, but did not include industries that use PFAS or link specific sites to contamination (Hu et al., 2016). Based on these studies, we hypothesized that location within the 0.1 km, 0.5 km, and 1 km buffer zones of PFAS-related industrial sites, Coldwater Shale bedrock type, well-drained soils, and impervious land cover would show a significant positive correlation with PFAS detection in wells, whereas well depth would show a significant negative

correlation with PFAS detections. Coldwater Shale bedrock type was chosen because it was the most common bedrock type at contaminated well sites (35%). Based on previous literature and the prevalence of industries within the buffer zones (as indicated in Table 2), we also hypothesized specifically that the number and percentage of current and historic electroplating facilities, airports, and landfills within the buffer zones would be positively correlated with PFAS detections in wells (Awad et al., 2011; Hepburn et al., 2019; Milley et al., 2018). To test for effects of industry presence on PFAS well contamination in Michigan, we used a maximum likelihood method, Probit analysis and Moran's I as described below.

3.2.3 Probit Models

Using a Probit function, the spatial siting of industries and the bedrock characteristics were used to predict the probability of a positive well test for PFAS. To test for a relationship between industry presence on PFAS detections in wells, buffer zones of 0.1 km, 0.5 km, and 1 km were constructed around each well tested for PFAS. In this study, industry presence within these buffer zones was analyzed as an effect on detection and non-detection in wells while controlling for other factors such as bedrock type, land cover, and well depth. Wells were given a value of 0 if PFAS were not detected (ND), and given a value of 1 if any level of PFAS were detected. A value of 1 was given for wells located within the Coldwater Shale bedrock formation, and a value of 0 given for wells within all other bedrock formation types. Coldwater Shale was selected as it is the most common bedrock formation for wells with detected levels of PFAS. Well depth was based on the numerical value of the well's depth, in feet, and well depth squared is the squared value of the depth of each well in feet squared. A value of 1 was given for wells

with a “developed, low intensity” land cover classification (NLCD code 22), and a value of 0 given for wells with any other land cover classification. A value of 1 was given for wells with “well drained”, “excessively drained”, or “somewhat excessively drained” soil drainage classifications. A value of 0 was given for wells with any other soil drainage classification. A few specific industries were chosen as separate variables because they were present at the highest numbers within the well buffers (see Table 2): landfill, electroplating, metal foil manufacture, and airport sites. All models were estimated as either percent, meaning the total percentage of sites within the given radius (0.5 km or 1 km) of a well that belong to the specific industry, or raw number, which is the number of industry sites classified as the specific industry within the given radius of a well. The percentage of “all others”, which includes all the industry sites included in the analysis apart from the specified industries just outlined, was also estimated in each model. Lastly, a variable was assigned for the total number of quarters within the past three years that industry sites in a given radius had failed to comply with USEPA environmental standards, with a maximum value of 12. A summary of the variables used in the Probit models is shown in Table 3.2.

Table 3.2: Summary statistics of variables used in Probit regression analysis – 0.5 km and 1 km buffers (N= 1081).

Variable	Variable Description	Model(s)	Expected Effect on Dependent Variable (+/-)	Mean/(sd)	Min.	Max.
Detect	0 if non-detect (ND), 1 if detect (D)	All	n/a	0.099	0	1
Bedrock	0 if other bedrock type, 1 if “Coldwater Shale”	All	+	0.31 (0.46)	0	1

	formation					
Welldepth	Well depth (ft.)	All	-	173.90 (107.76)	21	815
Welldepthsq	Well depth squared	All	-	4184.86 (60263.90)	576	664225
Landcover	0 if other land classification, 1 if “developed, low intensity” (NLCD code 22)	All	+	0.23 (0.42)	0	1
Soildrainage	0 if other drainage classification, 1 if “well drained”, “excessively drained”, or “somewhat excessively drained”	All	+	0.74 (0.44)	0	1
Percentlandfill	Percent of sites as landfills within 0.5 km of wells	1	+	0.01 (0.09)	0	1
Percentmetalfoil	Percent of sites as metal foil within 0.5 km of wells	1	+	0.01 (0.07)	0	1
Landfill	Number of sites as landfills within 0.5 km of wells	2	+	0.01 (0.16)	0	3
Metalfoil	Number of sites as metal foil within 0.5 km of wells	2	+	0.01 (0.07)	0	1
FacQtrsWit	Total number of quarters within last 3 years where all sites within 0.5 km buffer have failed to comply with USEPA environmental standards	1 and 2	+	0.05 (0.66)	0	12

Percentairport	Percent of sites as airports within 1 km of wells	3	+	0.01 (0.07)	0	1
Percentlandfill	Percent of sites as landfills within 1 km of wells	3	+	0.03 (0.17)	0	1
Percentelectroplating	Percent of sites as electroplating within 1 km of wells	3	+	0.01 (0.12)	0	1
Percentallothers	Percent of sites as all other industry types within 1 km of wells	3	+	0.93 (0.25)	0	1
Airport	Number of sites as airports within 1 km of wells	4	+	0.01 (0.11)	0	2
Landfill	Number of sites as landfills within 1 km of wells	4	+	0.07 (0.53)	0	10
Electroplating	Number of sites as electroplating within 1 km of wells	4	+	0.02 (0.16)	0	2
Allothers	Number of sites as all other industry types within 1 km of wells	4	+	0.06 (0.30)	0	3
FacQtrsWit	Total number of quarters within last 3 years where all sites within 1 km buffer have failed to comply with EPA environmental standards	3 and 4	+	0.08 (0.88)	0	12

Model 1: 0.5km buffer, percent of industry sites

Model 2: 0.5km buffer, number of industry sites

Model 3: 1km buffer, percent of industry sites

Model 4: 1km buffer, number of industry site

Four Probit models were considered to test the effect of land use and type on the probability of detection, such as the number and types of industries within a certain buffer of the well, bedrock, land cover, soil type, well depth, and well depth squared on the probability of PFAS detection in a well using the equation as follows

$$0,1 = f[\#sites, depth, percentindustry, percentmajorfacility, \#violations] \quad (1)$$

where the dependent variable is assigned values of 0 or 1. The four models separate the amount/percent and type of industries found within each buffer from the data found within other buffers. In this study, the detection of PFAS pollution at well sites is the dependent variable where a value of 1 indicates any detected level of PFAS pollution, otherwise the variable takes a value of 0. The limit of detection was 2 or 4 ppt depending on the analyte (AECOM, 2018). Several independent variables were included in the Probit regression model: number of industrial sites (*#sites*) within each spatial buffer of the wells (0.1 km, 0.5 km, 1 km), well depth in feet (*depth*), the percentage of sites within 1 km of specific industry types thought to be more likely to contribute to contamination (airports, landfills, and electroplaters) (*percentindustry*), and the total number of quarters in which an industrial site had USEPA violations in the past three years¹ (*#violations*). The Probit regression model in Equation 1 was analyzed using IBM SPSS Statistics 26, with statistically significant variables having a *p*-value no greater than 0.10. Results are in sections 2.3.1 and 2.3.2 (IBM Corp., 2019).

1 Other variables, such as classification as a “major” facility, liquid waste dumping permit holders, and percent or number of metal foil facilities were considered in earlier versions of the models but dropped due to few data points or high correlation between variables

3.2.4 Cluster analysis

A negative Local Moran's I Index was performed to identify any spatial correlation between detections of PFAS in wells in relation to each other, separate from industry presence. This analysis indicates spatial outliers, where the data at one location is independent of the data at nearby locations (Anselin, 1995). In this study, spatial outliers indicate that the level of PFAS pollution at one well is independent of the level of PFAS pollution at nearby wells. A positive Local Moran's I Index value indicates spatial clustering, where the data at one location is similar to the data at nearby locations. In this study, spatial clusters indicate that the level of PFAS pollution at one well significantly resembles the levels at nearby wells. Spatial clustering defined by high-high (high values near other high values) and low-low (low values near other high values) clusters. High-high PFAS clusters indicate potential hotspots of PFAS pollution, whereas low-low clusters indicate areas of low pollution levels. Spatial outliers are represented by low-high (low value at one location near high values at nearby locations) and high-low outliers (high value at one location near low values at nearby locations). Local Moran's I results are significant in this study if the p -value is no greater than 0.05. The Index values I_i range from -1 to +1 and are determined using the following equations:

$$I_i = \frac{x_i - \bar{X}}{S_i^2} \sum_{j=1, j \neq i}^n w_{i,j} (x_j - \bar{X}) \quad (2)$$

where x_i is the level of PFAS pollution at well site i , \bar{X} is the mean PFAS level across all wells, and $w_{i,j}$ is the spatial weight between well sites i and j , and

$$S_i^2 = \frac{\sum_{j=1, j \neq i}^n (x_j - \bar{X})^2}{n-1} \quad (3)$$

where n is the total number of well sites with detected levels of PFAS. An index value of -1 indicates negative correlation between positive PFAS detections or an outlier, a value of 0 indicates no correlation, and a value of +1 indicates a positive correlation or cluster.

3.3 Results and Discussion

3.3.1 Industrial and well sites

Using the NAICS codes listed in Table 3, 2696 relevant industry sites were identified in Michigan. Figure 1 shows the number of industrial sites present in each county. Among the well sites included in this study, 107 tested positive for PFAS with an average concentration of 28.794 ppt, whereas 974 sites did not contain PFAS at detectable levels. No identified industrial sites fell within 0.1 km of a well that tested positive for PFAS, and only two industrial sites fell within 0.1 km of any well identified in this study. A total of eight industrial sites were located within 0.5 km of wells that tested positive for PFAS, three of which were landfills. Other industries within half a kilometer of PFAS wells were metal coating, metal foil, plastics manufacturing, paper mill, and oil and grease manufacturing facilities. Table 3.3 summarizes the industry sites found within each radius. Twenty-six industrial sites fall within 1 km of wells that tested positive for PFAS; of these sites, eight were landfills, six were metal foil manufacturing, three were airport sites, two were paper mills, two were plastics manufacturing, one electroplating, one metal coating, one commercial printing, one oil and grease manufacturing, and one miscellaneous textiles facility. The totals for 1 km are inclusive of the sites found within 0.5 km.

Table 3.3: Michigan Industries within defined buffer sizes (0.1,0.5,1.0 km) of drinking water wells with detected PFAS concentrations. For total number of identified industrial sites in Michigan, $n = 2,696^n$

NAICS Code	Industry Classification	Number of facilities within each size buffer zone around contaminated wells		
		0.1 km	0.5 km	1.0 km
313320	Fabric Coating Mills (n = 9)	0	0	0
313310	Textile and Fabric Finishing Mills (n = 4)	0	0	0
336310	Motor Vehicle Gasoline Engine and Engine Parts Manufacturing (n = 48)	0	0	0
324110	Petroleum Refineries (n = 11)	0	0	0
325320	Pesticide and Other Agricultural Chemical Manufacture (n = 10)	0	0	0
325992	Photographic Film, Paper, Plate, and Chemical Manufacture (n = 7)	0	0	0
326112	Plastics Packaging Film and Sheet (including Laminated) Manufacture (n = 9)	0	0	0
325211	Plastics Material and Resin Manufacture (n = 116)	0	1	2
316110	Leather and Hide Tanning and Finishing (n = 7)	0	0	0
322220	Paper Bag and Coated and Treated Paper Manufacture (n = 14)	0	0	0
332813	Electroplating, Plating, Polishing, Anodizing, and Coloring (n = 317)	0	1	2
314110	Carpet and Rug Mills (n = 2)	0	0	0
812310, 812320	Dry Cleaning and Laundry Services (n=133)	0	1	8
325199	All Other Basic Organic Chemical Manufacture (n = 70)	0	0	0

325510	Paint and Coating Manufacture (n = 104)	0	0	0
323111	Commercial Printing (except Screen and Books) (n = 102)	0	0	1
313210	Broadwoven Fabric Mills, Manmade Fibers and Silk (n = 4)	0	0	1
424690	Chemicals and Allied Products, Not Elsewhere Classified (n = 14)	0	0	0
488119	Airports (n = 69)	0	0	3
322121	Paper Mills (n = 33)	0	1	2
332999	Metal Foil and Leaf Manufacture (n = 205)	0	1	6
324191	Lubricating Oils and Greases (n = 46)	0	1	1
562212	Solid Waste Landfill (n = 1373)	0	3	8
928110	Department of Defense Sites (n = 7)	0	0	0
323120	Support Activities for Printing (n = 13)	0	0	0
322219	Sanitary Food Containers, Except Folding (n = 3)	0	0	0
325611	Perfumes, Cosmetics, and other Toilet Preparations (n = 46)	0	0	0
333249	Surgical and Medical Instruments and Apparatus (n = 45)	0	0	0
325612	Specialty Cleaning, Polishing, and Sanitation Preparations (n = 27)	0	0	0
333318	Service Industry Machinery, Not Elsewhere Classified (n = 16)	0	0	0
334413	Semiconductor and Related Device Manufacture (n = 20)	0	0	0
326113	Unsupported Plastics Film and Sheet (n = 19)	0	0	0
314999	Waterproof Outerwear (n = 8)	0	0	0
Total (n = 2696)		0	8	26

^an = number of industries of each code in Michigan. Some sites classified as multiple industries on list and are counted totals for each industry, but once in grand total.

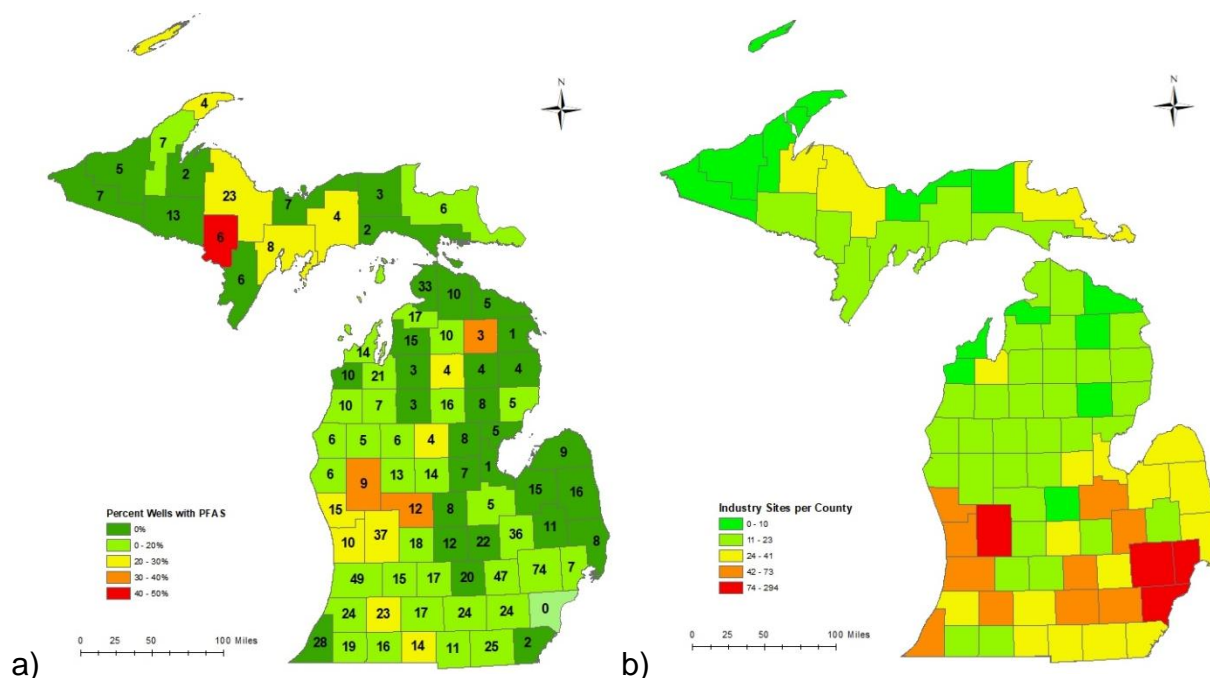


Figure 3.1: (a) Total groundwater wells per county, indicated by the numerical value on each county, and percentage of wells with PFAS in each county as shown by color scale. (b) Number of PFAS industry sites in Michigan by county.

3.3.2 Linking industrial sites to PFAS contamination

We hypothesized that the presence of the selected industries would have significant positive correlations with detections of PFAS in wells, as would the depth of the well, and that greater significance would be attributed to facilities belonging to industries already shown to contribute to PFAS contamination (i.e., airports, landfills, electroplaters) and to major facilities. In addition to likelihood of contamination decreasing with well depth, we also hypothesized that as the depth of the well increased, the likelihood of contamination would further decrease, indicated by well depth squared. Because of the lack of industrial sites within 0.1 km of wells, no Probit model was estimated for that buffer, but the model was estimated using both the number of each industry in the buffers as well as the percentage each industry in the

buffers for 0.5 km and 1.0 km. It should be noted that in the case of the 0.5 km buffers, electroplating was replaced with metal foil due to limited values for metal foil in the 0.5 km buffers. Omnibus Tests determined that our four Probit models were all significant at greater than 99% confidence. The model results are shown in Tables 3.4 and 3.5.

Table 3.4: Probit regression analysis results for 1 km buffers (n = 1081).

Variable	Model 1: 1 km buffer, %sites Wald Chi-Square	B	Sig.	Model 2: 1 km buffer, #sites Wald ChiSquare	B	Sig.
(Intercept)	0.027	0.062	0.869	17.743	0.791	0.000***
Bedrock	0.077	0.033	0.782	0.009	0.011	0.924
Welldepth	27.196	0.007	0.000***	27.190	0.007	0.000***
Welldepthsq	19.258	-9.900*10 ⁻⁶	0.000***	19.148	-9.853*10 ⁻⁶	0.000***
Landcover	1.291	0.155	0.256	1.221	0.150	0.269
Soildrainage	7.758	-0.384	0.005***	7.771	-0.382	0.005***
Percentairport/ Airport	0.036	-0.129	0.850	2.669	-0.603	0.102
Percentlandfill/ Landfill	1.626	0.552	0.202	0.109	0.035	0.741
Percente electroplating/ Electroplating	2.987	2.150	0.084*	1.104	0.549	0.293
Percentallothers/ Allothers	4.924	0.735	0.026**	0.893	-0.172	0.345
FacQtrsWit	0.127	-0.021	0.722	0.101	-0.018	0.751
	Wald Chi-Square	Degrees of Freedom	Sig.	Wald Chi-Square	Degrees of Freedom	Sig.
Omnibus test	44.864	10	0.000	40.760	10	0.000
Observations	1081					

*, **, *** indicates statistical significance at p≤0.10, p≤0.05, and p≤0.01 respectively

Table 3.5: Probit regression analysis results for 0.5 km buffers (n = 1081).

Variable	Model 3: 0.5 km buffer, % sites Wald Chi-Square	B	Sig.	Model 4: 0.5 km buffer, #sites Wald Chi-Square	B	Sig.
(Intercept)	18.050	0.793	0.000***	17.973	0.792	0.000***
Bedrock	0.104	0.038	0.747	0.100	0.037	0.752
Welldepth	26.119	0.007	0.000***	26.106	0.007	0.000***
Welldepthsq	18.241	-9.589*10 ⁻⁶	0.000***	18.239	-9.596*10 ⁻⁶	0.000***
Landcover	1.054	0.139	0.305	1.062	0.139	0.303
Soildrainage	7.437	-0.371	0.006***	7.508	-0.373	0.006***
Percentlandfill/ Landfill	0.421	-0.310	0.516	0.151	-0.107	0.697
Percentmetalfoil/ Metalfoil	0.524	-0.456	0.469	0.520	-0.454	0.471
FacQtrsWit	0.937	-0.062	0.333	0.932	-0.062	0.334
	Wald Chi-Square	Degrees of Freedom	Sig.	Wald Chi-Square	Degrees of Freedom	Sig.
Omnibus test	37.040	8	0.000	36.783	8	0.000
Observations	1081					

*, **, *** indicates statistical significance at $p \leq 0.10$, $p \leq 0.05$, and $p \leq 0.01$ respectively

3.3.3 Probit models, 1 km

The 1.0 km buffer models both showed that well depth, well depth squared, and well-drained soil were significantly likely to increase the probability of PFAS detection at greater than 99% confidence level (Table 4). In both cases, well depth positively affected the likelihood of detection, while well depth squared had a negative effect. This indicates that the likelihood of PFAS detection increases with deeper wells, but that the rate of increase declines as depth increases. The positive effect of greater well depth on the probability of PFAS detection runs counter to our hypothesized relationship. One explanation for this could be that wells in vulnerable areas are dug deeper as a

preventative measure, but further study is necessary to confirm this. There was a positive relationship between percentage of electroplaters, along with percentage of all other industry and the likelihood of PFAS detection in the 1.0 km model, which corroborates our hypothesis.

The relatively high number of metal foil sites (compared to the other industries included in this study) within 1 km of positive-detect wells is surprising. Although this industry appeared on a list of PFAS-using industries created by the Minnesota Pollution Control Agency (MPCA), it has not yet become an industry of focus across literature examining PFAS pollution. Additional research on metal foil practices could help confirm if this industry contributes significantly to PFAS contamination in wells near facilities.

3.3.4 Probit models, 0.5 km

For both Probit models estimated at the buffer size of 0.5 km, well depth, well depth squared, and well-drained soil showed significant effects on likelihood to detect positive PFAS levels (Table 5). Similar the 1.0 km models, well depth and well-drained soil had a positive effect while well depth squared had a negative effect on the probability of detection. It appears based on these analyses that more permeable soil near a well is more important than presence of specific industry types when predicting PFAS contamination in wells. Despite the higher numerical value of metal foil sites within the 0.5 km buffers compared to other sites, the number and percent metal foil sites did not prove significant in this model. This is likely due to the number of metal foil sites still being low, despite being higher than other industry types. Percent and number of landfill sites were also not significant at this level, along with bedrock type, land cover, and quarters with violations.

3.3.5 Cluster analysis

A local Moran's I test examining clusters and outliers of high versus low concentrations of PFAS within wells that tested positive showed eight low-high outliers, three high-high clusters, and one high-low outlier all concentrated in southwest Michigan. A map of clusters and outliers can be seen in Figure 2. It is interesting to note that the high-high clusters and both types of outliers are predominantly located in Kalamazoo and Allegan counties, both of which have relatively high numbers of industry sites compared to other counties. About half of the industrial sites in these counties were landfills, which corresponds to the percentage of landfills compared to total industrial sites in the state as a whole. In these two counties, however, only one of the landfills (1.6% of total landfills) was flagged as actively operating, whereas more than 4% of the state's total landfills were labeled active. A higher percentage of inactive landfills may indicate older landfills. Because landfills were not required to be lined until the Resource Conservation and Recovery Act of 1976, older landfills are more likely to cause leaching of contaminants into groundwater (U.S.Congress, 1976). Thus, a higher proportion of inactive landfills in Kalamazoo and Allegan counties may explain the clustering found in these counties from the Moran's I test. The presence of outliers, or wells with high concentrations having a significant number of wells with low concentrations nearby and vice versa, could be explained by landfill leachate permeating wells to different degrees. Further study of wells in this region, the groundwater flow near these wells, and their proximity to landfills could help explain the outliers found in this study. In addition to the clusters and outliers in southwest Michigan, ten low-low clusters were identified throughout the state. All other clusters and outliers determined using Local Moran's I

have *p*-values exceeding the 0.05 threshold, and are not statistically significant to include in the study. Table 7 identifies the location of statistically significant Moran's I results, the Index values, and Z-scores.

Table 3.6: Significant clusters and outliers identified using Local Moran's I for PFAS clusters in Michigan (detected wells only).

Well Location City/Town	Cluster/Outlier Type	Moran's I index value	Z-score	p-value ¹
Plainwell	High-high	0.000036	1.390	0.03
Kalamazoo	High-high	0.00014	2.813	0.012
Plainwell	High-high	0.000105	1.684	0.05
Parchment	High-low	-0.0009	1.842	0.048
Houghton	Low-low	0.000002	0.272	0.004
Sherman Township	Low-low	0.000002	0.314	0.02
Richmond Township	Low-low	0.023118	0.140	0.01
Richmond Township	Low-low	0.023118	0.174	0.01
Marquette	Low-low	0.00003	0.190	0.01
KL Sawyer AFB	Low-low	0.000004	0.407	0.002
Escanaba	Low-low	0.000004	0.321	0.018
Gladstone	Low-low	0.000004	0.363	0.006
Kawkawlin	Low-low	0.000008	0.263	0.016
Northport	Low-low	0.000003	0.227	0.046
Parkwood Village	Low-low	0.000006	0.706	0.028
Climax	Low-high	-0.000058	-2.904	0.032
Delton	Low-high	-0.000034	-2.438	0.046
Gun Plain Township	Low-high	-0.000124	-2.904	0.032
Lockport Township	Low-high	-0.00003	-1.890	0.044
Otsego	Low-high	-0.000061	-1.594	0.042
Portage	Low-high	-0.000058	-3.485	0.012
Kalamazoo	Low-high	-0.000049	-2.159	0.048

Kalamazoo	Low-high	-0.000146	-3.898	0.032
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¹Threshold for significance was defined at p-values of 0.05 or below.

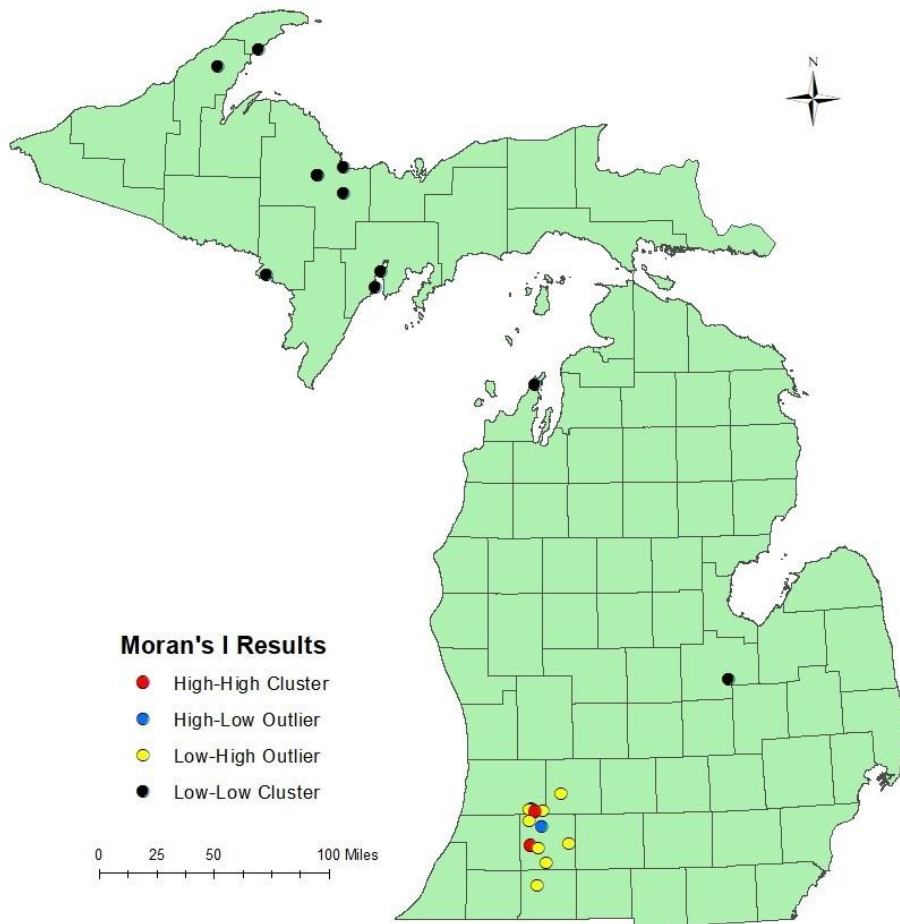


Figure 3.2: Local Moran's I for PFAS clusters in Michigan (detected wells only).

3.4 Conclusions

Overall, this study underscores the difficulty of tying industrial presence to PFAS contamination in drinking water wells as a means of targeting groundwater testing at a landscape scale. Spatially, the Moran's I results pointed to landfills as a possible smoking gun for PFAS detection, due to a high portion of clusters coinciding with counties that host a high number of inactive landfills, but the more detailed, site-specific

Probit model did not show significance between landfill presence and positive PFAS detections in wells. Future research could investigate the relationship between age of landfills and detections of PFAS, as this data set did not include landfill age. Although multiple variables were investigated in our predictive probit models to predict PFAS well contamination, the only factors that proved significant in all models were well depth, well depth squared, and soil type. The positive correlation found between well depth and PFAS detection contradicted our hypothesis, and a possible explanation for this is wells being dug deeper in vulnerable areas. The recalcitrance of PFAS prevents them from breaking down, and this allows them to eventually reach greater depths. It was found in one of the 1.0 km models that the higher the percentage of electroplating facilities within 1 km of the well compared to total industries studied, the more likely a well was contaminated with PFAS. Based on these results, it can be stated that wells constructed in well-drained soil and with electroplating facilities within a kilometer are likelier to be contaminated with PFAS. This information can be useful for identifying wells to prioritize for testing, but additional predictive parameters would be helpful for more accurate targeting. Future research in this area should consider additional parameters that may lead to trends in PFAS well contamination, such as slope, elevation, and groundwater flow direction surrounding wells.

Chapter 4: Implications for PFAS Contamination in Biosolids End of Life Disposal

4.1 Introduction

The prevalence of PFAS in waste products has led to concern regarding their presence in municipal biosolids, and studies have shown that sewage sludge does serve as a sink for PFAS compounds (Higgins et al., 2005). Concentrations of PFASs in sewage sludge tend to fall in the parts per billion (ppb) range, three orders of magnitude above recommended levels in drinking water (Arvaniti and Stasinakis, 2015; Zhang et al., 2018). The USEPA estimates that several million dry metric tons of biosolids are produced annually in the United States, and more than half of these biosolids are applied to land for uses including agriculture, horticulture, and forestry (USEPA, 2002). Thus the presence of PFAS in biosolids and the widespread use of biosolids on land, including land used for food production, has led to concern regarding the contribution of land-applied biosolids to PFAS contamination in the environment.

Several studies have begun to investigate the implications of land-applying biosolids contaminated with PFAS. For example, Sepulvado et al (2011) found a linear relationship between the PFAS concentration in soils and the loading rate of biosolids, and that PFAS were present in soils at 120 cm, the maximum depth analyzed (Sepulvado et al., 2011). They also found a higher transport potential for shorter-chain PFAS compounds, which is in agreement with a later study that saw this trend occur in PFASs with chain lengths greater than four carbons (Guelfo and Higgins, 2013). Another study looked at surface and groundwater PFAS concentrations in the vicinity of fields that received biosolids from a wastewater treatment plant (WWTP) that takes in

waste from a fluorochemical production facility, and found that 82% of water samples contained at least one PFAS compound and that 22% had concentrations exceeding recommended USEPA limits (Lindstrom et al., 2011a). It should be noted that the recommended limits at the time Lindstrom et al performed that study were significantly higher (200 ppt for PFOS and 400 ppt for PFOA) compared to current standards of 70 ppt. In addition to use as fertilizer, biosolids are disposed of via incineration at some treatment plants. There is concern that this process may volatilize PFAS in the biosolids rather than destroy them.

While a few studies have investigated PFAS sorption and desorption in soils, this work is the first of our knowledge to investigate desorption of PFAS from contaminated biosolids, and tested for a wider suite of PFAS chemicals than prior studies. The goal of this chapter was to provide insight into the implications PFAS contamination in municipal biosolids. In order to study PFAS behavior in biosolids, a batch experiment was performed using biosolids obtained from three different WWTPs. Data obtained from batch experiments was then used to calculate desorption kinetics from biosolids into water in order to begin to understand the mechanisms of transport of PFAS compounds from biosolids to soil and groundwater. In addition, a small incineration experiment was conducted to provide a first look at if biosolids incineration contributes to airborne PFAS pollution.

4.2 Methods

4.2.1 Biosolids Sampling and Preparation

Biosolids samples were gathered in conjunction with the Wisconsin State Lab of Hygiene's (WISLH) sampling efforts during the summer of 2020. Wet cake was

gathered from three different sewage treatment plants and kept refrigerated prior to use.

The solids were dried in a drying oven at 100° C for 24 hours and percent moisture calculated. Dried solids were kept in covered beakers at room temperature until use in batch and incineration experiments. Initial PFAS concentrations of the biosolids were determined at WISLH and reported based on dry weight of the samples. Table 4.1 describes the wastewater treatment facilities where each of the solids were obtained.

Table 4.2 shows the initial PFAS concentrations in the biosolids.

Table 4.1: Information about the wastewater treatment facilities that provided biosolids for this project, received from representatives from the facility (S1) or the WISLH (S2, S3). Facilities wish to remain anonymous so names are withheld.

Facility	Approximate Population Served	Daily Flow (MGD)	Input Breakdown	Notes
S1	470,000	130	~13% Industrial, ~37% Commercial, ~50% Residential	Solids are combined from two facility sources
S2	27,000	2.6	~10% Industrial/Commercial, ~90% Residential	Industrial input is primarily brewery and vegetable processing waste
S3	75,000	7.8	~10% Industrial/Commercial, ~90% Residential	Industrial input contains wide variety of sources

Table 4.2: Initial concentrations of PFAS in the three facilities' biosolids, in ppb based on dry weight. Concentrations were reported as wet weight for S3, so the S3 values in this table have been corrected based on the calculated percent moisture of the S3 solids (94.7%).

Compound	Full Name	ppb		
		S1	S2	S3
PFPeA	Pefluoropentanoic acid	6.84	16.2	1.11
PFPeS	Perfluoropentane sulfonate	1.17*,**	ND	ND
PFHxA	Perfluorohexanoic acid	36.1	1.51*	1.56**
6:2 FTSA	6:2 Fluorotelomer sulfonate	14.2	ND	ND
PFOS	Perfluorooctane sulfonate	31.6	121	9.74
N-MeFOSE	N-methyl perfluorooctane sulfonamidoethanol	2.04	18.3	9.55

10:2 FTSA	10:2 Fluorotelomer sulfonate	5.09	4.39	1.54
N-MeFOSAA	N-Methyl perfluorooctane sulfonamidoacetic acid	10.3	34.2	20.0
N-EtFOSAA	N-Ethyl perfluorooctane sulfonamidoacetic acid	5.86	14.6	10.0
PFOA	Perfluorooctanoic acid	3.69	2.11	0.87*
PFBA	Perfluorobutanoic acid	ND	23.1**	ND
PFHxS	Perfluorohexane sulfonate	ND	1.13*	1.03
PFNA	Perfluorononanoic acid	.931*	1.52*	0.57
8:2 FTSA	8:2 Fluorotelomer sulfonate	3.45	1.94	0.46*,**
PFNS	Perfluorononansulfonic acid	ND	.645*	ND
PFDA	Perfluorodecanoic acid	2.31	4.34	4.15
FOSA	Perfluorooctane sulfonamide	.824*	3.2	3.70
PFUnA	Perfluoroundecanoic acid	.647*	1.71*	0.85
PFDoA	Perfluorododecanoic acid	1.21*	2.08	1.91
N-EtFOSE	N-ethyl perfluorooctane sulfonamidoethanol	1.27*	5.18	2.15
PFTeDA	Perfluorotetradecanoic acid	ND	.827*	0.63
PFHxDA	Perfluorohexadecanoic acid	ND	.597*,**	0.47**
PFTTrDA	Perfluorotridecanoic acid	ND	ND	0.39*
PFDS	Perfluorodecanesulfonic acid	.730*	ND	2.28
PFHpA	Perfluoroheptanoic acid	5.06	ND	ND

*Compound detected between LOD and LOQ. Value is an estimate.

**Interference or internal standard recovery flagged

4.2.2 Centrifuge Tests

Samples required centrifugation to be sure that any PFAS chemicals in the water were not due to their binding to suspended particles, but were present in the water itself. In order to determine an appropriate time and rpm for which to centrifuge samples, several tests were run using commercially-purchased biosolids. Fifteen grams of biosolids particles were shaken in 150 mL of Type 1 ultra-pure water (E-pure water) for three hours at 150 rpm, then centrifuged at different times and rpms in order to achieve at least 90% reduction in turbidity. Table 4.3 shows the first two tests of 3000 rpm for 15 minutes and 10,000 rpm for two minutes, which did not provide sufficient reduction in turbidity. The time was then increased to one hour at 10,000 rpm and samples were tested in a Zetasizer (Malvern Nano-ZS) for particle size before and after as well. Table

4.4 shows the results of this test, which proved sufficient for reduction in turbidity and particle size.

Table 4.3: Results of first test to determine appropriate centrifuge time and rpm for batch experiment water samples. “Slow” indicates a rpm of 3,000 for 15 minutes and fast indicates a rpm of 10,000 for 2 minutes. Biosolids were shaken at 150 rpm in DI water prior to centrifugation to mimic batch experiment conditions. Each test was done in triplicate.

Sample	Mass Biosolids	V water	Unit: NTU		% Reduction
			Turbidity Before	Turbidity After	
Slow 1	15.0007 g	150 mL	5.3	1.07	79.8%
Slow 2	14.9847 g	150 mL	5.76	1.55	73.1%
Slow 3	15.0181 g	150 mL	6.78	2.24	67.0%
Fast 1	15.0080 g	150 mL	4.04	0.94	76.7%
Fast 2	15.0112 g	150 mL	3.51	1.09	68.9%
Fast 3	15.0007 g	150 mL	6.23	1.39	77.7%

Table 4.4: Turbidity and particle sizes following centrifugation at 10,000 rpm for one hour. Test done in triplicate.

Sample	Mass Biosolids	V water	Unit: NTU			Unit: nm	
			Turbidity Before	Turbidity After	% Reduction	Avg Size Before	Avg Size After
Rep 1	15.0057 g	150 mL	10.68	0.74	93.1%	1592.667	45.923
Rep 2	14.9985 g	150 mL	8.45	0.79	90.7%	1830.667	149.627
Rep 3	15.0004 g	150 mL	9.82	0.75	92.4%	1763.333	125.700
			Averages	0.76	92.0%	1728.889	107.083

4.2.3 Batch Desorption Experiment

A batch experiment was conducted with all three biosolids, each in triplicate. Dried biosolids were placed in a beaker with E-pure water, covered using Parafilm M, and shaken at 150 rpm. The ratio of dried biosolids to water was 1:10 by mass. Aliquots were taken at 1, 3, 12, 24, and 48 hours and at two weeks (336 hours). All aliquots were run in separate beakers so as not to disrupt the biosolids to water ratio. After being removed from the shaker, water from the beakers were transferred to polycarbonate

centrifuge bottles and centrifuged at 10,000 rpm for one hour. The water samples were then diluted by ten in sample bottle provided by the WISLH and kept below 6° C until they were transported to WISLH for analysis. The biosolids from the end of the two weeks were also sent for analysis. The E-pure water from the lab was analyzed as well in order to identify any PFAS resulting from the water.

4.2.4 Calculation of Sorption Constants and Retardation Factors

Using the data from the batch experiment, organic carbon sorption constants were calculated for the PFAS that were present. The constants were calculated using the following equation:

$$K_d = \frac{C_s}{C_w} \quad (\text{Equation 4.1})$$

where K_d is the desorption constant for the given solid, C_s is the final concentration of the PFAS compound in the solids at the end of the two weeks, and C_w is the concentration found in the water at the end of two weeks. The K_d value was then corrected for the fraction of organic carbon in the biosolids to get the organic carbon sorption constant (K_{oc}). For S1, which was used in the incineration, the fraction organic carbon was calculated (.696), whereas for the other two solids an estimated value of 0.7 was used.

Based on the K_{oc} values calculated from the batch experiment, retardation factors (R_f s) were then calculated for each compound in four different soil scenarios. The R_f accounts for factors beyond water velocity that control (slow) movement of a contaminant through soil, from factors such as sorption, reaction, and a compound breaking down. A high R_f value indicates slower movement of a contaminant through

soil. Because PFAS are not reactive and do not readily break down, the R_f s in this scenario are driven by sorption to soil. The three characteristics of soil that affect a compounds R_f are the soil's f_{oc} , bulk density, and porosity. Using a high f_{oc} value of 0.05 and a low f_{oc} value of 0.007, R_f values were calculated in a “worst case” and “best case” scenario of bulk density and porosity for both f_{oc} values. Typical soil bulk densities range from 1.6-2.1 g/cm³ and soil porosity from 0.2-0.4. The higher the bulk density and lower the porosity of a soil, the higher the retardation factor. Thus, the “best case” scenario for each f_{oc} used bulk density of 2.1 g/cm³ and porosity of 0.2, and the “worst case” used bulk density of 1.6 g/cm³ and porosity of 0.4. The equation for calculating R_f is shown below:

$$R_f = 1 + \frac{\rho_b}{n} K_d \quad (\text{Equation 4.2})$$

where ρ_b is the bulk density of the soil and n is the porosity of the soil.

4.2.5 Incineration Experiment

The first-look incineration experiment consisted of one blank run and one biosolids sample. For each of these runs, a benchtop furnace was heated to 800° C and that temperature was maintained for four hours. In order to collect exhaust air, a high-density polyethylene (HDPE) funnel was positioned above the exhaust port. The funnel was connected to HDPE tubing, sealed with insulation tape, which then attached to the CORBO sampling device provided by Eurofins TestAmerica. Inside the CORBO sampler is a resin that is designed to capture PFAS chemicals that pass through in the exhaust. The sampler was attached on the other end to an SKC Inc. Airchek Sampler air pump (Model 224-44XR). This setup, used for both the blank (furnace run with no

sample inside) and the sample, is shown in Figure 4.1a. Prior to attaching to the funnel and tubing, the air pump was calibrated to a flow rate of ten mL/min (with the CORBO attached to account for experimental conditions as much as possible)—see Figure 4.2.

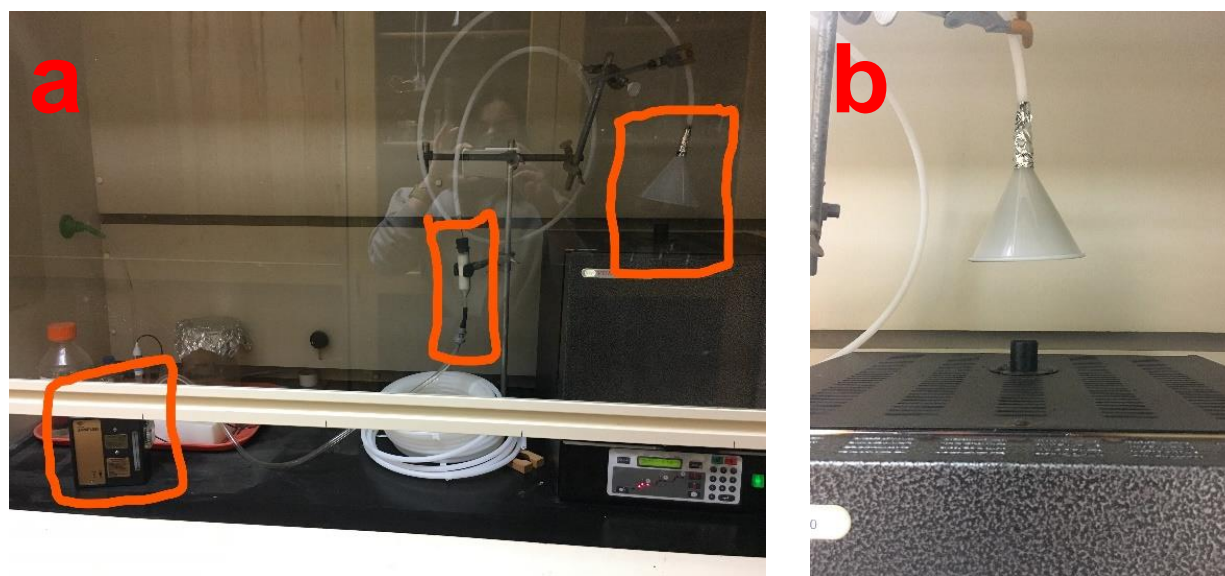


Figure 4.1: Photos of (a) Experimental setup with air pump, CORBO sampler, and funnel (respectively from left to right) outlined in orange; (b) a closer view of the funnel, after adjusting slightly higher to prevent melting



Figure 4.2: Photo of air pump and CORBO attached to calibration device, to achieve a flow rate of 10 mL/min. The pump was calibrated before both the blank and the sample run.

During the blank run, a small hole began to melt in the funnel while the furnace was still heating. The setup was adjusted so that the funnel was slightly higher (~7-8cm above port, as shown in Figure 4.1b) and no additional melting occurred. After the four hours were complete, the CORBO device was removed, capped, and placed in a cooler in a fridge. The furnace was allowed to cool overnight between the blank run and the sample run. On the following day, the funnel was replaced with an identical HDPE funnel for the biosolids sample run. The air pump was recalibrated on the second day prior to heating the biosolids sample in the furnace. For the biosolids run, 12.04g of dried solids were placed in a crucible in the furnace, enough to fill the crucible about halfway (Photo 3a). The sample was then heated to 800° C and left there for four hours as with the blank. After the experiment was complete, the second CORBO was removed and capped. The two CORBOS were packed on ice in a cooler that was shipped overnight to Eurofins for testing. Eurofins used a modified version of USEPA Method 537 to test for PFAS (USEPA, 2009). Their version tests for 39 different PFAS compounds, listed in Appendix B. The incinerated remains of the biosolids were brought to the WISLH for analysis.

4.3 Results

4.3.1 Batch Desorption Experiment

Although prior research had indicated that equilibrium was reached by 24 hours in batch experiments, our findings were inconsistent in this regard (Sepulvado et al., 2011). For S1, only two out of six compounds with results in more than one replicate clearly reached equilibrium, whereas the other four rose in concentration between 48 hours and two weeks. Two out of those four, however appeared to stop increasing and often

even begin to decrease in concentration by 48 hours, then had concentrations increase by the two-week aliquot. The first replicate for S1 was done as a test batch prior to changing the methodology to dilute the samples, so in many cases the results were less reliable due to the high concentrations interfering with the equipment. In addition, many compounds that were identified in S1 were not found in other replicates due to dilution; results for those compounds are shown in Appendix B.

In the case of the S2 solids, all six compounds had begun to decrease in concentration from 24 to 48 hours only to increase again at two weeks. For S3, however, seven out of ten clearly reached equilibrium. Many compounds in the S3 water samples also showed the same trend of decreasing at the 48-hour mark. Compounds detected only in some aliquots or replicates for S2 and S3 are not graphed but raw data can be found in Appendix B. Figures 4.3-4.7 show the results for PFHxA, PFHpA, PFOA, PFHxS, and PFOS, respectively. Results for the remaining compounds, which were not found in all three of the solids, are shown in Appendix B.

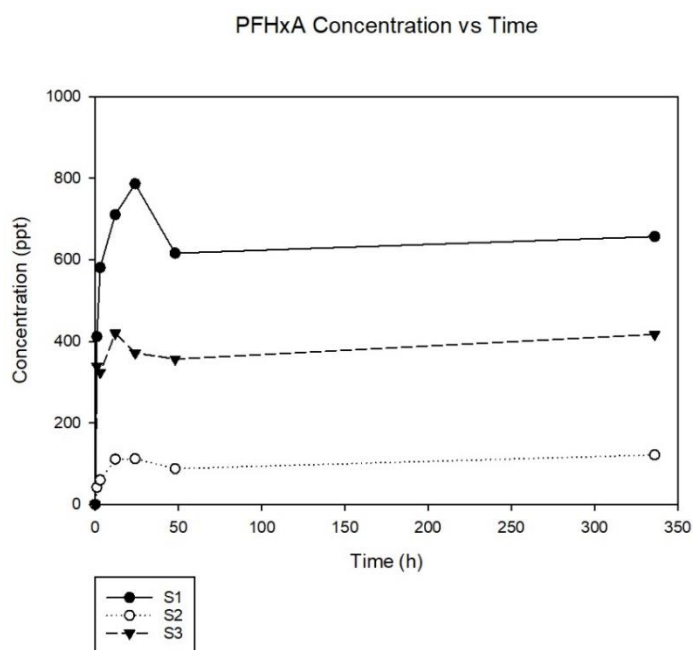


Figure 4.3: PFHxA concentration versus time in S1, S2, and S3.

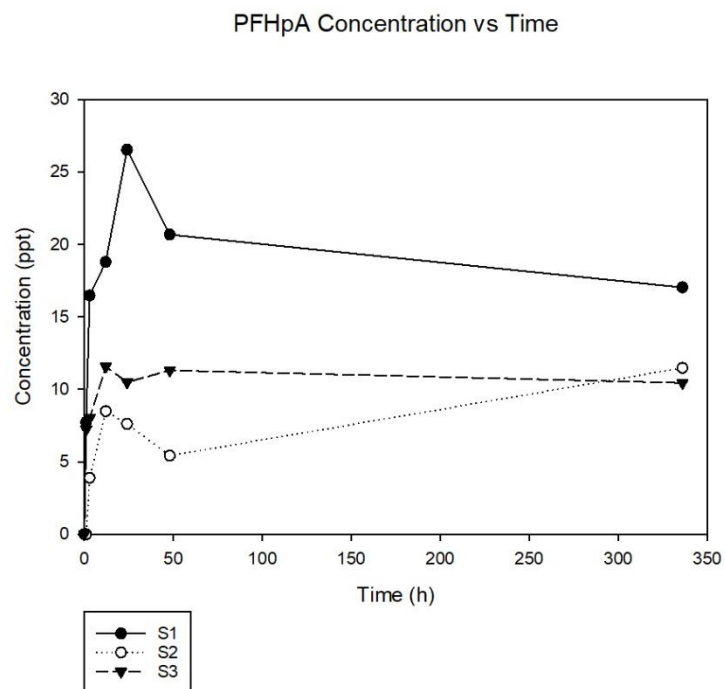


Figure 4.4: PFHpA concentration versus time in S1, S2, and S3.

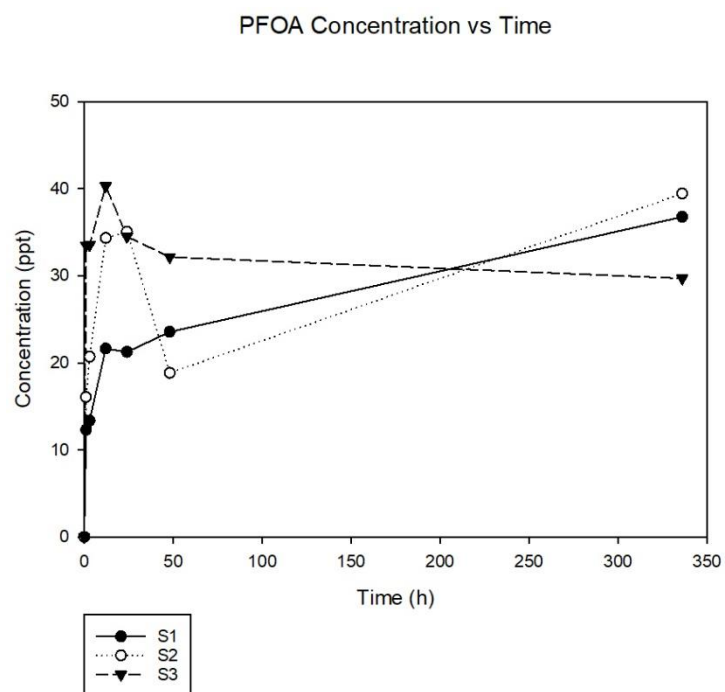


Figure 4.5: PFOA concentration versus time in S1, S2, and S3.

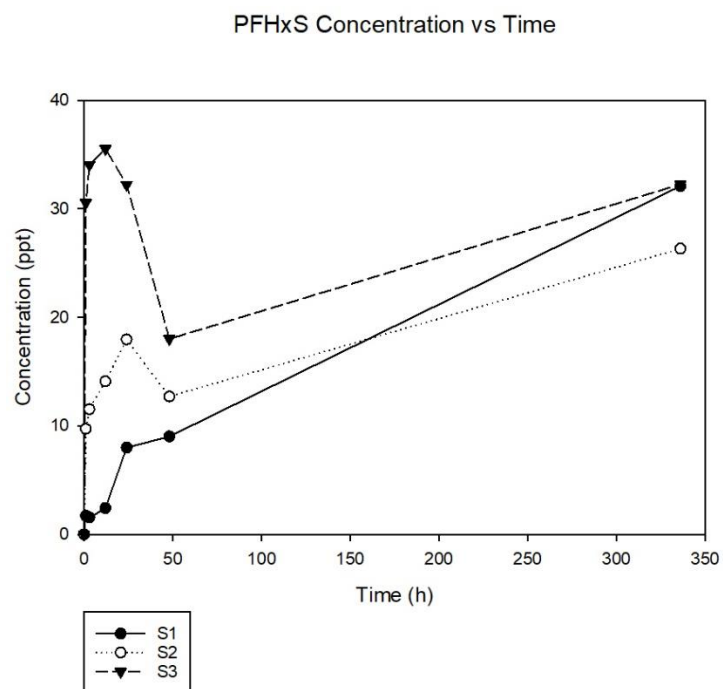


Figure 4.6: PFHxS concentration versus time in S1, S2, and S3.

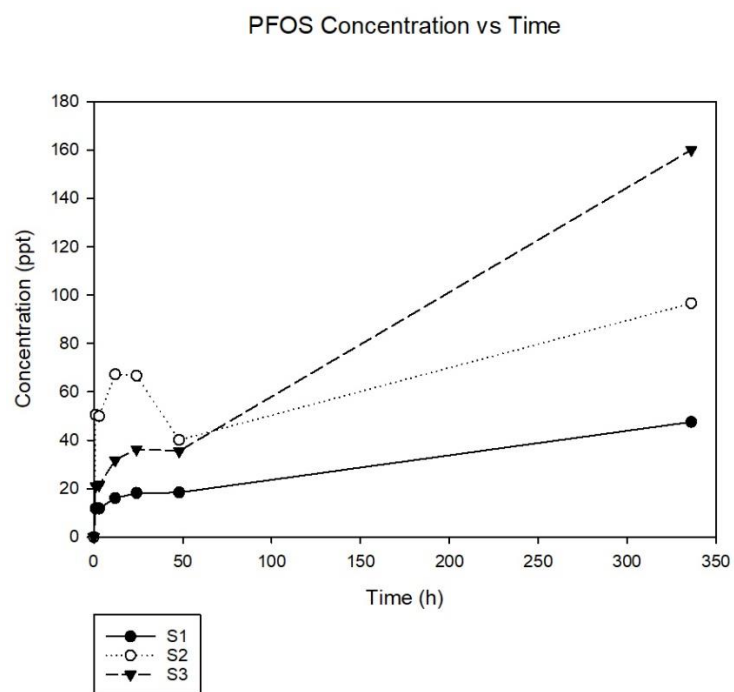


Figure 4.7: PFOS concentration versus time in S1, S2, and S3.

4.3.2 Calculation of Sorption Constants and Retardation Factors

Log K_{oc} values were able to be calculated for four compounds in S1 and S2, and nine compounds in S3. The average log K_{oc} values calculated for the compounds found in the batch experiment, along with their standard deviations, are shown in Table 4.5 below.

Table 4.5: Average Log K_{oc} values calculated from batch results.

Compound	S1 Average	Standard Deviation	S2 Average	Standard Deviation	S3 Average	Standard Deviation	Average
PFHxA	1.24	±0.53	0.89	±0.12	0.962	±0.09	1.03
PFOA	1.75	±0.24	1.76	±0.17	1.97	±0.05	1.83
PFOS	2.95	±0.34	3.14	±0.11	3.17	±0.03	3.09
6:2 FTSA	1.78	±0.17			1.99	±0.10	1.89
PFHxS			1.46	±0.11	1.80	±0.20	1.63
PFDA					3.19	±0.03	3.19
N-MeFOSAA					3.31	±0.12	3.31
N-EtFOSAA					3.42	±0.09	3.42

The R_f s calculated for the different soil scenarios range from 1.30 for PFHxA in the low f_{oc} worst-case scenario to 1,382 for N-EtFOSAA in the high f_{oc} best-case scenario and are shown in Table 4.6.

Table 4.6: Calculation of retardation factors (R_f s) for each PFAS compound in different soil scenarios.

Compound	Average log K_{oc}	K_{oc}	f_{oc}	K_d	R_f Best Case	R_f Worst Case
PFHxA	1.03	10.7	0.007	0.075	1.79	1.30
PFOA	1.83	67.1	0.007	0.470	5.93	2.88
PFOS	3.09	1221	0.007	8.5	91	35.2
6:2 FTSA	1.89	76.7	0.007	0.537	6.64	3.15
PFHxS	1.63	42.7	0.007	0.299	4.14	2.19
PFDA	3.19	1549	0.007	10.8	115	44.4
N-MeFOSAA	3.31	2042	0.007	14.3	151	58.2
N-EtFOSAA	3.42	2630	0.007	18.4	194	75

PFHxA	1.03	10.7	0.05	0.537	6.63	3.15
PFOA	1.83	67.1	0.05	3.35	36.2	14.4
PFOS	3.09	1221	0.05	61.0	642	245
6:2 FTSA	1.89	76.7	0.05	3.84	41.3	16.3
PFHxS	1.63	42.7	0.05	2.13	23.4	9.5
PFDA	3.19	1549	0.05	77.4	814	311
N-MeFOSAA	3.31	2042	0.05	102	1073	409
N-EtFOSAA	3.42	2630	0.05	132	1382	527

4.3.3 Incineration Experiment

After heating, the mass of the biosolids ash (Figure 4.6b) was 3.66g. Results from Eurofins were received via email on 1/25/2020. A summary of the PFAS compounds found in the biosolids as well as the incineration exhaust is shown in Table 4.7. For the biosolids, only concentrations above the limit of quantification were included. It was noted by Eurofins that all the PFAS found in the exhaust, blank or sample, were below the limit of quantification (but above the level of detection) so the amounts found are estimated. The lab control standard for N-MeFOSE was flagged as high biased. The incinerated solids were found to contain almost no PFAS. Thus, either the PFAS present in the solids prior to incineration were broken down into byproducts or the exhaust collection was largely unsuccessful. Unfortunately, because we were not able to analyze the exhaust for possible breakdown products, it is unclear based on this experiment if the PFAS were destroyed or simply not captured. Prior studies, however, have indicated that >99% of PFAS are destroyed at temperatures of 600C, which supports the possibility that the PFAS in this experiment were broken down (Kucharzyk et al., 2017).

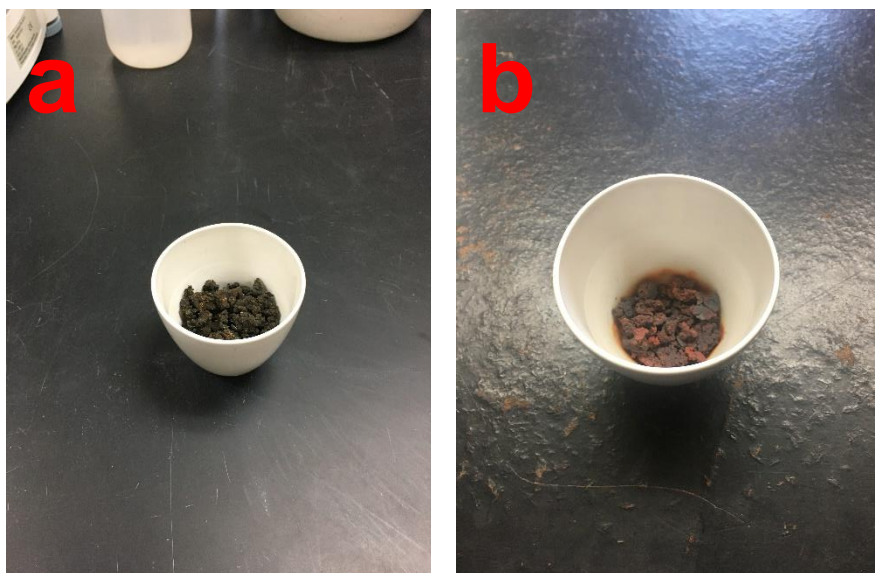


Figure 4.8: (a) Dried biosolids in crucible prior to incineration: mass 12.04 g; (b) remaining ash of biosolids sample after incineration: mass 3.66 g.

Table 4.7: PFAS concentrations found in the biosolids used in the incineration experiment and in the furnace exhaust from the blank run and the biosolids run. The units of concentration are ng/g, which is equivalent to ppb.

Compound*	Concentration in Solids, Initial (ng/g)	Total Amount (ng)	Total in Exhaust (ng)	Total in Blank (ng)	Concentration in Incinerated Solids (ng/g)	Total Amount (ng)	Mass Lost (ng)
PFPeA	6.840	82.354	-	-	-	-	82.354
PFHxA	36.100	434.644	0.309	-	0.218	0.798	433.537
6:2 FTSA	14.200	170.968	-	-	-	-	170.968
PFOS	31.600	380.464	-	-	-	-	380.464
N-MeFOSE	2.040	24.562	4.38	16.5	-	-	24.562
10:2 FTSA	5.090	61.284	-	-	-	-	61.284
N-MeFOSAA	10.300	124.012	-	-	-	-	124.012
N-EtFOSAA	5.860	70.554	-	-	-	-	70.554
PFOA	3.690	44.428	0.417	0.247	0.134	0.490	43.767
PFHpA	5.06	60.922	0.448	-	-	-	60.474
PFDA	2.310	27.812	-	-	-	-	27.812
8:2 FTSA	3.450	41.538	-	-	-	-	41.538

*See Table 4.2 for compounds' full names

4.4 Discussion

4.4.1 Batch Experiment

The results of the batch experiment show a strange phenomenon where, in most cases, the concentration of the compound decreased from 24 to 48 hours rather than continuing to increase at a slower rate as time went on. The proposed explanation for this is, due to the process of drying the solids from wet sludge, the clumps that formed were very concentrated with PFAS on the outer surface area. Thus, a high concentration of the PFAS was released at the outset, but as the clumps broke into smaller pieces during the time on the shaker, more sites on the inner part of the clumps became available for binding, so some of the PFAS were resorbed by 48 hours before reaching final equilibrium. It would be interesting to have had additional aliquots between 48 hours and two weeks to identify any other anomalies, or to run the same experiment after having ground the biosolids to uniform particle sizes to see if the same drop is observed at 48 hours.

4.4.2 Calculation of Sorption Constants and Retardation Factors

The K_{oc} values calculated from the batch experiment results match reasonably well with prior studies that have investigated sorption of PFAS. In addition, we were able to calculate K_{oc} for 6:2 FTSA, which no prior study to our knowledge has done thus far. Table 4.7 shows the average K_{oc} values calculated in this study alongside values calculated in previous studies.

Table 4.8: Comparison of K_{oc} values calculated in this study to prior studies on PFAS sorption.

Compound	Schulz Average	Standard Deviation	Guelfo 2013	McGuire 2013	Sepulvado 2011	Higgins & Luthy 2006	Average
PFHxA	1.03	±0.18	1.31	2.06	1.91		1.76
PFOA	1.83	±0.12	1.89	2.22	2.31	2.06	2.12

PFOS	3.09	±0.12	2.80	3.14	3.34	2.57	2.96
6:2 FTSA	1.89	±0.15					
PFHxS	1.63	±0.24	2.05	2.28	2.70		2.34
PFDA	3.19	±0.03	2.96				2.96
N-MeFOSAA	3.31	±0.12				3.11	3.11
N-EtFOSAA	3.42	±0.09				3.23	3.23

In addition to lining up well with prior research, our values follow expected trends in chain length. Generally, with PFAS, the longer-chain compounds have higher K_{oc} values than shorter-chain compounds with the same functional group due to longer carbon chains contributing to higher hydrophobicity. Interestingly, one study found that this trend reverses with PFAS of 3-4 carbons in length, because with the very short carbon chains hydrophobic interactions no longer dominate sorption and clay sorption takes over (Guelfo and Higgins, 2013). We did not find compounds this short in the water in our study, however, and were therefore unable to confirm these results. Figure 4.7 indicates the relationships between chain length and log K_{oc} values.

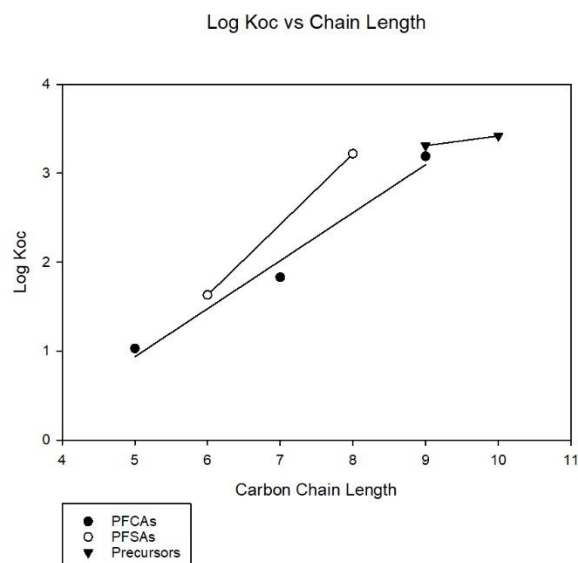


Figure 4.9: Calculated K_{oc} value versus chain length within each family of PFAS studied (PFCAs, PFSA, and precursors), along with trend lines. Precursors in this figure include N-MeFOSAA and N-EtFOSAA.

The calculated R_f values show a wide range of retardation between the different PFAS compounds and soil scenarios. Unsurprisingly, N-MeFOSAA and N-EtFOSAA have very high retardation due to their dual carbon chains and generally large size. In the worst-case scenario for low f_{oc} , low bulk density, and low porosity, several compounds still had R_f s above 30, indicating that the implications for the soil are more pronounced than for the groundwater at biosolids application sites, as the compounds present in this study show a propensity for sorbing to soil rather than remaining in the water that passes through. In addition, a rainfall event is unlikely to last more than a few hours, meaning that the contaminants wouldn't be present in the water at such high levels as were found at the 2-week mark in our study, leading to even less danger of major contamination events in groundwater wells near biosolids application fields. Testing wells near fields that receive biosolids would confirm these suggestions.

4.4.3 Incineration Experiment

Overall, very few PFAS compounds were found in the exhaust from the incineration experiment. The results for N-MeFOSE showing a higher amount of the compound in the blank than the sample is questionable, but that compound's results had been flagged as high biased based on the lab standard. Looking at the other compounds found in the exhaust, the amounts were far less than the total amount in the solids themselves. About 1% of the PFHxA in the biosolids was found in the exhaust, and about 3.5% of the PFOA in the biosolids was present in the exhaust. Although PFHpA was below the limit of detection in the biosolids, it was one of the compounds present in the exhaust. It is possible that the transformations of precursors (6:2 FTSA, 10:2 FTSA, N-MeFOSAA, or N-EtFOSAA) during the incineration process led to the presence of

PFHpA in the exhaust. It is also possible that PFHpA was present in the biosolids below the limit of detection, which was .630 ppb or 630 ppt. These results indicate that only a minimal amount of any PFAS present in biosolids are volatilized during incineration, but transformation of precursors may cause some compounds to be present in exhaust that were not present in biosolids. More complete benchtop studies or large-scale stack analysis will help confirm these results.

Chapter 5: Conclusions and Future Research

The issue of PFAS contamination in the environment is complex and multifaceted. These compounds have been a concern over the last two decades, but with lower detection capabilities in the last three years and the subsequent detection in many environmental compartments, many aspects of PFAS, fate, transport and the implications of this low level ubiquitous distribution remain unclear. The goal of the research described in this thesis is to begin to understand the role of branched isomers, the ability to connect PFAS contamination in wells with industrial presence, and the implications of land-applying and incinerating contaminated biosolids.

Although the majority of studies consider PFOS, PFOA, and PFHxS concentrations as a sum total, a growing number look at the branched isomers separately from the linear isomers. The clearest difference seen between linear and branched PFAS is the distinct sorption behavior. Several studies showed that the branched isomers are less hydrophobic than the linear isomers, and are present at higher proportions in surface and groundwater compared to their ratios when manufactured. Conversely, the linear isomers are found at higher proportions in soils and sediments due to their higher hydrophobicity. More research is necessary to confirm these findings, but several studies showed linear versus branched isomers to have different health associations from one another. Interestingly, opposite trends seemed to occur when looking at PFOA and PFOS isomers; when branched PFOS isomers showed negative health associations but linear did not, such as for renal function, linear isomers of PFOA showed negative impacts but branched did not, and when branched PFOA isomers showed negative health associations but linear did not,

such as for higher odds ratios of obesity, the opposite was true for PFOS. It should be noted that most health outcomes only had one or two studies that looked at isomers separately, so additional research is needed to confirm these findings and to start to explain the mechanisms for these phenomena. In general, more insights could be gained if future research separated branched isomers from their linear counterparts in addition to looking at the sum totals when considering both environmental behavior as well as adverse health outcomes.

Because industries have been using PFAS for decades without regulations on disposal and emissions, many states are finding themselves in need of widespread testing efforts in order to identify where drinking water may be contaminated. Identifying factors that increase likelihood of contamination could help to prioritize wells and increase the efficiency of testing programs. We were able to identify an easy method for pinpointing the exact locations of PFAS-using industries based on their NAICS codes via the USEPA's ECHO tool. Using this data, coupled with PFAS testing data from Michigan, we found that soil type (well-drained soil) and well depth were positively associated with PFAS contamination in wells across all four models. One of the two models showed a positive correlation between the presence of electroplaters within 1.0 km of a well and the likelihood of contamination in wells. Future research into the impact of other environmental factors such as elevation could help expand on this work and provide more insights into environmental fate and transport of PFAS.

With widespread use, wastewater and specifically biosolids are a natural repository of PFAS compounds. This creates a new issue as WWTP biosolids are used as fertilizers in agriculture and urban parks, and are at times sold commercially.

Biosolids in turn may be the source of widespread contamination of PFAS. However, there have only been a few studies that investigate the wide range of PFAS compounds that may be present in biosolids and their potential release into the environment. The organic carbon sorption constants calculated from the results of our batch experiment align with prior research where available. In addition, these values followed expected trends with increasing chain length. The log K_{oc} values, which ranged from ~1-3.5, indicate that PFAS will move very slowly through soil, ten through thousands of times more slowly than water percolates, reducing the impacts on groundwater contamination from biosolids spreading. Although we only performed one replicate on one type of biosolids in our incineration experiment, the results indicate minimal volatilization of PFAS from incineration. Very little research on the effects of incineration on PFAS in biosolids has been done, leaving much room for future studies. Investigating volatilization on an industrial scale, such as stack analysis at an actual wastewater treatment facility would provide additional insights. In addition, an analysis that could test for possible PFAS byproducts would further help to discern how incineration affects the PFAS known to be present in solids.

Based on the findings in this thesis, future research should continue to separately analyze branched isomers of PFAS in addition to the sum totals in order to gain more complete understandings of how isomers differ in behavior. This is especially true for human health studies, as more research is needed to confirm the findings that humans preferentially uptake branched over linear, as well as the findings, seen in several studies, of disparate adverse health outcomes between isomers. In addition, further study into factors that affect wells' contamination with PFAS is needed; our study was

not able to find many definite predictors, and future research could focus on factors such as proximity to biosolids land application, elevation, and groundwater flow, factors that were outside the scope of our data set. Lastly, expanding on our batch experiment to do full column studies and eventually field studies would help to further illuminate the contamination risk introduced by spreading contaminated solids on fields and determine whether or not current PFAS levels in biosolids pose a threat to drinking water wells.

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Appendix A

Nationwide PFAS use survey

I. Industry survey

In consultation with a focus group of industry specialists, a survey instrument was designed to assess industrial use of PFAS and to identify specific compounds used by each industry, as these two pieces remain gaps in scientific knowledge. The goal of this survey was to identify which industries used PFAS, what compounds were used and whether anticipated regulations had induced changes in industrial use of PFAS compounds. Data were collected via an email survey administered in Qualtrics to potential industry and municipal users of PFAS. Industrial and municipal categories of users were identified based on an extensive literature review. Using this list of likely PFAS users, paired with the North American Industry Classification System (NAICS), categories of likely PFAS industries were identified. Table A1 lists the industries included in the survey and their NAICS codes.

Table A1: Industries included in nationwide PFAS use survey and their associated NAICS codes.

NAICS Code	Industry Classification
313320	Fabric Coating Mills
313310	Textile and Fabric Finishing Mills
336310	Motor Vehicle Gasoline Engine and Engine Parts Manufacturing
324110	Petroleum Refineries
325320	Pesticide and Other Agricultural Chemical Manufacture
325992	Photographic Film, Paper, Plate, and Chemical Manufacture
326112	Plastics Packaging Film and Sheet (including Laminated) Manufacture
325211	Plastics Material and Resin Manufacture
316110	Leather and Hide Tanning and Finishing
322220	Paper Bag and Coated and Treated Paper Manufacture
332813	Electroplating, Plating, Polishing, Anodizing, and Coloring

314110	Carpet and Rug Mills
325199	All Other Basic Organic Chemical Manufacture
325510	Paint and Coating Manufacture

II. Company Records

Business records for 14 industry types that were likely or known to use PFAS across the United States were identified and purchased from siccode.com, where lists are regularly updated to include only active businesses. For businesses with multiple email addresses on file, one address was selected to receive the emailed survey link based on the listed position type within the company. Science, engineering, and technical roles were prioritized if available, followed by executive, managerial, and operational roles. Emails were sent to a total of 1319 businesses on October 16th, 2019. When 346 emails were returned as invalid, 86 firms listed additional email contacts. A replacement email was sent to the next person in the firm, 49 of the secondary emails were invalid, and 28 listed a third email contact. At three and seven weeks, follow up emails were sent to 1307 and 1296 individuals, respectively. The final return rate out of valid email addresses was 18/1018 or 1.8%. Responses were anonymous and Institutional Review Board (IRB) approval was obtained on October 8th, 2019 (IRB #20.069).

III. Survey Question Design

Survey questions solicited company characteristics including home state of operations, age and size of company, and annual revenue. Industrial use of PFAS, both current and past, was assessed. Companies that indicated yes to either current or past use were asked about specific compounds. A matrix of “agree/disagree” statements regarding search for or investments in PFAS alternatives followed use questions, as well as a similar matrix regarding concerns for how regulation may affect their business and

operations. Demographic questions soliciting information regarding the survey-taker were included at the end of the survey, along with an open-ended entry form for comments.

IV. Results

A total of 1018 survey emails were successfully sent to companies after accounting for bounced emails. There were 33 responses received but the final tally of 18 complete surveys constitutes a 1.8% response rate. Of the 18 respondents, 72% reported no current or prior use of PFAS, 22% reported current use, and 6% reported past but not current use. One responder listed the chemical they use as “fluorosulfonate”. This is a functional group rather than a PFAS chemical, and is not a complete chemical name. It is possible they meant PFOS, which was listed, or they use a chemical such as methyl fluorosulfonate that contains this functional group. Due to the survey’s anonymity, it was not possible to confirm which chemical was identified in this survey. Table A2 shows the PFAS use response breakdown. Responders who indicated current PFAS use were directed to a set of questions gauging their attitudes towards the potential regulation of PFAS. Of the five responders who participated in the matrix of attitudinal questions, 60% agreed or strongly agreed that they felt concerned about the impacts on their company of state and federal efforts to regulate PFAS and the monetary costs that would accompany compliance with regulations. Three of five also expressed that their firms were exploring both alternatives to PFAS, as well as available cleanup technologies, but only one firm indicated monetary investment in research on alternatives and two indicated monetary investments in cleanup/treatment technologies.

Table A2: Breakdown of response subset from internet survey aimed at PFAS-using industries (n=1081).

Industry Type	# of Respondents	Currently Use (compounds)	Prior Use (compounds)	No Current or Prior Use
Electroplating, Plating, Polishing, Anodizing, and Coloring	11	3 (PFOS, 6:2 fluorotelomer sulfonate FTSA)	1 (PFOS)	7
Textile and Fabric Finishing	1	0	0	1
Paint and Coating Manufacturing	3	0	0	3
Plastics Material and Resin Manufacturing	1	0	0	1
Pesticide Manufacturing	1	0	0	1
Paper Bag and Coated and Treated Paper Manufacturing	1	0	0	1
Photolithography	1	1 ("fluorosulfonate")	0	0
Chemical Milling (Industrial Etching)**	1	0	0	1
Total	18*	4	1	13*

Appendix B

Raw results from biosolids batch experiment.

Table B1: Batch results from solids S1. Concentrations are in ppb. Yellow highlight indicates that results were flagged for interference, transition ion ratio failure, or failure to meet QA/QC standards. Blue highlight indicates that results were between LOD and LOQ, so the concentration is an estimate. Yellow highlight with blue outline indicates that both the aforementioned qualities apply.

Compound	Time	R1	R2	R3	Average
PFHxA	0	0	0	0	0
	1	428	413	393	411
	3	495	695	553	581
	12	644	761	726	710
	24	524	939	895	786
	48	495	701	652	616
	336	98.0	993	880	657
PFHpA	0	0	0	0	0
	1	10.5	6.5	6.18	7.73
	3	0	30.6	18.8	16.5
	12	8.65	27.5	20.2	18.8
	24	9.28	35.2	35.1	26.5
	48	7.74	26.7	27.6	20.7
	336	15.2	20.3	15.6	17.0
PFOA	0	0	0	0	0
	1	12.4	12.7	11.8	12.3
	3	12.9	15.8	11.4	13.4
	12	17.8	27.1	20.0	21.6
	24	20.4	21.9	21.4	21.2
	48	41.0	15.6	14.1	23.6
	336	51.3	34.0	25.0	36.8
PFHxS	0	0	0	0	0
	1	5.17	0	0	1.72
	3	0	4.66	0	1.55
	12	7.30	0	0	2.43
	24	12.6	5.72	5.65	7.99
	48	15.0	5.6	6.47	9.02
	336	64.4	13.0	18.9	32.1
PFOS	0	0	0	0	0
	1	16.1	8.95	10.2	11.8
	3	15.5	10.0	9.68	11.7
	12	22.5	12.9	12.8	16.1

	24	27.0	14.0	13.6	18.2
	48	31.9	11.5	11.8	18.4
	336	80.2	37.4	25.1	47.6
6:2 FTSA	0	0	0	0	0
	1	217	310	305	277
	3	310	229	215	251
	12	309	329	294	311
	24	372	377	351	367
	48	333	289	285	302
	336	535	1220	757	837
PFNA	0	0	0	0	0.00
	1	2.35	0	0	0.783
	3	2.32	0	0	0.773
	12	3	0	0	1.00
	24	3.16	0	0	1.05
	48	2.91	0	0	0.970
	336	6.71	5.12	0	3.94
PFPeA*	0	0	0	0	0.0
	1	437	0	0	146
	3	108	0	0	36.0
	12	364	0	0	121
	24	280	0	0	93.3
	48	170	0	0	56.7
	336	0.712	0	0	0.237
PFDA	0	0	0	0	0.00
	1	1.17	0	0	0.39
	3	1.18	0	0	0.39
	12	1.42	0	0	0.47
	24	1.92	0	0	0.64
	48	1.90	0	0	0.63
	336	5.65	0	0	1.88
PFBS	0	0	0	0	0.0
	1	133	0	0	44.3
	3	203	0	0	67.7
	12	156	0	0	52.0
	24	159	0	0	53.0
	48	144	0	0	48.0
	336	26.1	0	0	8.7
PFPeS	0	0	0	0	0.00
	1	0	0	0	0.00
	3	0	0	0	0.00
	12	3.86	0	0	1.29
	24	0	0	0	0.00

	48	0	0	0	0.00
	336	9.31	0	0	3.10
8:2 FTSA	0	0	0	0	0.00
	1	1.7	0	0	0.57
	3	2.59	0	0	0.86
	12	2.07	0	0	0.69
	24	2.57	0	0	0.86
	48	2.62	0	0	0.87
	336	7.21	0	0	2.40
N- MeFOSAA	0	0	0	0	0.00
	1	1.27	0	0	0.42
	3	2.32	0	0	0.77
	12	1.68	0	0	0.56
	24	2.21	0	0	0.74
	48	2.41	0	0	0.80
	336	9.39	0	0	3.13

Table B2: Batch results from solids S2. Concentrations are in ppb. Yellow highlight indicates that results were flagged for interference, transition ion ratio failure, or failure to meet QA/QC standards. Blue highlight indicates that results were between LOD and LOQ, so the concentration is an estimate. Yellow highlight with blue outline indicates that both the aforementioned qualities apply.

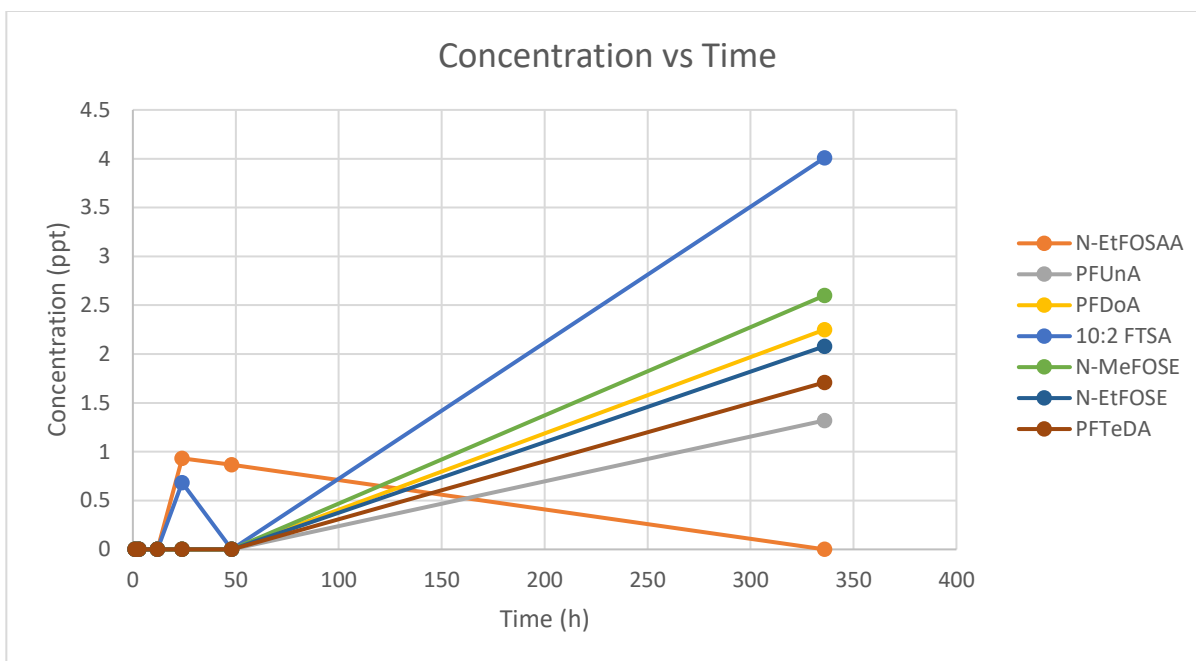
Compound	Time	R1	R2	R3	Average
PFHxA	0	0	0	0	0
	1	44.5	41.6	39.4	41.8
	3	65.1	56.8	56.7	59.5
	12	107	118	107	110.7
	24	96.7	120	118	111.6
	48	88.6	88.1	86.0	87.6
	336	127	107	130	121.3
PFHpA	0	0	0	0	0
	1	0	0	0	0
	3	5.81	0	5.86	3.89
	12	9.58	7.46	8.4	8.48
	24	8.95	8.51	5.37	7.61
	48	5.48	5.17	5.6	5.42
	336	14.0	8.29	12.1	11.5
PFOA	0	0	0	0	0
	1	18.5	15.5	14.2	16.1
	3	21.5	20.3	20.3	20.7
	12	34.1	34.5	34.4	34.3

	24	34.2	35.3	35.7	35.1
	48	18.1	18.1	20.3	18.8
	336	43.1	27.8	47.4	39.4
PFHxS	0	0	0	0	0
	1	9.79	9.06	10.3	9.7
	3	11.1	11.8	11.7	11.5
	12	0	19.2	23.1	14.1
	24	21	18.9	14.0	18.0
	48	13.8	13.0	11.3	12.7
	336	26.0	21.5	31.5	26.3
PFOS	0	0	0	0	0
	1	52.4	49.4	49.7	50.5
	3	50.7	50.4	48.8	50.0
	12	67.2	66.2	68.2	67.2
	24	63.4	70.0	66.7	66.7
	48	40.3	37.0	43.0	40.1
	336	92.8	70.2	127	96.7
PFNA	0	0	0	0	0
	1	0	0	0	0
	3	0	0	0	0
	12	4.98	5.52	4.55	5.02
	24	4.44	4.74	4.71	4.63
	48	0	0	0	0
	336	5.96	0	7.36	4.44
6:2 FTSA	0	0	0	0	0
	1	0	0	0	0
	3	0	0	0	0
	12	0	0	0	0
	24	0	0	0	0
	48	0	0	0	0
	336	5.86	0	5.56	3.81
N-MeFOSAA	0	0	0	0	0
	1	0	0	0	0
	3	0	0	0	0
	12	0	0	0	0
	24	0	0	0	0
	48	0	0	0	0
	336	5.45	0	8.08	4.51

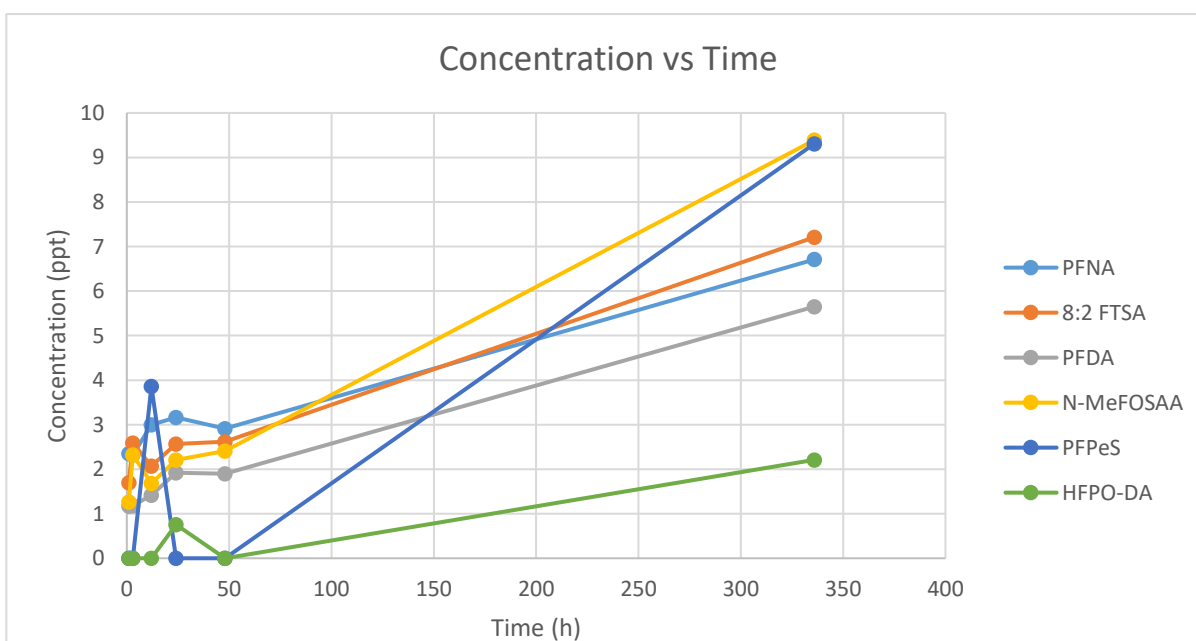
Table B3: Batch results from solids S3. Concentrations are in ppb. Yellow highlight indicates that results were flagged for interference, transition ion ratio failure, or failure to meet QA/QC standards. Blue highlight indicates that results were between LOD and LOQ, so the concentration is an estimate.

Compound	Time	R1	R2	R3	Average
PFHxA	0	0	0	0	0
	1	358	341	317	339
	3	312	372	287	324
	12	395	434	430	420
	24	407	368	339	371
	48	379	318	372	356
	336	527	324	399	417
PFHpA	0	0	0	0	0
	1	7.99	6.6	7.09	7.23
	3	7.82	9.52	6.69	8.01
	12	10.6	12.3	11.8	11.6
	24	10.7	10.9	9.87	10.5
	48	13.9	8.90	11.1	11.3
	336	11.4	11.2	8.7	10.4
PFOA	0	0	0	0	0
	1	34.9	32.8	32.8	33.5
	3	35.8	36.2	28.6	33.5
	12	39.4	40.4	41.1	40.3
	24	35.0	34.3	34.2	34.5
	48	33.5	30.3	32.7	32.2
	336	32.8	28.2	28.1	29.7
PFHxS	0	0	0	0	0
	1	30.0	27.8	33.9	30.6
	3	35.1	35.5	31.6	34.1
	12	39.0	34.1	33.5	35.5
	24	30.0	37.4	29.3	32.2
	48	26.7	27.4	0	18.0
	336	35.0	30.6	31.2	32.3
PFOS	0	0	0	0	0
	1	16.9	18.5	18	17.8
	3	17.3	18.9	19.0	18.4
	12	20.9	20.1	21.4	20.8
	24	19.1	19.1	19.1	19.1
	48	18.4	19.5	19.7	19.2
	336	19.3	21.1	21.5	20.6
PFNA	0	0	0	0	0
	1	0	0	4.39	1.46

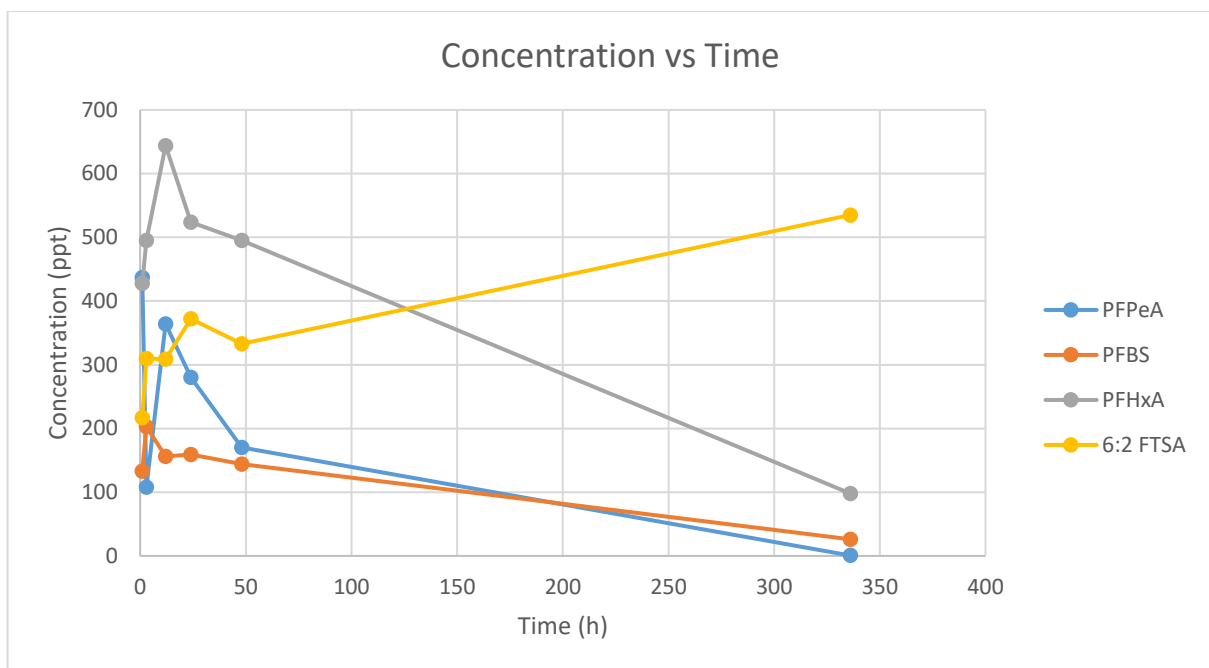
	3	4.7	4.87	0	3.19
	12	5.78	0	5.06	3.61
	24	5.04	0	0	1.68
	48	0	0	0	0
	336	0	0	0	0
6:2 FTSA	0	0	0	0	0
	1	18.2	14.7	16.8	16.6
	3	15.3	17.5	12.0	14.9
	12	20.2	19.7	21.0	20.3
	24	16.2	16.9	17.5	16.9
	48	16.8	14.1	11.5	14.1
	336	15.7	11.2	11.6	12.8
N- MeFOSAA	0	0	0	0	0
	1	9.92	11.8	11.9	11.2
	3	11.3	12.3	7.52	10.4
	12	11.7	13.8	17.7	14.4
	24	15.2	17.0	14.9	15.7
	48	16.7	17.6	11.0	15.1
	336	16.3	22.7	25.6	21.5
N- EtFOSAA	0	0	0	0	0
	1	0	0	0	0
	3	0	0	0	0
	12	0	4.65	5.67	3.44
	24	4.82	5.25	4.72	4.93
	48	5.99	5.73	4.41	5.38
	336	6.4	8.04	9.32	7.92
PFDA	0	0	0	0	0
	1	4.16	5.01	4.99	4.72
	3	4.68	4.85	0	3.18
	12	6.15	5.64	6.51	6.10
	24	6.10	5.36	5.41	5.62
	48	5.21	5.11	5.38	5.23
	336	6.68	6.52	7.13	6.78
4:2 FTSA	0	0	0	0	0
	1	0	0	0	0
	3	0	0	0	0
	12	0	0	0	0
	24	0	0	0	0
	48	45.9	0	0	15.3
	336	0	0	0	0



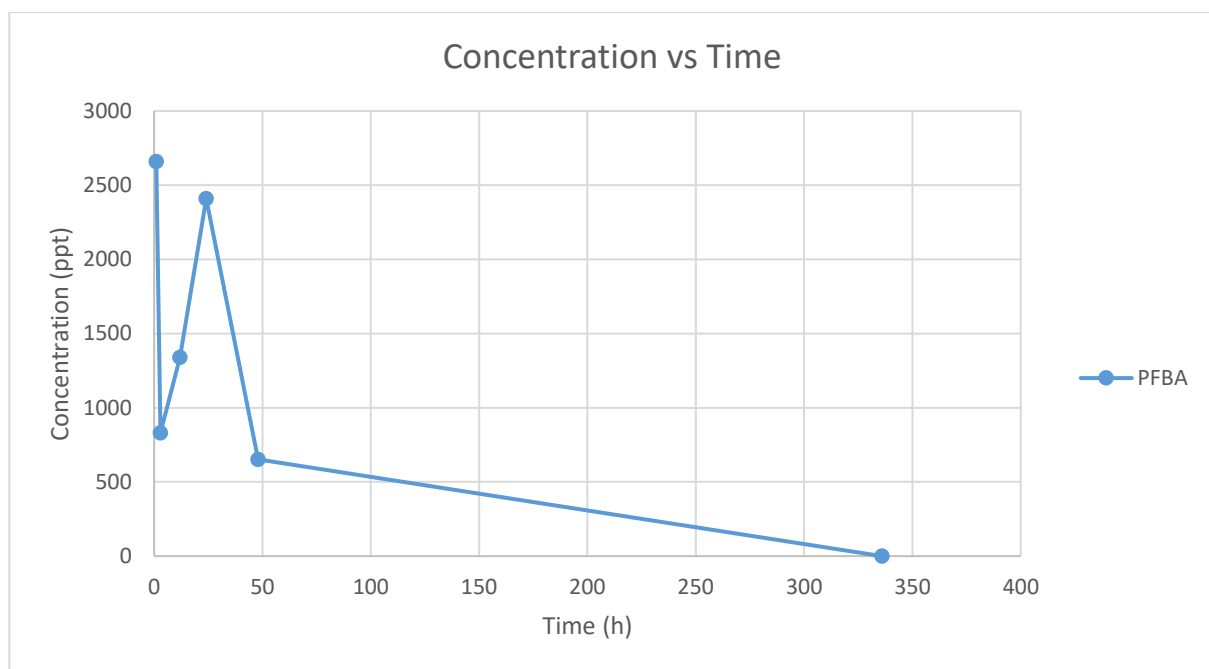
a)



b)



c)



d)

Figure B1: Results from the test batch, also used as R1 for S1. All compounds shown in (a), (b), and (d) were not present in R2 and R3 due to dilution of samples or, in the case of PFBA, due to flawed methodology that was later modified. In (c), PFPeA and PFBS were not seen in remaining replicates, but PFHxA and 6:2 FTSA were and are also shown in Figure 4.3 (c) and (f), respectively.

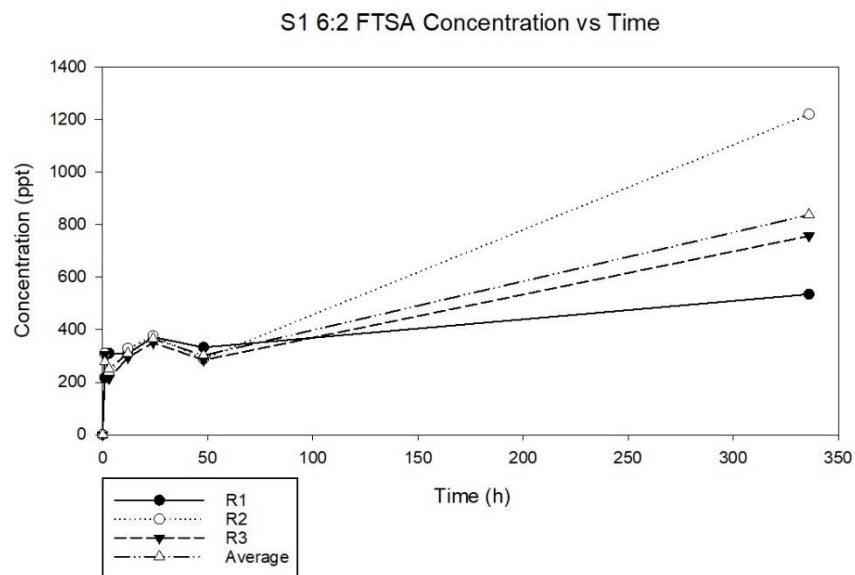


Figure B2: Concentration of 6:2 FTSA versus time in S1.

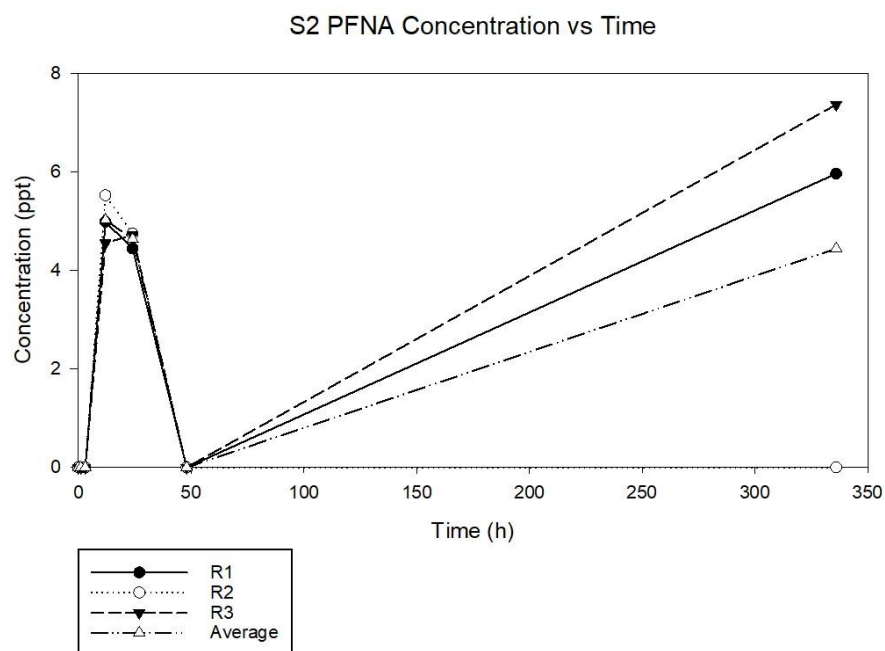


Figure B3: Concentration of PFNA versus time in S2.

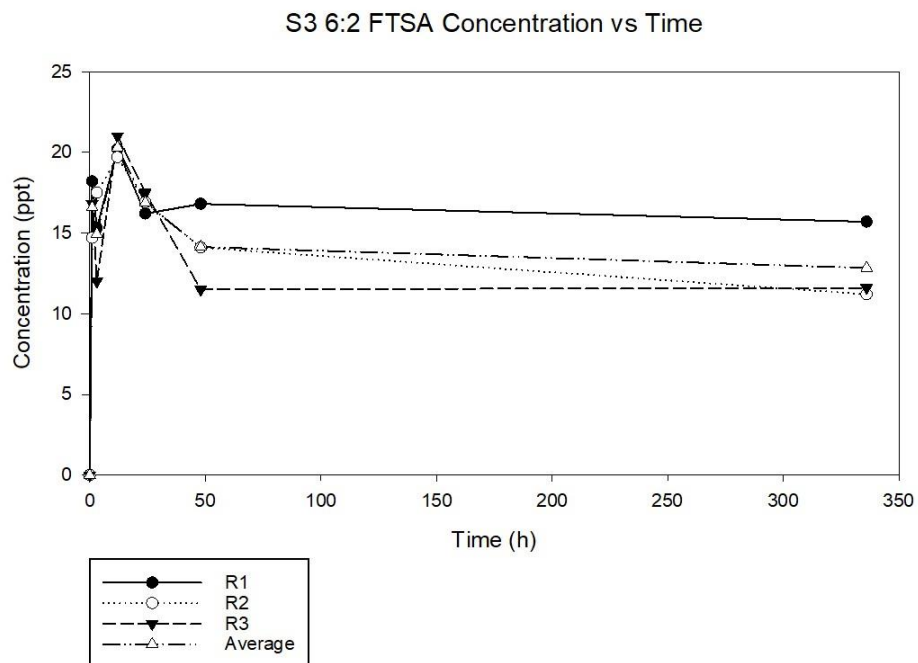


Figure B4: Concentration of 6:2 FTSA versus time in S3.

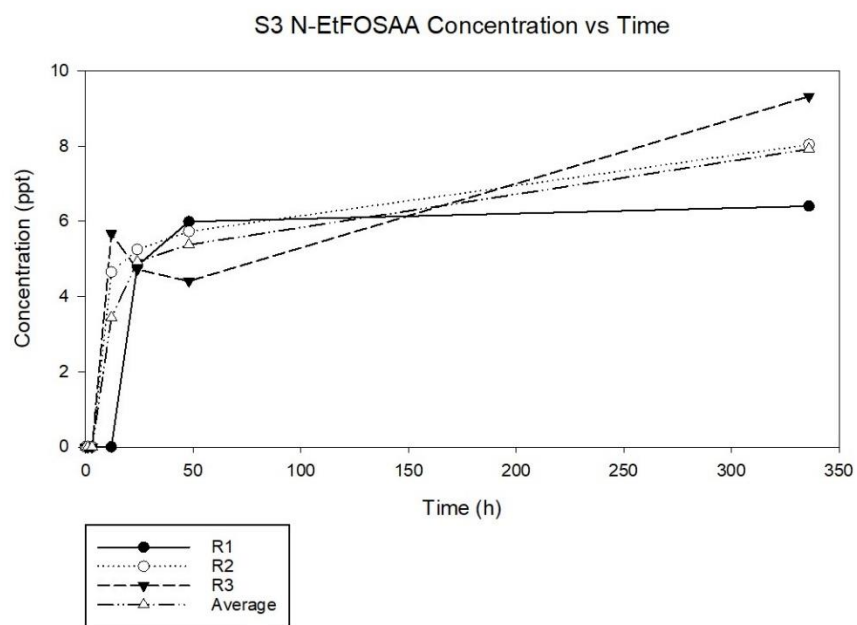


Figure B5: Concentration of N-MeFOSAA versus time in S3.

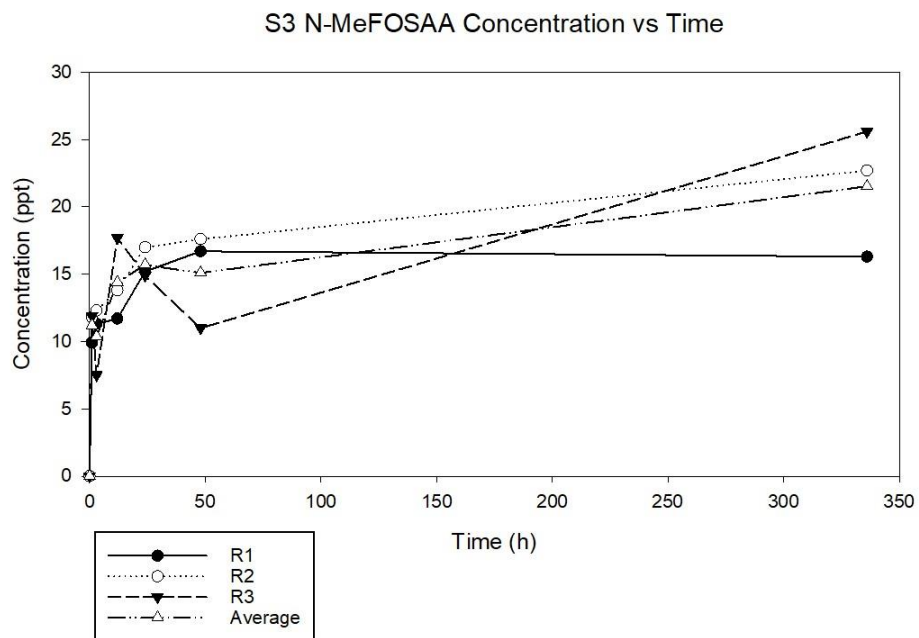


Figure B6: Concentration of N-EtFOSAA versus time in S3.

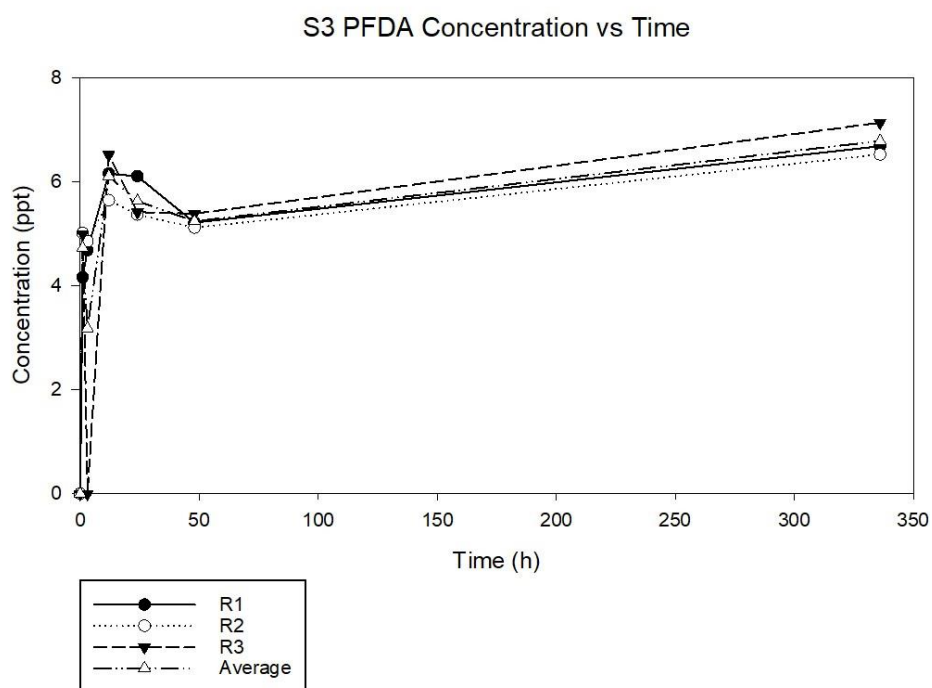


Figure B7: Concentration of PFDA versus time in S3.