The Pennsylvania State University
The Graduate School

SPATIAL AND TEMPORAL PATTERNS OF PFAS OCCURRENCE AT A WASTEWATER BENFICIAL REUSE SITE IN CENTRAL PENNSYLVANIA

A Thesis in
Agricultural and Biological Engineering
by
Olivia R. Mroczko

Submitted in Partial Fulfillment
of the Requirements
for the Degree of
Master of Science

December 2023

The thesis of Olivia R. Mroczko was reviewed and approved by the following:

Heather E. Preisendanz
Associate Professor of Agricultural and Biological Engineering
Thesis Advisor

Tamie L. Veith
Adjunct Associate Professor of Agricultural and Biological Engineering
Research Agricultural Engineer, USDA-ARS-Pasture Systems and Watershed Management Research Unit

Patrick Drohan
Professor of Pedology & Graduate Program Chair

Hershell A. Elliot.
Professor Emeritus of Agricultural and Biological Engineering

Suat Irmak
Professor and Head of Department of Agricultural and Biological Engineering

Abstract

Per- and polyfluoroalkyl substances (PFAS) is a collective name for a growing range of synthetic fluorinated compounds that have been produced to enhance both consumer and industrial products since the 1940s. Due to their chemical composition, PFAS do not easily degrade and can persist in the environment, negatively impacting ecosystem and human health. With recent advances in analytical technology, the fate and transport of PFAS in the environment is becoming better understood, as are the risks they pose to human and environmental health. Because PFAS persist in treated wastewater, reusing wastewater effluent as an irrigation source can inadvertently introduce PFAS into agroecosystems. The Pennsylvania State University has been spray-irrigating all of its treated wastewater at a site known as the "Living Filter" since the early 1980s. The site contains ~250 ha of mixed use agricultural and forested land and 13 monitoring wells. To understand the effects of this long-term irrigation on the occurrence and the spatial and temporal patterns of PFAS at the site, groundwater water samples were collected bimonthly from October 2019 to February 2021 from the wastewater influent and effluent and from each of the groundwater monitoring wells, with all samples analyzed for 20 PFAS compounds. Additionally, crop tissue samples were collected at the time of harvest for corn silage and fescue to determine the potential impacts of spray-irrigation activities on PFAS occurrence in the crops harvested as livestock feed. To better understand potential human health impacts of PFAS occurrence at the Living Filter site, aqueous PFAS concentrations were compared to national and international drinking water policies, including throughout the United Kingdom, to determine if the long-term spray irrigation activities associated with beneficial reuse are significant enough to warrant human-health related concerns under different policy regimes.

Data from the monitoring wells demonstrated that of the 20 analyzed PFAS compounds, 10 PFAS compounds were found to be present in the ground water. Concentrations of total measured PFAS ranged from below the detection limit to 155 ng/L, with concentrations increasing in the direction of groundwater flow. PFOA and PFOS across the Living Filter were detected at concentrations above the drinking water standards proposed by US Environmental Protection Agency (USEPA) at 10 of the 13 monitoring wells and above the Pennsylvania Department of Environmental Protection's drinking water standards in 7 wells. However, all but

3 of the 13 wells met UK policy standards. Because the Living Filter is operated to maintain groundwater concentrations below the USEPA's primary drinking water standard of nitrate of 10 mg NO_3-N/L (USEPA, 2009), strict regulations for PFAS in potable water could limit the long-term feasibility of beneficial reuse of treated wastewater. However, these wells do not serve as supply wells for potable water and therefore do not pose a direct risk to human health.

Research results provide insight into potential impacts of beneficial reuse of treated wastewater on groundwater and crop tissue quality. Crop tissue was also found to contain detectable levels of PFAS, with short chain compounds being the largest contributor (>84%). These results were used to estimate the amount of PFAS ingested by dairy cattle through their feed, which was found to range from 2.46 – 7.67 mg/animal/yr. These results suggest that beneficial reuse of wastewater effluent can impact groundwater and feed quality; however, the results to livestock and human health are not yet fully understood. Without these beneficial reuse programs, the treated wastewater would be discharged to surface water. Therefore, additional research is needed to better understand the risks and benefits associated with beneficial reuse programs as they relate to PFAS fate and transport in agroecosystems.

TABLE OF CONTENTS

List of Tables

List of Figures

Acknowledgments

This research was funded, in part, by The Pennsylvania State University Office of the Physical Plant and a cooperative agreement from the USDA-ARS. H. E. Preisendanz, M. L. Mashtare, H. A. Elliott, and J. E. Watson are supported, in part, by the USDA National Institute of Food and Agriculture Federal Appropriations under Project PEN04574 and Accession number 1004448. H. E. Preisendanz is supported, in part, by the Penn State Institutes of Energy and the Environment. The findings and conclusions of this research do not necessarily reflect the view of the funding agency (USDA) or the Pennsylvania State University. Mention of trade names, laboratory names, or commercial products in this publication is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the Pennsylvania State University or the USDA. All entities involved are equal opportunity providers and employers.

There are so many people I wish to extend my gratitude to for helping and supporting me through this journey to complete this project. I would like to start by thanking my advisor, Dr. Heather Preisendanz, without whom, I would not be who I am and where I am today. She has shown so much compassion and support throughout this project. She has challenged me and guided me since the beginning of my journey, and I would like to extend my utmost thanks to her and for how lucky I am to have had her as my advisor. Thank you for sticking by my side and supporting me through all of it and being my number one advocate. And an extended thanks to Heather's daughter, Maya, for being her mom's number one cheerleader and supporting Heather in the crazy times to help push her students, myself included, to success.

I would like to extend a huge thank you to the Penn State Office of the Physical Plant staff, including David Swisher, Joshua Gates, James Loughran and Holly Martinchek, for their assistance coordinating and collecting samples. This project would not have been possible during the COVID pandemic without their help and collaboration.

To my original thesis committee, Dr. John Watson and Dr. Hershel Elliot, thank you for pushing me and believing in me to make this project what it has become. You were there in the beginning and stuck with me through the learning curve that was the pandemic. To my current

committee, Dr. Patrick Drohan and Dr. Tamie Veith, who so kindly and sportingly stepped up when I needed to form a new committee. You all have supported and believed in me, and I wouldn't be here without any of you.

To those in, and formerly in, the Preisendanz-TV lab group, thank you all for all your help and support. If it were not for all of you, I would not have been offered this position, nor would I have been able to make it through. Thank you from the bottom of my heart to Rachel Taylor, Faith Kibuye, Talia Leventhal, Katie Hayden, Bill Clees, Christopher Wilson, and Carla Ndoun Tangmo. Whether it was late night pizza and wine sessions, field, or lab work, you all were there to lend support and advice. I could not ask for a better group of people to call colleagues or friends.

I would like to extend my uttermost gratitude and thanks to my family and partner. Thank you to my family for pushing me and supporting me, for offering advice and listening to me explain things, even when you had no idea what I was saying. I am enormously grateful to my parents, George and Patricia Mroczko, and my younger sister, Emmeline, as well as my entire extended family. Your support, love, and belief in me throughout my entire Penn State journey has meant everything to me and I thank you all so much. Thank you all for calling and checking in, as well as reading and sending me articles that you thought had anything to do about my research so that you all can learn with me.

Finally, to my partner, Igor Kobzarenko. Thank you in every way possible for being my person. Thank you for all you have done and for standing by my side through this adventure we call life. Thank you for being the person I can go to for anything, a laugh, a cry, questions, help, or friendship. I would not have been able to complete this journey without your unwavering support and strength. You were my rock through it all and I am so lucky and grateful that you are my person for all that we have in store on our adventure as well.

Thank you again to everyone who had the smallest contributions to the largest of them all. Each and every one of you helped me in some way, and I will always be immensely thankful. Never doubt that even the smallest action did not make some sort of difference.

Chapter 1. Introduction

Synthetic chemicals that are released into the environment can negatively impact ecosystem health and accumulate in the food chain, posing potential risks for human health, resulting in environmental regulations having to be updated as new pollutants emerge (Ghisi et. al., 2019; Manzetti et al., 2014). With the rise of plastics and other synthetic materials in the mid 1900s, synthetic polymers were seen as versatile and transformative for everyday life. The use of plastics and synthetic materials brought about waterproof material and long lasting products that were both durable and light weight (Thompson et al., 2002). However, with the widespread usage of synthetic materials in products ranging from personal care products and nonstick cookware to industrial machinery and advanced medical technologies, their presence in the environment has become inevitable and warrants concern, even at trace level concentrations (USEPA, 2019; OECD, n.d.). Contaminants of emerging concern (CECs), a collective class of contaminants that include pharmaceuticals and personal care products (PPCPs), have gained widespread attention over the past two decades after Kolpin et al. (2002) conducted a nationwide reconnaissance on the occurrence of CECs in surface water. This seminal study has led to the inclusion of CECs in water quality assessments worldwide. Concerns regarding per- and polyfluoroalkyl substances (PFAS) as a specific group within CECs have been increasingly documented since 2003 (Ranjan et al., 2006; Sharma et al., 2016).

Due to the nature and composition of these chemicals, accumulation of PFAS in the environment and wildlife has persisted through the decades. Studies have demonstrated that PFAS has been found in water and crop sources, as well as in urban environments. Due to the migration and prevalence of PFAS in crops and water, exposure and accumulation of PFAS within the food chain is a realistic probability (Blaine et al., 2013; Ghisi et. al., 2019). PFAS are often observed in the influent to municipal wastewater treatment plants and water reclamation facilities, entering through both domestic and industrial pathways. Because of their resistance to degradation, they persist in the treated effluent and can then be introduced back into the environment through land-application (e.g., wastewater irrigation, biosolid applications. There is a need to better understand the potential unintended consequences of beneficial reuse programs on the fate and transport of PFAS in agroecosystems and potential impacts to human and ecological health.

Land-based application of wastewater is an increasing form of recycling water to reduce reliance on fresh water for other uses, like drinking water, especially in the south and western regions of the United States (FLDEP, n.d.; USDOE, n.d.; USEPA, 2020). The Living Filter at Penn State is a 2.5 km^2 mixed land site to which the University Park campus has been land-applying 100% of its treated wastewater for irrigation since the early 1980s. These reclamation and irrigation activities inadvertently introduce PFAS compounds into the environment, as they are typically present in domestic wastewater effluent at concentrations from 62 - 418 ng/L in North America (Arvaniti and Stasinakis, 2015; Hamid and Li, 2016). Although the concerns regarding PFAS in wastewater effluent and the environment are recent, the compounds have likely been in the wastewater spray-irrigated at the Living Filter since the beginning of irrigation activities. After approximately four decades of these spray-irrigation activities, it is likely that PFAS occurrence at the site is widespread, with PFAS potentially having been taken up into crop tissue and affecting groundwater quality.

The goal of this research study was to assess the long-term impacts of spray-irrigation activities at the Living Filter site on groundwater quality and crop tissues used as livestock feed. The objectives were to: (a) quantify total measured PFAS in influent entering effluent leaving the Penn State wastewater reclamation facility (PSU WRF); (b) characterize PFAS spatial and temporal patterns across the site's 13 groundwater monitoring wells and compare the results to existing and proposed standards for drinking water; and (c) determine the presence PFAS in corn and tall fescue entering the food chain. Samples from the 13 ground monitoring wells throughout the Living Filter, as well as a 24-hr composite sample of both the influent and effluent of the wastewater treatment plant, were collected bimonthly and analyzed for 20 PFAS compounds using EPA Method 537.1. The influent and effluent concentrations were determined to assess the potential for the PSU WRF to remove PFAS prior to wastewater irrigation over the period of study (October 2019 – February 2021). Additionally, the results from the groundwater monitoring wells were investigated spatially and temporally to identify potential patterns across the study site during the study period. For all harvesting seasons, irrigated fescue and irrigated and non-irrigated corn silage samples were collected, dried, and analyzed for the same 20 PFAS

analytes. These results were used to estimate the PFAS masses that livestock consumed through their feed, which included corn silage and fescue grown at the site.

Because of the lack of data available to provide context to the results of this study, they will be compared to existing and proposed PFAS policies for the United States and the United Kingdom. For purposes of this dissertation, this comparison will also fulfill the requirements of the International Agricultural and Development (INTAD) degree. Further, this discussion will provide an understanding of the long-term viability of wastewater irrigation systems. For example, the Living Filter site is permitted by the Pennsylvania Department of Environmental Protection. Under its current policy requirements, the groundwater concentrations of nitrate must not exceed the EPA's drinking water standards for nitrate (10 mg NO_3-N/L). If such facilities may be mandated to meet drinking water standards for PFAS, it is important to compare the results of the groundwater concentrations at the site to current and proposed drinking water standards to determine whether long-term spray-irrigation of treated wastewater leads to concentrations that meet or exceed policies/standards. Additionally, interpreting the data in the context of international policies, such as those of the U.K., would have important implications for long-term viability of spray-irrigation programs internationally. These comparisons would help to understand under what policy regimes/settings long-term wastewater irrigation may be sustainable, and whether investments in further treatment of wastewater effluent may be necessary to ensure that spray-irrigation continues to remain feasible in the long-term.

1.1 Per- and Polyfluoroalkyl Substances in the Environment

1.1.1 Definition of PFAS

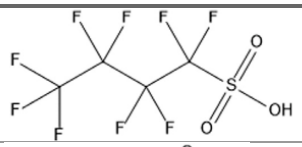
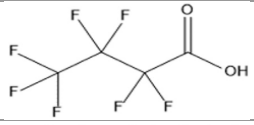
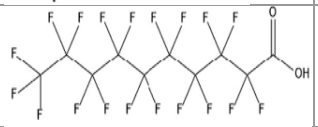
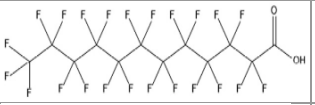
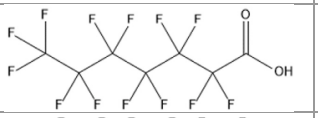
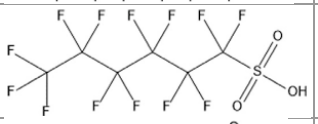
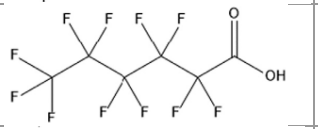
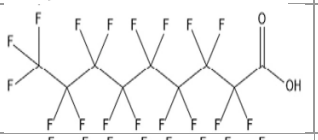
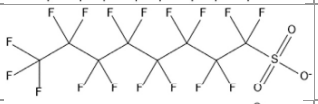
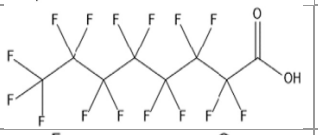
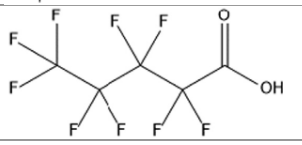
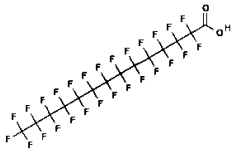
PFAS is a collective name for over 15,000 compounds, as of October 2023, of fully synthetic polymers that have been historically produced by a process of electrochemical fluorination (ECF) or telomerization (Newland et al., 2023). PFAS were first manufactured in the mid 1940s, arising due to the mass production of products for World War II and General Motors Assembly manufacturing companies when extensively use chemicals during the mass production of synthetic and plastic-based products (Hodgkins et al., 2019; Jahnke et al., 2009). PFAS chemicals have non-polar phases and a low aqueous surface tension, leading them to exhibit amphiphilic behavior (Buck et al., 2011; Krafft and Riess, 2015). As a result, industries began to

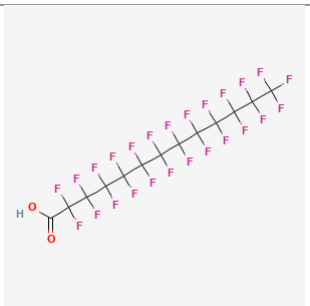
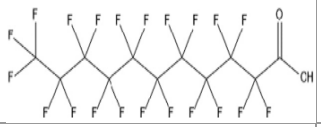
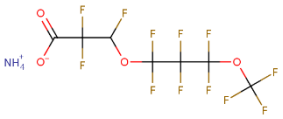
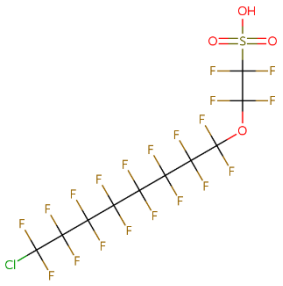
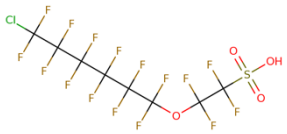
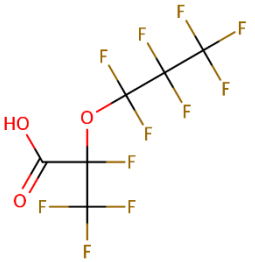
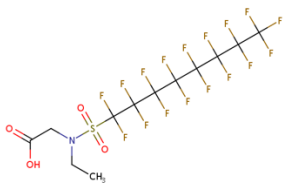
exploit these unique properties of repelling water, oil, and stains, as well as surfactant properties and thermal resistance for commercial applications. They have been widely used in many industrial and manufacturing processes and in fire-fighting foams. Their properties make them highly desirable in consumer products such as water and stain-resistant clothing, textiles, personal care products, makeup, and non-stick cookware. Other products containing PFAS are paper and cardboard packaging, including fast food packaging and consumer products.

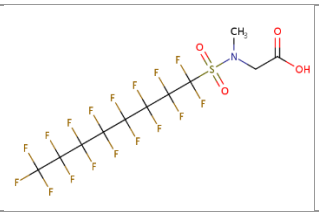
PFAS are a unique family of molecules that are composed of a branched or linear carbon chain that can be fully or partially fluorinated (Buck et al., 2011). Their unique physicochemical characteristics are due to the strength of the carbon-fluorine bond and the ratio between the fluorine atom and hydrogen atoms (Buck et al., 2011; Ghisi et. al., 2019) as seen in Table *1*. Two of the earliest and most studied PFAS compounds include perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS). Due to concerns regarding their carcinogenicity, manufacturing of these two compounds ended in the mid 2000's, with chemicals referred to as GenX generally replacing them (Buck et al., 2011; Environment Protection Agency, 2019). GenX is a trade name for a processing aid technology that creates high-performance fluoropolymers, or the waterproof lining and nonstick surfaces of many industry products today, as a replacement for PFOA (USEPA, 2018; USEPA, 2019). While GenX has been taking the place of PFOA and was initially seen as a safer alternative, HFPO dimmer acid, ammonium salts and other fluoro-based chemicals that help compose GenX have been found in rainwater, groundwater, drinking water, surface water, etc., and are receiving increasingly more interest for toxicity studies (Dery et al., 2019; Hopkins et al., 2018).

Despite the number of chemicals considered to be PFAS being in the thousands, the currently approved analytical method for PFAS analysis (EPA Method 537.1) identifies 20 compounds, as shown in Table *1,* including the six PFAS chemicals that the EPA has proposed be considered under federal regulation for drinking water statutes as of March 2023.

Table 1. A list of 20 PFAS analytes in this study, with their chemical formula, structure, and molecular weight (CompTox chemicals dashboard 2023; Ghisi et. al., 2019; Mueller and Yingling, 2017).

Analyte	Acronym	Formula	Structure	Molecular Weight
Perfluorobutanesulfonic acid	PFBS	$C_4F_9SO_3H$		300.10
Perfluorobutanoic acid	PFBA	C_3F_7COOH		214.04
Perfluorodecanoic acid	PFDA	$C_9F_{19}COOH$		514.08
Perfluorododecanoic acid	PFDoA	$C_{11}F_{23}COOH$		614.10
Perfluoroheptanoic acid	PFHpA	$C_6F_{13}COOH$		364.06
Perfluorohexanesulfonic acid	PFHxS	$C_6F_{13}SO_3H$		400.11
Perfluorohexanoic acid	PFHxA	$C_5F_{11}COOH$		314.05
Perfluorononanoic acid	PFNA	$C_8F_{17}COOH$		464.08
Perfluorooctanesulfonic acid	PFOS	$C_8F_{17}SO_3H$		500.13
Perfluorooctanoic acid	PFOA	$C_7F_{15}COOH$		414.07
Perfluoropentanoic acid	PFPeA	C_4F_9COOH		264.05
Perfluorotetradecanoic acid	PFTA	$C_{14}HF_{27}O_2$		714.11

Perfluorotridecanoic acid	PFTrDA	$C_{12}F_{25}COOH$		664.10
Perfluoroundecanoic acid	PFUnA	$C_{10}F_{21}COOH$		564.09
Ammonium 4,8-dioxa-3H-perfluorononanoate	ADONA	$C_7H_5F_{12}NO_4$		395.10
11-Chloroperfluoro-3-oxaundecanesulfonic acid	11Cl-PF3OUdS	$C_{10}HClF_{20}O_4S$		632.59
Perfluoro(2-((6-chlorohexyl)oxy)ethanesulfonic acid	9Cl-PF3ONS	$C_8HClF_{16}O_4S$		532.58
Perfluoro-2-methyl-3-oxahexanoic acid	FRD-903 / HFPODA	$C_6HF_{11}O_3$		330.05
2-(N-Ethylperfluorooctanesulfonamido)acetic acid	Net-PFOSA	$C_{12}H_8F_{17}NO_4S$		585.23

2-(N-Methylperfluorooctanesulfonamido)acetic acid	NMePFOSA	$C_{11}H_6F_{17}NO_4S$		571.20

PFAS can be categorized into two subsets: polymers and non-polymers. Polymers are comprised of long-chains molecules with multiple segments within, typically based off carbon segments. Non-polymers are also based off carbon segments, typically between 2-13 in chain length, and are made in a repeating pattern. When people refer to polymers, they are typically referring to long-chain PFAS, however, both polymers and non-polymers can be short- and long-chain PFAS. Polymer and non-polymer PFAS compounds create a cycle with one another. Non-polymer PFAS, including the use of perfluorocarboxylic acids (PFCAs) and perfluoroalkyl acids (PFAAs) are typically used in the production of polymers, such as fluoropolymers (e.g., PFTE). The cycle closes with these polymers potentially degrading in the environment to compounds such as PFCA and PFAA (Fidra UK, 2018). With the rapid industrialization in PFAS, the characteristics of these compounds are attributable to their structure, chemical composition, and their nature of use. Short-chain PFAS are comprised of less than 6 carbons, such as PFBA where as long-chain PFAS are comprised of 6 or more carbons, with the most notable being PFOA and PFOS (American Water Works Association, 2019). Typically, due to the nature of the composition of short-chained PFAS, they show more hydrophilicity (like of water) than their long-chained counterparts (Zeng and Zemba, 2023). This makes short-chained PFAS compounds more desirable in products such as firefighting foams and photography film, while long-chained chemicals are more desired for their water repellent tendencies in products such as non-stick cookware, waterproofed textiles, and plastic production (American Water Works Association, 2019).

Due to widespread use of PFAS in a variety of products, from cookware, food packaging, and laundry detergent, to coatings of ship hulls to prevent barnacle and algae growth, the spread of PFAS throughout the environment and food chain is global. Direct exposure to PFAS chemicals such as PFOA and PFOS for humans has been voluntarily phased out from most industry uses entirely since 2015 in the United States and was ceased in production in the United Kingdom in

2002 (Stockholm Convention, 2017; NSW Government, 2011). However, there are still products that are in use from before the voluntary phase out as well as products being produced in other major manufacturing countries that have not phased out PFOS and PFOA, which can in turn be introduced into the wastewater systems in countries that have phased out the use of PFOA and PFOS in production.

1.1.2 Environmental Protection Standards

Due to the inability of PFAS to easily degrade over time, they have been coined as "forever chemicals". Additionally, given concerns that these chemicals pose to human and ecological health, guidelines and standards have been proposed or established at state, federal, and international levels to regulate what are considered harmful levels of PFAS in drinking water. The United States Environmental Protection Agency (EPA) established a drinking water health advisory on the concentration of PFAS in potable water sources, in May of 2016, of 70 parts per trillion (ppt) or 70 nanograms per liter (ng/L). This health advisory was for the combined concentrations of PFOS and PFOA. In comparison, this is equivalent to 4 grains of sugar in an Olympic size swimming pool (USEPA, 2017). If levels were below 70 ppt, then the water source was considered to have a margin of protection from the examined toxicity level (USEPA, 2018). However, over time, this level was updated. Regulations are constantly evolving as more science and understanding becomes available about PFAS. As of August 2023, the state regulations pertaining to the different levels of PFAS compounds are outlined below in Table 2.

Table 2. State Guidelines for PFAS in Drinking Water Standards in the United States (August 17, 2023)

States with Standards Lower than 70 ppt	Concentration Level (ppt)	Type of Regulation
California	3, 5.1, 6.5	PFHxS, PFOA, PFOS,
Connecticut	2, 5, 10, 12, 16, 19, 49	6:2FTS & 9Cl-PF3ONS, 8:2FTS & 11Cl-PF3OUdS, PFOS, PFNA, PFOA, GenX or HFPO-DA, PFHxS
Hawaii	40 combined	PFOS and PFOA

Illinois	2, 14, 21	PFOA, PFOS, PFNA
Maine	20 combined	PFOA, PFOS, PFHxS, PFNA, PFHpA, and PFDA
Massachusetts	20 combined	PFOA, PFOS, PFHxS, PFNA, PFHpA, and PFDA
Michigan	6, 8, 16, 51	PFNA, PFOA, PFOS, PFHxS
Minnesota	15, 35, 47	PFOS, PFOA, PFHxS
Nevada	6.67	PFSA
New Hampshire	11, 12, 15, 18	PFNA, PFOA, PFOS, PFHxS
New Jersey	13, 14	PFNA & PFOS, PFOA
New York	10	PFOA & PFOS
North Carolina	10	GenX or HFPO-DA
Ohio	21	PFNA, PFNA, GenX or HFPO-DA
Oregon	30 combined	PFOS, PFOA, PFHxS, and PFNA
Pennsylvania	14, 18	PFOA, PFOS
Rhode Island	20 combined	PFOA, PFOS, PFHxS, PFNA, PFHpA, and PFDA
Vermont	20 combined	PFHpA, PFHxS, PFNA, PFOS, and PFOA
Washington	9, 10, 15, 65	PFNA, PFOA, PFOS, PFHxS
States with Standards Equal to 70 ppt	Concentration Level (ppt)	Type of Regulation
Alaska	70 combined	PFOA, PFOS, PFNA, PFHxS, and PFHpA

Colorado	70 combined	PFOS, PFOA, and PFNA
Delaware	70 combined	PFOS and PFOA
New Mexico	70 combined	PFOS and PFOA
Ohio	70 combined	PFOS and PFOA
Wisconsin	70 combined	PFOS and PFOA
States with Standards Higher than 70 ppt	Concentration Level (ppt)	Type of Regulation
California	500	PFBS
Colorado	700, 400,000	PFHxS, PFBS
Connecticut	760, 240, 1,800	PFBS, PFHxA, PFBA
Illinois	140, 2,100, 3,500	PFHxS, PFBS, PFHxA
Maryland	140	PFHxS
Michigan	370, 420, 400,000	GenX or HFPO-DA, PFBS, PFHxA
Minnesota	100, 200, 7,000	PFBS, PFHxA, PFBA
Nevada	1,000	PFBS
Ohio	140, 140,000	PFHxS, PFBS
Washington	345	PFBS
18 Individual PFAS Standards	Regulated PFAS (ppt)	
Hawaii	PFDA (4 ppt); PFNA (4.4 ppt); PFUnDA (10ppt); PFDoDA and PFTrDA (13ppt); PFHxS (19ppt); PFHpS and PFDS (20ppt); PFOSA (24ppt); PFHpA (40ppt); PFTeDA (13 ppt); HFPO-DA	

	(160ppt); PFBS (600ppt); PFPeA (800ppt); PFHxA (4,000ppt); and PFBA (7,600ppt)

PFOS and PFOA were included in the USEPA's 2016 contaminant candidate list as the fourth unregulated toxic contaminant to occur in public drinking water systems, with perfluorohexane sulfonate (PFHxS) and perfluorobutonic acid (PFBA) under review by the Stockholm convention to be added to the PFAS POPs (USEPA, 2017; USEPA, 2019). As of March 2023, the USEPA has issued an individual Maximum Contaminant Level (MCL) for PFOS and PFOA at 4.0 ng/L (4.0 ppt). There is also an issued Health Index (HI) for mixtures of PFHxS, PFNA, PFBS, and HFPO-DA and its ammonium salts. The HI for the mixture is 1.0 for any mixture containing one or more of the four PFAS compounds. The unitless level is due to the representation of a level that no known or anticipated adverse effects of the health of persons is expected to occur within and it allows for a margin of safety as more about the effects that PFAS has on a person's health is determined (USEPA, 2023).

1.1.3 International Policy and PFAS

PFAS have been a Contaminant of Emerging Concern (CEC) in recent studies internationally due to the Stockholm Convention, an international environmental treaty, adopted on May 22, 2001 and entered into force in 2004, concerning the restriction or elimination of persistent organic pollutants. As of February of 2022, there are 185 parties that share the same overarching objective and implement the scope of the agreements, one of which stated that PFHxS, PFOA and PFOS are considered harmful and potentially toxic persistent pollutants within the environment and food chain and are listed under the Stockholm Convention as industrial persistent organic pollutants (POPs) (Stockholm Convention, 2017; Templeton, 2020). The World Health Organization (WHO) initiated the development of a level of concern for PFAS substances, particularly PFOS and PFOA. There has been a rolling revision on the focus of these two substances, with working drafts discussed July 2018, April 2019, March 2021, and October 2021. The most recent has since closed as of November 2022, however, no updated standards have been released yet. As of 2020, the standards released were PFOS at 0.4 µg/L and PFOA at 4 µg/L (European Union, 2020; World Health Organization, 2022). The EU and US have set more stringent guidelines, with 2020 value advisories at 0.07µg/L for the combination of PFOS and

PFOA in a water source, showing that lower parametric values are achievable (European Union, 2020). However, as of 2023, the values have officially changed for the US EPA and in February of 2023, the European Union submitted a proposal to further restrict PFAS in the European Economic Area. The values depicted below are what the US policy and the EU policy currently stand at as of October 2023.

Table 3. List of regulated PFAS in the United States and the European Union as of 2023 (European Chemicals Agency, 2021; United States Environmental Protection Agency, 2023)

Compound	United States EPA	European Union
PFOA	4.0 ppt	4.4 ppt
PFOS	4.0 ppt	4.4 ppt
PFNA	1.0 (unitless) Hazard Index	4.4 ppt
PFHxS		4.4 ppt
PFBS		Identified as substances of very high concern
HFPO-DA or GenX		

Values for accepted levels within drinking water were derived from Stockholm Convention High Level Political Forum and ongoing research, with the phase out and outlaw of PFOA and PFOS usage in industrial processes for most industries in the US and the EU. Guidelines were established stemming from population, sedimentation, water quality, groundwater and surface water delineations, and surveillance of important water supplies (USEPA, 2018). Countries, and in the case of the US, states, should adapt their own guidelines for drinking water standards, which can differ from the guidelines of international levels; however, they are encouraged, and potentially required, to maintain a level either less than or equal to the established guideline for specific compounds and POPs.

Like the United States, the United Kingdom (UK) has made significant progress to phase out, ban, or place extensive restrictions on PFAS chemicals, in particular PFOS, PFOA, PFNA and PFHxS, with GenX chemical salts and PFBS also listed as compounds of high concern. Many policies pertaining to PFAS are similar between the UK and the US, such as the areas of highest concern being at military bases, airports, and historical reclaimed wastewater dump sites (NSW Government, 2011; Hodgkins et al., 2019).

Within the UK, there has been an increased interest in monitoring for PFAS contaminants in potential drinking water sources (European Parliament, 2015; Fidra, 2020). Monitoring and extensive research on PFAS compounds, particularly PFOA and PFOS, has taken place throughout most of the United Kingdom since their detection in the early 2000s. The EU and UK started measuring for PFAS, especially PFOA and PFOS, in surface waters and ground water in the mid 2010s, with over 17,000 ground and surface water sites across the UK and Europe (Salvidge, 2023). While the UK phased out the use of PFOS and PFOA in 2002 and 2009 respectively, PFOS derivatives and PFOA -related compounds and salts were still used in the EU and UK up until 2019 for a limited number of industrial uses, such as hydraulic fluid for aviation and paper or printing plates (UK Environmental Agency, 2019; Public Health of England, n.d.). Variations of these chemicals are still used in production today as well, though they are being more heavily monitored than ever before.

EU standards do consider both PFOS and PFOA in their regulation values like the United States, however, the United Kingdom is falling behind in regulation of PFAS (Salvidge, 2023). Measuring concentrations of PFAS found in surface and ground waters throughout the United Kingdom range between from below the environmental quality standard (EQS) to 4 times greater the EQS (UK Environmental Agency, 2019). The UK uses both surface and groundwater as potable water supplies. Because PFAS are known to persist through wastewater treatment facilities, there are concerns that utilizing this treated wastewater to recharge groundwater aquifers and beneficially reusing treated wastewater as an irrigation source could impact groundwater quality, as well as surface water sources that are currently being tapped for potable water. The EQS for inland surface waters in the EU and UK is listed as 6.5×10^{-4} µg/L (0.65 ng/L) and the annual average EQS for other surface waters is 1.3×10^{-4} µg/L (0.13 ng/L) as seen in Table 4 (UK Environmental Agency, 2019). This value, however, was derived based upon the PFOS compound only. As of 2023, new standards are under review but have not been released yet.

Table 4. Summary of PFOS concentrations in WwTWs as discharges measured as part of UK Water Industry Research (UKWIR) Chemical Investigation Programme (CIP2) tranche 3, that commenced in 2015 (UKWIR, 2019).

Sample	Units	Mean	Standard Deviation (between Wastewater Treatment Works (WwTWs)	Median
Effluent	µg/l	0.010	0.024	0.0039
Upstream	µg/l	0.0043	0.0068	0.0021
Downstream	µg/l	0.0059	0.0091	0.0029

1.1.4 PFAS Introduction into Agroecosystems

Historically, farmers have used animal manure to help with crop production and fertilization for centuries. In the 1920s, farmers started using municipal sludge, or "biosolids", as a fertilizer. Biosolids, while sometimes misunderstood to be raw sewage, are organic solids that have been treated to have reduced disease-causing pathogens and stabilized organic matter (Gaskin and Risse, 2022). Biosolids in agriculture have federal regulations were developed by the EPA and took effect in 1993, known as the 503 regulations (40 CFR part 503) (Gaskin and Risse, 2022). These regulations divide biosolids into two classes, determining their value and application acceptance: Class A and Class B. Class A are for exceptional quality biosolids, meeting the most stringent of requirements and can be used without a site permit. Class B meet regulatory requirements for fertilizers, but are lower quality to Class A (USEPA, 2023a).

With the extensive use of consumer products containing PFAS for decades, PFAS has been found in domestic and industrial wastewaters for decades. Even with the stringent regulations in place for biosolid reuse, PFAS have historically not been regulated. This also applies to reclaimed wastewater used for irrigation purposes. Reclaimed wastewater for agricultural water reuse has the benefits of reducing nutrient rich water from entering sensitive waterways and providing nutrient rich water to crops. Reclaimed water can be applied to include commercial and non-commercial crops including, but not limited to: pasture grasses and haylage, vineyards, orchards, Christmas tree farms, commercial food crops, and nursery stock (USEPA, 2023c). Along with the application of biosolids as a fertilizer, reclaimed wastewater can be used to

irrigate agricultural systems under more than 70 regulations or guidelines across the globe, including the US EPA, WHO, EU Commission, and the United Nations (Shoushtarian and Negahban-Azar, 2020). Reports of PFAS has been found in multiple different media sources including groundwater, surface water, rainwater, and soils across the globe, began in 1999 and only continued to rise since 200 (Leeuwen, 2023; Szabo et al., 2018). With the increased use of PFAS in the mid 1940s to 1950s for both industrial and consumer products, and a sharp increase in food production per capita that began in the 1960s, agricultural practices, both commercial and non-commercial, have been impacted by PFAS compounds for decades (Gowdy and Baveye, 2018). Across multiple research sites, 100% of the sites with historical application of biosolids and reclaimed wastewater have been found to have PFAS in the soil, surface-waters and groundwaters, with samples ranging up to 20m deep (Johnson, 2022; Szabo et al., 2018; Treat, 2021). While reclaimed water and biosolid application may not be the main source of PFAS, it is a contributing factor to PFAS found in agricultural practices and systems.

1.1.5 Plant Uptake of PFAS

Plant uptake has become a recent emphasis in the PFAS research community. Since 2018, studies have been conducted that have shown that PFAS and their precursors are taken up by crops (Costello and Lee, 2020). PFAS precursors are PFAS that can degrade into perfluoroalkyl carboxylic acids (PFCAs) or perfluoroalkyl sulfonic acids (PFSAs), which are terminal metabolites and can be referred to collectively as PFAAs (Costello and Lee, 2020). While low accumulations of PFOS and PFOA, which belong to the PFCA group, have been found in plants and crop tissues, short-chain compounds, such has PFBA and PFHxA, have been found to accumulate in higher concentrations in plant tissues, particularly in leafy vegetables and fruits (Costello and Lee, 2020; Ghisi et al., 2019). Factors that determine the amount of PFAS a crop uptakes includes, but is not limited to; PFAS chain length, functional group, plant root depth and species (Ghisi et al., 2019). Due to greater mobility in the environment and a more water-soluble attribute, short-chained PFAS are transported into the crop during water uptake and transpiration, accumulating in the upper portion of the plant like the leaves and stem (Ghisi et. al., 2019; Nassazzi et al., 2023; Vierke et al., 2012; Wang et al., 2015). In contrast, long-chained PFAS are structurally larger and less water-soluble, leading to less long-chained adsorption into the roots and other plant tissues (Costello and Lee, 2020; Nassazzi et al., 2023). Research has shown that

agricultural areas that are irrigated, or surrounding areas that are irrigated, with reclaimed wastewater or biosolid application, near a military base, airport, or landfill, could have higher a higher PFAS accumulation in tissue and root uptake due to more PFAS entering and leaching into the environment (Ghisi et al., 2019).

1.1.6 Implications for the Food Chain

Because dietary intake is a predominant route for human and animal exposure to PFAS and other emerging contaminants, polluted soil and/or water will cause an increase in potential exposure within the food chain, with primary exposure routes including drinking water, meat, fish, milk, and crops (Costello and Lee, 2020; Sungur et al., 2023; Weber et al., 2017). Due to the nature of PFAS and how different groups react in crop and plant uptake, livestock that are fed with crops produced alongside, or similarly to crops produced for humans, along with dietary fillers, could be inferred to having PFAS present in these agricultural products (cereals, grains, fruits, and vegetables). In cows specifically, PFOS has been found in milk through an experimental feeding trial that demonstrates how, when ingested, PFAS compounds react within an animal (van Asselt et al., 2013; Treat, 2021). In a study that was conducted in 2016, retail cow's milk can be found with higher detection rates of PFOS (24.5 ng/L) than that of PFOA (16.2 ng/L), however, in raw milk, there was only PFOS detected (Xing et al., 2016). It can then be deduced that PFOA is introduced to the food chain between the collection of the raw milk to the table of the consumer. This could be from the tubing and machinery that is used to collect the milk, or the different systems that the milk is processed through that could have PFTE lined tubes and pipes. It should be pointed out, that without studying the entire process to determine the exact point in which PFOA is introduced, entry points can only be hypothesized. However, with the knowledge that PFOS and PFOA can be found in cow's milk, as well as other sources such as fish and meat, which is then sold nationwide, it can be expected that PFOS and PFOA, as well as other PFAS analytes, can be found in other dairy products that are ingested by humans, such as cheese, yogurt, and butter (Costello and Lee, 2020; Xing et al., 2016).

The US Food and Drug Administration (FDA) has focused on testing foods most commonly eaten by people in the US and have been assessing the potential health concern levels found in

food and non-commercial crop sources for seven (7) PFAS that are considered high risk PFAS compounds (ATSDR, 2021; USFDA, 2020). The FDA has helped identify minimal risk levels (MRLs) for these seven compounds (PFOA, PFOS, PFNA, PFHxS, HFPO-DA, PFBS, and PFBA) and are used as screening tools to help identify chemicals that could be of concern and levels that lead to adverse health effects (ATSDR, 2021). If the FDA finds detectable limits of PFAS within a consumer product, the agency conducts an investigation to assess whether the product presents a potential human health concern and warrants further action or is below the MDL (USFDA, 2020).

1.2 The Living Filter at Penn State

1.2.1 Establishment of the Living Filter

The Pennsylvania State University is located in the Spring Creek watershed, which is designated as a high quality, cold water fishery (PA Code 25, Ch 93). In the mid 1950's, a high profile fish kill occurred in Spring Creek, with chemicals linked back to Penn State's wastewater effluent determined to be partly responsible. The University needed a way to manage its wastewater responsibly, especially because of the population growth the University was experiencing. After evaluating various options, the University decided to beneficially reuse its treated wastewater as an irrigation source at a site that became known as the "Living Filter". It was established in 1963 for the purpose of agricultural research with reclaimed water and to prevent extensive fish kills due to thermal shocks in the cold-water fishery. The Living Filter site is currently comprised of over 240 hectares of land, divided into two sections: the Astronomy side and the State Game Lands side. The site is composed of approximately 50% agricultural land and 50% forested and densely wooded areas and the soil is a mixture of Hagerstown soil, Hublersburg soil, and Morrison soil (NRCS). The agricultural lands contain both irrigated and non-irrigated portions, and the crops grown at the site include corn silage, fescue grasses, oats, and wheat.

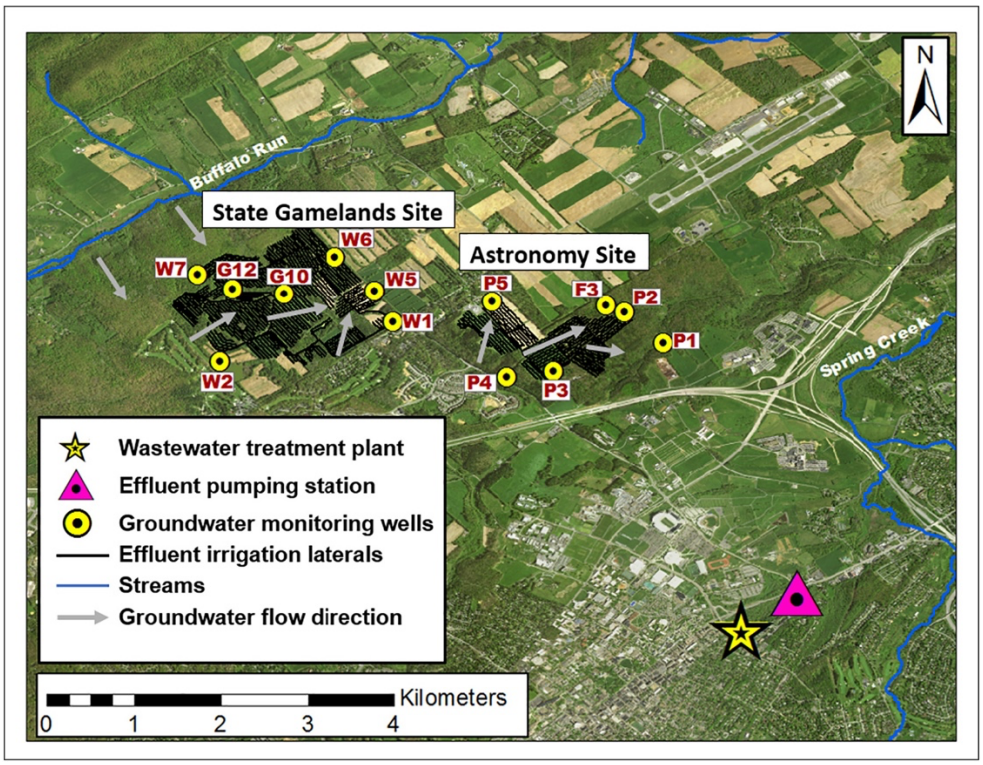


Figure 1. Map of The Pennsylvania State University beneficial reuse facility, including the treatment plant (yellow star), pumping station (pink triangle), and the wastewater spray-irrigation sites that together make the "Living Filter" (Kibuye et al., 2019)

Treated wastewater from the University's WRF is pumped out to the fields, through two (2) miles, or 3.2 km, of subterranean pipes, where it is then spray-irrigated onto the agricultural and forested land. All treated effluent from the University's WRF has been spray irrigated since 1983 (Richardson, 2010). Within the Living Filter are thirteen (13) monitoring wells that monitor the groundwater aquifer below the site recharged by the spray irrigation consisting of 177 lateral pipes used to irrigate the crops with the reclaimed wastewater. The reclaimed water within the irrigated areas then trickles through the soil profile and replenishes the ground water aquifers below the Living Filter Site, of which samples are taken from the monitoring wells throughout the sites. Based upon previous research conducted at the sites, it takes between a year to two years for the sprayed reclaimed water, once irrigated, to reach the groundwater aquifers (Richardson, 2010).

Operation of the Living Filter is permitted by the Pennsylvania Department of Environmental Protection (PA DEP). The permitted application rate for the Living Filter is 2"/acre/week (or 6.3 cm/hectare/week), with only 45-60% of the permitted application actually being used, depending

on season and usage of water on campus (Richardson 2010). For example, the amount of wastewater generated decreases over the summer months and winter break when undergraduate students are typically not on campus, with the volume increasing during the fall and spring semesters. Additionally, the permit requires that the facility be operated in a way that keeps the groundwater concentrations of nitrate below the drinking water standard (10 mg-N/L). To comply with this portion of the permit, 13 monitoring wells were installed across the site, which are sampled at least quarterly (sometimes bi-monthly) to ensure that the concentrations are below these levels. The groundwater wells vary in depth from ~15 to 65 meters, with water from the irrigation activities estimated to take approximately one to two years to reach the underlying groundwater (Crook et al., 1996; Richardson, 2010).

While PFAS are not currently part of the permit under which the WRF or the Living Filter site are operated, there is concern that PFAS compounds likely to be present in the influent will persist in the treated effluent and be inadvertently introduced to the Living Filter site during irrigation activities. Because PFAS compounds have been produced for decades and generally do not degrade, it is likely that the irrigation activities have been introducing PFAS into the Living Filter site for the entire duration of its operation, thereby potentially leading to widespread occurrence and potential accumulation of PFAS at the site. This research seeks to understand the implications of long-term wastewater irrigation activities on PFAS occurrence in groundwater and crop tissue. Study results have important implications to ensure that beneficial wastewater reuse activities achieve desired goals to reuse water and nutrients while ensuring PFAS levels are safe from a human health perspective.

Chapter 2. Research Objectives and Questions

2.1 Research Objectives

The research objectives for this study are as follows:

1. Quantify total measured PFAS in influent and effluent at the Penn State WRF and determine the extent to which PFAS are removed through the WRF;
2. Characterize PFAS spatial and temporal patterns across the site's 13 groundwater monitoring wells and compare the concentrations to proposed/existing drinking water standards; and
3. Determine PFAS concentrations in crop tissues at the time of harvest and estimate the amount of PFAS in livestock feed.

2.2 Research Questions

This study was motivated by the ensuing research questions:

1. What PFAS compounds are in the influent to the Penn State WRF, and is the WRF able to reduce those concentrations prior to irrigation?
2. How does PFAS concentration in groundwater vary across the Living Filter site, and to what extent does the PFAS concentration in each monitoring well change over the study period?
3. How does long-term beneficial reuse affect the occurrence of PFAS in crop tissue, and what are the implications for PFAS entering the food chain?
4. Given differences in policies at the state, federal, and international level for PFAS in drinking water, how would the ability to continue beneficial reuse of treated wastewater change if the groundwater concentrations were to need to meet potable water standards for PFAS?

Chapter 3. Methodology

3.1 General Overview and Flow Chart Methodology

A timeline and process for the study is detailed below in the flow chart, depicting the major steps taken as part of this study.

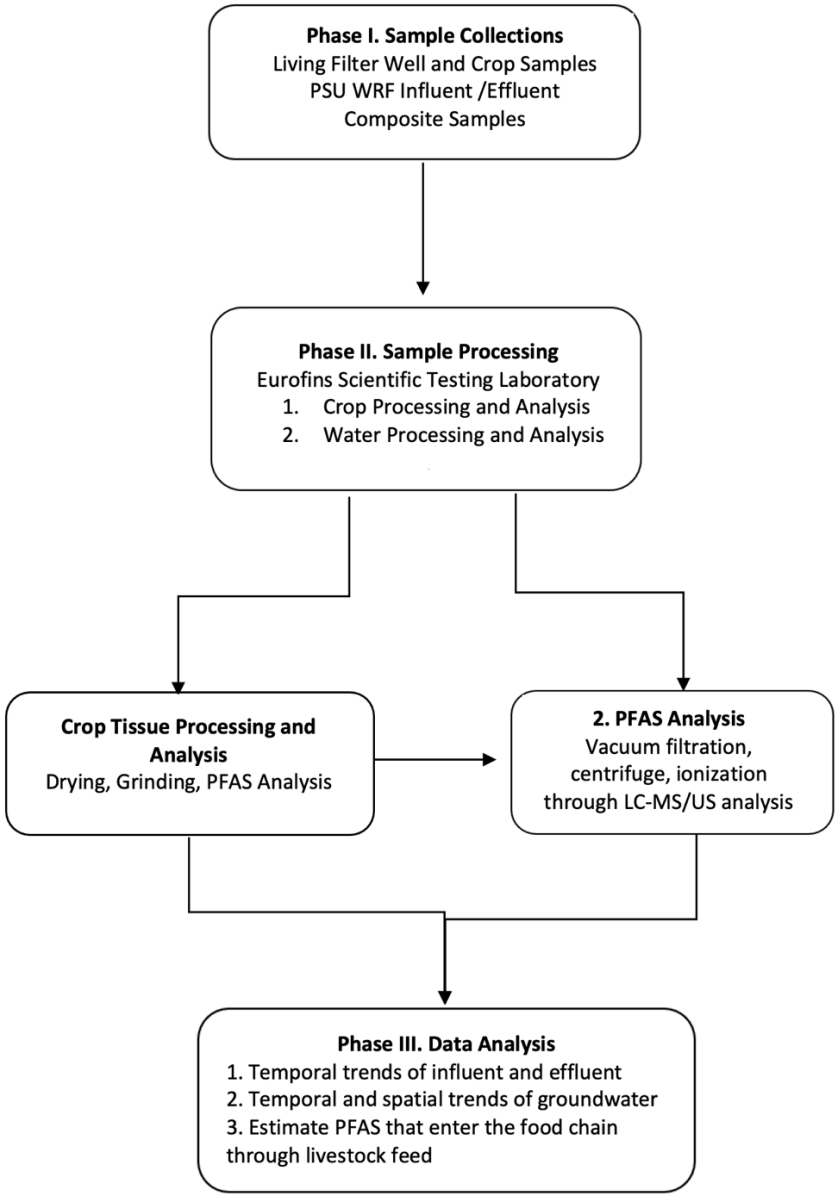


Figure 2. Research Flow Chart

3.2 Sampling and Analysis Methodology

3.2.1 Water Sample Collection and Analysis

The EPA has established recommended guidelines to be followed when sampling for PFAS known as EPA Method 537.1, Field Sampling Guidelines for PFAS (Blanks, 2020). Any samples that were collected during this study follows the EPA's Standard Operating Procedure. Sampling procedures states that those collecting any PFAS compounds should consider anything that might contain PFTE, Gore-Tex®, Tyvek®, or personal care products that are listed under the contamination list and avoid the use of anything containing these products. This includes sunscreen, hand lotions, cosmetics, and waterproof textiles like hiking books, raincoats, and gloves. Sampling procedures also states that any sampling materials that contain any of the listed products, such as PFTE and low-density polyethylene (LDPE), cause cross-contamination and should be avoided during sampling. Using high-density polyethylene (HDPE), stainless steel, silicone, acetate, or polypropylene are the only sampling materials allowed that will not cause PFAS contamination in the field or lab (Blanks, 2020; EPA Office of Research, 2019).

Samples were collected from three points of interest throughout the beneficial reuse system: (i) the wastewater treatment plant (influent and effluent); (ii) the Living Filter monitoring wells; and (iii) crop tissue (corn silage and fescue) from fields within the Living Filter site. All samples were collected in high density polypropylene plastic (HDPE plastic) per the EPA standard method 537.1 (USEPA, 2020).

Water samples from the PSU WRF were collected approximately bi-monthly from fall 2019 through winter 2021: specifically in October 2019; February, May, July, October, and December 2020; and February 2021. For both influent and effluent, 24-h composite samples were collected using automated (Teledyne ISCO) samplers equipped with flow sensors. Thus, smaller percentages of the cumulative sample were collected during low-flow periods of the day and higher percentages were collected during periods of high-flow at the treatment plant. Standard sampling equipment contains polytetrafluoroethylene (PTFE)-lined tubing, which can be a source of PFAS contamination. Therefore, all tubing in the samplers was replaced with HDPE alternatives.

Samples for the 13 monitoring wells were collected approximately bi-monthly from fall 2019 through winter 2021 during the same months as influent and effluent samples were collected. Each well was pumped for approximately 20 minutes prior to sample collection, following standard protocols for nitrate sampling required by the site's PA DEP permit. Once the well was pumped, water levels (elevation) were measured and recorded. During sampling at each of the 13 monitoring wells, a field blank was collected by opening a sample bottle filled with deionized (DI) water such that any PFAS contaminants present in the air that could affect the field sample were captured in the field blank. Samples were held in coolers on ice during sample collection in the field. When field sampling was complete, the monitoring well samples and field blank were transferred back to the PSU WRF where they were refrigerated at 4°C until they were shipped on ice overnight to Eurofins Lancaster Laboratories for PFAS analysis. The maximum sample hold time between sample collection and extraction is 90 days for aqueous samples (Shoemaker & Tettenhorst, 2018), and all samples were extracted within 30 days of collection. All samples were analyzed for 20 PFAS analytes (see Table 5) following EPA Method 537.1 to accommodate non-potable water samples.

Although the laboratory methods contain some proprietary information, the analysis method is summarized here briefly. First, aqueous samples were fortified with isotopically labeled extraction standards, extracted onto a solid-phase extraction cartridge, and eluted. The extract was then concentrated to a target volume of 400-500 µL using nitrogen in a heated water both and then reconstituted with methanol to a volume of 1 mL. Isotopically labeled injection standards were then added to the sample extract. The PFAS analysis was done by liquid chromatography-tandem mass spectrometry operated in negative electrospray ionization mode to detect and quantify the analytes, with quantitative analysis performed using isotope dilution. Samples were analyzed in batches no bigger than 20, with the following quality control samples included: on method blank, one laboratory control sample, one laboratory control duplicate, one matrix spike, and one matrix spike duplicate.

Table 5. The 20 Compound Analytes with common abbreviations and Limit of Detection for both Crop and Water samples

Analyte	Acronym	Method Detection Limit	
		Water (ng/L)	Crop Tissue (μg/kg wet weight)
11-chloroeicosafluoro-3oxaundecane-1-sulfonic acid	11Cl-PF3OUdS	0.42 - 0.50	0.18 - 0.20
9-chlorohexadecafluoro-3oxanonane-1-sulfonic acid	9Cl-PF3ONS	0.42 - 0.50	0.18 - 0.20
ammonium 4,8-dioxa-3H-perfluorononanoic acid	ADONA	0.42 - 0.50	0.18 - 0.20
2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3heptafluoropropoxy)-propanoic acid	HFPO-DA	0.42 - 0.50	0.37
N-ethyl perfluorooctanesulfonamidoacetic acid	N-EtPFOSAA	0.42 - 0.50	0.18 - 0.20
N-methylperfluorooctane sulfonamidoacetic acid	N-MePFOSAA	0.53 – 0.57	0.18 - 0.20
Short-Chain PFCAs			
Perfluoro-n-butanoic acid	PFBA	1.80 – 1.90	0.74 – 0.79
Perfluoro-n-pentanoic acid	PFPeA	0.42 - 0.50	0.18 - 0.20
Perfluorohexanoic acid	PFHxA	0.42 - 0.50	0.18 - 0.20
Perfluoroheptanoic acid	PFHpA	0.42 - 0.50	0.18 - 0.20
Long-Chain PFCAs			
Perfluorooctanoic acid	PFOA	0.42 - 0.50	0.18 - 0.20
Perfluorononanoic acid	PFNA	0.42 - 0.50	0.18 - 0.20
Perfluorodecanoic acid	PFDA	0.42 - 0.50	0.18 - 0.20
Perfluoroundecanoic acid	PFUnA	0.42 - 0.50	0.18 - 0.20
Perfluorododecanoic acid	PFDoDA	0.42 - 0.50	0.18 - 0.20
Perfluorotridecanoic acid	PFTrDA	0.42 - 0.50	0.18 - 0.20
Perfluorotetradecanoic acid	PFTeDA	0.42 - 0.50	0.18 - 0.20
Short-Chain PFSA			
Perfluorobutanesulfonic acid	PFBS	0.42 - 0.50	0.37
Long-Chain PFSAs			
Perfluorohexanesulfonic acid	PFHxS	0.42 - 0.50	0.18 - 0.20
Perfluorooctanesulfonic acid	PFOS	0.42 - 0.50	0.18 - 0.20

3.3.2 Crop Tissue Methodology and Analysis

Crop tissue samples were collected from fields at the Living Filter to determine the amount (i.e., mass) of PFAS in spring and fall 2020 harvest seasons, with samples collected in September 2020 for corn (harvested for silage) and June and October 2020 for endophyte free fescue (harvested for haylage). Because the crops are used in feed for the dairy cattle and other Penn State livestock, determining concentrations of PFAS in the crop tissue will help elucidate potential exposure to the livestock raised on campus.

At the time of harvest (September 22, 2020), farm services staff collected bulk samples of 500g (at harvest moisture) of corn into a PFAS-free HDPE container to be subsampled into five replicates for PFAS analysis. The fescue was used for haylage and could only be collected from areas of the Living Filter that were directly spray-irrigated due to fescue not being grown in the

non-irrigated portions of the site. Previous research has suggested that PFAS concentrations may be greater in later cuttings of a crop compared to the first (Ghisi et. al., 2019). Therefore, samples were collected (n=5) from the first and third cuttings (16 June and 23 October 2020) of fescue used for haylage that had been directly spray-irrigated. The second cutting was not included because it was harvested for baled hay instead of haylage.

Corn silage samples were collected using a forage harvester, dump truck, and table-baggers. Fescue samples were divided into silage and hay harvests. For silage production, a merger, forage harvester, dump truck, and table-bagger were all used. For hay production, a tedder or rake option, a round baler, and an optional bale mower were all used. For both harvests, a mower-conditioner were used. The Penn State Farm Operations and Services protocol does not consider the possibility of PFAS contamination, and so, there may be equipment and personal equipment that could add to the overall PFAS occurrence. This may include, but may not be limited to, harvesting machinery hoses, collection bins, heat or oil proofed machinery coatings, like paint, personal care products, and waterproof personal clothing articles. However, these harvesting methods represent the typical processes, and are appropriate here given that the goal was to assess PFAS in crop tissue under typical irrigation and harvesting methods.

Five replicates of each crop type (irrigated corn silage, non-irrigated corn silage, first cutting of fescue, third cutting of fescue) were taken to ensure that the results were consistent and representative of the crop harvest across the entire field. Given that the effects of the irrigation may result in samples closer to the irrigation laterals having higher PFAS masses than samples further away from the laterals, this replicate sampling aimed to avoid these effects skewing the results.

The samples were processed, once obtained from the Farm Operations, following the EPA Method 537.1. EPA Method 537.1 was established to create a standard protocol for sample collection and processing that would reduce any additional PFAS from being added to a sample and compromising results. Sampling to create the replicates was done using proper protective gear that was listed as approved by the EPA and put into 500 mL HDPE bottles. The bottles were labeled with the crop field identification, cut date, and if they were irrigated or non-irrigated.

These samples were then shipped on ice to Eurofins Lancaster Laboratories, where they were processed and analyzed according to EPA Method 537.1. Samples were analyzed for 20 target PFAS compounds (Table *1*) at Eurofins Lancaster Laboratories based on a modification of EPA Method 537.1 (Shoemaker & Tettenhorst, 2018) to accommodate plant tissue samples. Although the laboratory methods contain some proprietary information, the analysis method is summarized here briefly. Upon arrival at Eurofins, the samples were fortified with isotopically labeled extraction standards and extracted using ultrasonic extraction, and the extracts were then vortexed and centrifuged. A portion of the supernatant (2.0 mL) was transferred and concentrated with nitrogen in a heated water bath, reconstituted with methanol to 1.0 mL, and analyzed for target PFAS along with isotopically labeled PFAS injection standards by liquid chromatography-mass spectrometry following the same methods as for the aqueous samples. For each batch of samples, where a batch is no more than 20 samples, the following quality control samples were used: one method blank, one laboratory control sample, one laboratory control sample duplicate, one matrix spike, and one matrix spike duplicate.

It should be noted that based on current sampling methods, the results do not differentiate between the amount of PFAS present in the corn and fescue samples due to direct spray-irrigation (i.e., present on the surface of the crop) versus what was taken up by the crop. We are only able to report total PFAS compounds present in and on the plant tissue at the time of harvest. However, these samples are believed to be the first collected from an actual site that has been operating for agricultural production with treated wastewater as its spray-irrigation source for multiple decades. Additionally, the fields harvested for irrigated crops (corn silage and fescue) are adjacent and therefore irrigated at the same time and rates, such that differences in irrigation management of the laterals would not be a factor in this study.

3.3.3 Calculation methods for estimating PFAS loads consumed by livestock

Corn silage and haylage grown at the Living Filter site are used in the feed given to livestock raised on campus. Here, feed ration data were used for non-research dairy cattle due to concerns regarding transfer of PFAS into dairy products, and also due to the dairy cattle containing the highest percentage of their feed from corn silage and haylage grown at the Living Filter site. Feed ration data were obtained from Farm Operations (Table 6). Together, corn silage and

haylage represent approximately 42% of the diet (Table 6). PFAS concentrations reported by Eurofins were converted to a dry weight concentration using the wet weight of the sample and the moisture content of the sample at time of sample processing. Then, the dry weights of the feed rations were used to determine the total amount of PFAS in the feed at an annual scale. Any PFAS concentrations present in the crop tissue below the method detection limit was considered to be zero for purposes of these calculations. This approach may underestimate masses consumed.

Table 6. Daily feed rations for non-research milk cows raised at Penn State. Note that only corn silage and grass hay were analyzed for PFAS compounds.

Description	Dry Weight (kg/animal)	% Food Load
Roasted beans	2.50	8.76
Mineral + Optigen	0.57	1.99
Grass Hay	0.91	3.19
Canola Meal	3.41	11.95
Cookie Meal	2.04	7.17
Ground Corn	2.95	10.36
Whole Cotton Seed	1.36	4.78
Corn Silage	11.12	39.04
Alfalfa	2.27	7.97
Sugar (No glycerin)	1.36	4.78

3.3.4 Data Analysis Methods

Samples were processed by the Eurofins Lancaster Laboratories for all 20 of the PFAS analytes that were listed in Table 5. Some of the data were provided with a “J” notation associated with the concentration. The J notation indicated that the concentration was between the MDL and the LOQ. These numbers were estimated by Eurofins and were used included in the data analysis as though they were the reported values

In July 2020, Eurofins went through a system reporting change. There was no change in the methods for analyzing the samples, however, reports no longer included a J notation if the limit was between the MDL and LOQ. Rather, these values were reported as the given number. To ensure consistency in data analysis, all values included in reports that were between the MDL and LOQ were treated as though the number was a reported value. This was deemed a better approach than replacing all values between MDL and LOQ with the same number (e.g., average of MDL and LOQ or LOQ/2), as it allowed variability and took advantage of the estimates that Eurofins was able to provide.

Chapter 4. Results and Discussion

4.1 Wastewater Samples

Bi-monthly samples were collected from the WRF from October 2019 through February 2021, resulting in seven samples each of the influent and effluent. Of the 20 PFAS compounds that were analyzed, 10 analytes were observed at concentrations above the LODs (compound LODs provided in Table 5), with detectable concentrations of at least one compound in 100% of the samples. A summary of the PFAS concentrations in the influent and effluent is provided in Table *7*. Several of the analytes, including PFBA, PFNA, and PFHxS appear to have been reduced through the wastewater treatment process, with effluent concentrations lower compared to the influent concentrations (Table *7*). However, for the majority of PFAS compounds detected, concentrations either did not change significantly or were somewhat higher in the effluent compared to the influent, potentially due to the likely presence of precursor compounds that were not investigated as part of this current study. Interestingly, PFOS and PFOA were detected frequently (>85% of samples) despite being discontinued in the production of new consumer and industrial products in 2002 and 2015, respectively, but were generally each present at concentrations <10 ng L^{-1}. This could be from products imported from countries that have not phased out PFOS and PFOA, as well as older products still in use from before the phase out. Though both PFOA and PFOS persisted in the effluent, there was generally a decrease in the value from influent to effluent.

Table 7. Summary of PFAS concentrations (ng/L) for influent and effluent collected at the PSU WRF.

PFAS Compound	Influent			Effluent		
	% n > LOD	Range (ng/L)	Average (n > LOD) (ng/L)	% n > LOD	Range (ng/L)	Average (n > LOD) (ng/L)
PFBS	57.1	< LOD – 4.50	3.48	85.7	< LOD – 5.20	3.78
PFBA	57.1	< LOD – 27.0	15.60	57.1	< LOD – 13.0	9.40
PFDA	14.3	< LOD – 0.92	NA	42.9	< LOD – 1.30	0.84
PFHpA	57.1	< LOD – 3.00	2.80	100	3.50 – 12.0	6.81
PFHxS	100	9.40 – 41.0	15.7	85.7	< LOD – 5.00	3.55
PFHxA	57.1	< LOD – 3.90	3.38	100	12.0 – 41.0	26.7
PFNA	57.1	< LOD – 7.0	2.46	85.7	< LOD – 2.00	1.25
PFOS	100	< LOD – 63.0	14.1	100	4.00 – 11.0	6.99
PFOA	85.7	< LOD – 85.71	6.53	85.7	< LOD – 8.60	5.07

PFPeA	0	< LOD	NA	14.3	< LOD – 0.56	NA
Total measured PFAS	100	30.2 – 99.5	51.4	100	32.4 – 87.8	58.0

n = 7, with samples collected in Nov 2019, Feb, May, July, Oct, and Dec 2020, and Feb 2021.
LOD = 0.50 ng/L; Note that averages were calculated only for the concentrations above the LOD. NA = Not applicable, as less than 2 samples had a concentration above the LOD.

The concentrations of each of the PFAS compounds that were observed in the influent and effluent are depicted graphically in Figure 3. Little consistency was found within the overall contribution of each PFAS analyte over the period samples were taken for this study, though the newer, short chain PFAS compounds such as PFHxA and PFBA were found at higher concentrations than older, long chain compounds, such as PFOA and PFOS. The nearly threefold difference in concentrations observed for total measured PFAS over the study period may be due to the presence or absence of students on campus, especially given the unique situation from March 2020 through Summer 2020 when students were largely not on campus due to the COVID-19 pandemic, which resulted in substantially lower flowrates (up to 75% lower) compared with pre-pandemic flowrates.

Despite significant changes in the population contributing to the wastewater at the PSU WRF during the study period, the composition of the total measured PFAS observed in the effluent during the study period remained similar. Interestingly, PFOS and PFOA were detected frequently (>85% of samples) despite being discontinued in the production of new consumer and industrial products in 2002 and 2015, respectively, but were generally each present at concentrations <10 ng L^{-1}. The dominant PFAS observed in the effluent was PFHxA, which contributed to an average of 47% of the total measured PFAS in the effluent, with PFHpA and PFOS each contributing to ~12% and PFBA, PFBS, and PFOA contributing to an average of 5–8%. Although some students did return to campus in fall 2020, many classes were still offered in either mixed or fully remote mode, with most students not returning for in-person classes until mid-February 2021, near the end of our study period.

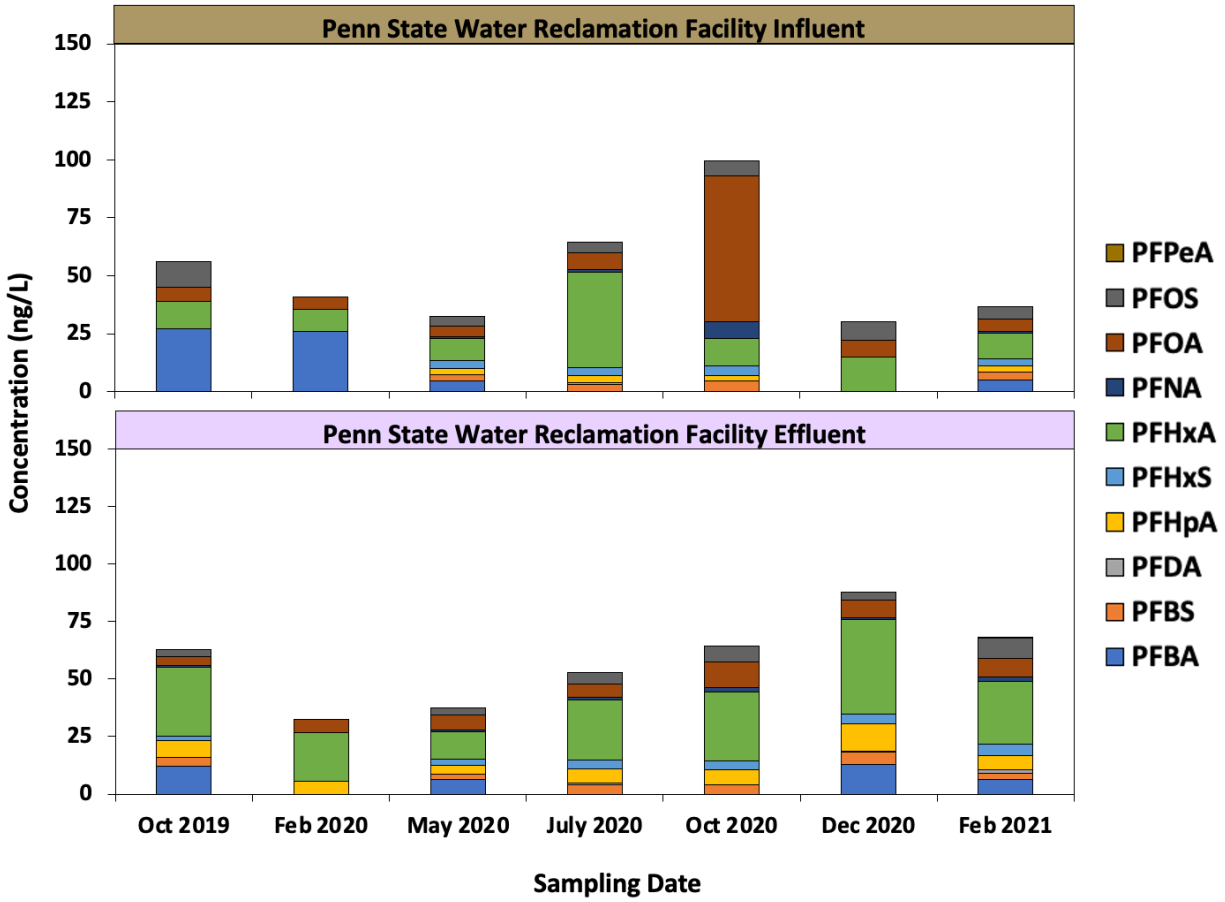


Figure 3. PFAS concentrations for each sampling date of the Influent and Effluent at the Penn State WRF. Note that the samples are 24-hr composite samples collected from the raw influent and final effluent, before being pumped to the Living Filter site

4.2 Well Water Samples

A total of 7 samples from each of the 13 monitoring well were collected between October 2019 and February 2021, for a total of 91 well water samples collected during the study period. Of the 20 PFAS compounds analyzed, the following were not found at detectable concentrations in any of the samples collected: 11-chloroeicosafluoro-3-oxaundecane-1sulfonic acid, 9-chlorohexadecafluoro-3-oxanonane-1-sulfonic acid, ammonium 4,8-dioxa-3H-perfluorononanoic acid, HFPO-DA, N-ethyl perfluorooctanesulfonamidoacetic acid, N-methylperfluorooctanesulfonamidoacetic acid, PFDA, perfluoroundecanoic acid, perfluorododecanoic acid (PFDoDA), perfluorotridecanoic acid, and perfluorotetradecanoic acid. A summary of the compounds with concentrations above the LOD for at least one sample is provided in Table 8 and

.

The total measured PFAS concentrations in the monitoring wells ranged from below the LOD to 155 ng L^{-1}. With the exception of Well W2, each of the monitoring wells had at least three PFAS present above the LOD (PFHxA, PFOA, and PFHxS), and the monitoring wells on the Astronomy site had at least eight PFAS present above the LOD (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFBS, PFHxS, and PFOS). The maximum observed combined concentration of PFOS+PFOA was 43 ng L^{-1} at Well W5 in December 2020.

Table 8. Summary of PFAS Concentrations per analyte (ng/L) for Monitoring Wells at the State Game Lands Site.

State Game Lands Site							
Well ID	W7	W2	G12	G10	W6	W5	W1
PFAS Compound	% n > LOD Range (ng/L) Avg. n > LOD (ng/L)	% n > LOD Range (ng/L) Avg. n > LOD (ng/L)	% n > LOD Range (ng/L) Avg. n > LOD (ng/L)	% n > LOD Range (ng/L) Avg. n > LOD (ng/L)	% n > LOD Range (ng/L) Avg. n > LOD (ng/L)	% n > LOD Range (ng/L) Avg. n > LOD (ng/L)	% n > LOD Range (ng/L) Avg. n > LOD (ng/L)
Short-chain PFCAs							
PFBA	0% < LOD NA	0% < LOD NA	100% 4.2 – 6.0 5.1	100% 10.0 -13.0 11.1	100% 14.0 – 19.0 16.3	100% 10.0 – 13.0 11.1	29% < LOD – 2.0 NA
PFPeA	0% < LOD NA	0% < LOD NA	57% < LOD – 9.4 5.3	100% 0.72 – 21.0 6.6	100% 0.80 – 31.0 9.2	86% < LOD – 21.0 7.2	29% < LOD – 3.1 NA
PFHxA	14.3% < LOD – 1.1 NA	0% < LOD NA	100% 6.0– 7.5 6.7	100% 15.0 – 19.0 17.7	100% 19.0 – 28.0 24.3	100% 15.0 – 19.0 17.1	100% 1.7 – 2.4 2.1
PFHpA	0% < LOD NA	0% < LOD NA	100% 2.4 – 2.6 2.5	100% 6.2 – 7.8 7.3	100% 9.1 – 12.0 10.3	100% 5.9 – 8.3 7.3	100% 1.1 – 1.5 1.3
Long-chain PFCAs							
PFOA	14.3% < LOD – 0.96 NA	0% < LOD NA	100% 5.3 – 7.6 6.17	100% 18.0 – 22.0 18.9	100% 24.0 – 30.0 26.9	100% 17.0 – 24.0 21.3	100% 2.4 – 3.6 3.0
PFNA	0% < LOD NA	0% < LOD NA	0% < LOD NA	100% 0.63 – 1.0 0.84	100% 0.6 – 1.2 1.01	100% 2.6 – 3.5 3.0	0% < LOD NA
Short-chain PFSA							
PFBS	0% < LOD NA	0% < LOD NA	100% 1.1 – 1.4 1.3	100% 3.4 – 4.0 3.7	100% 4.7 – 5.6 5.1	100% 2.7 – 3.3 2.9	100% 2.3 – 4.5 3.2
Long-chain PFSAs							
PFHxS	14.3% < LOD – 0.69 NA	0% < LOD NA	100% 3.1 – 4.6 4.0	100% 11.0 – 15.0 13.4	100% 17.0 – 25.0 10.1	100% 7.0 – 9.1 8.1	100% 1.5 – 1.8 1.7
PFOS	0% < LOD NA	0% < LOD NA	100% 1.0 – 2.0 1.6	100% 5.0 – 7.2 6.5	100% 5.0 – 7.7 6.4	100% 16.0 – 21.0 18.1	100% 3.4 – 8.0 5.4
Total measured PFAS	14.3% < LOD – 2.75 NA	0% < LOD NA	100% 24.8 – 41.1 30.4	100% 72.2 – 108.8 86.0	100% 102.6 – 155.3 106.0	100% 79.2 – 118.4 95.2	100% 13.6 – 22.5 18.1

n = 7, with seven samples for each well collected in: Oct 2019, Feb, May, July, Oct, Dec 2020, and Feb 2021.
LOD = Limit of detection; Note that averages were calculated using a value of 0 when the concentration was less than the LOD NA = not applicable because fewer than three samples contained concentrations above the LOD.

Table 9. Summary of PFAS Concentrations (ng/L) for Monitoring Wells at the Astronomy Site

Astronomy Site						
Well ID PFAS Compound	P5	P4	P3	F3	P2	P1
	% n > LOD Range (ng/L) Avg. n > LOD (ng/L)	% n > LOD Range (ng/L) Avg. n > LOD (ng/L)	% n > LOD Range (ng/L) Avg. n > LOD (ng/L)	% n > LOD Range (ng/L) Avg. n > LOD (ng/L)	% n > LOD Range (ng/L) Avg. n > LOD (ng/L)	% n > LOD Range (ng/L) Avg. n > LOD (ng/L)
Short-chain PFCAs						
PFBA	100% 6.9 – 9.0 7.9	43% < LOD – 2.5 2.3	100% 5.5 – 8.2 6.5	100% 11.0 – 13.0 11.7	100% 12.0 – 15.0 14.0	100% 11.0 – 15.0 12.9
PFPeA	43% < LOD – 15.0 9.8	29% < LOD – 1.3 NA	43% < LOD – 13.0 8.2	100% 0.46 – 23.0 6.8	100% 0.48 – 0.70 8.4	86% < LOD – 26.0 7.7
PFHxA	100% 9.9 – 16.0 12.6	100% 1.1 – 1.6 1.2	100% 9.5 – 16.0 11.4	100% 16.0 – 22.0 18.3	100% 20.0 – 25.0 22.6	100% 20.0 – 22.0 20.9
PFHpA	100% 4.1 – 6.1 5.2	100% 0.54 – 0.65 0.62	100% 4.7 – 6.1 5.3	100% 6.2 – 9.0 7.7	100% 9.0 – 11.0 10.1	100% 7.9 – 9.1 8.5
Long-chain PFCAs						
PFOA	100% 12.0 – 17.0 13.7	100% 1.1 – 1.4 1.3	100% 9.6 – 13.0 11.5	100% 9.1 – 21.0 17.4	100% 19.0 – 30.0 24.3	100% 16.0 – 20.0 19.3
PFNA	100% 0.80 – 1.2 1.06	0% < LOD < LOD	0% < LOD < LOD	71% < LOD – 0.83 0.71	100% 1.2 – 1.9 1.5	100% 2.0 – 2.9 2.4
Short-chain PFSAs						
PFBS	100% 2.2 – 2.7 2.4	100% 1.2 – 1.5 1.3	100% 1.9 – 2.5 2.1	100% 2.8 – 3.6 3.2	100% 3.4 – 4.2 3.8	100% 3.4 – 4.5 3.9
Long-chain PFSAs						
PFHxS	100% 6.1 – 8.9 7.5	86% < LOD – 0.55 0.51	100% 4.0 – 6.2 5.0	100% 7.5 – 9.5 8.6	100% 10.0 – 12.0 11.0	100% 9.3 – 12.0 10.6
PFOS	100% 7.9 – 9.0 8.34	86% < LOD – 0.53 0.51	100% 1.3 – 1.8 1.6	86% < LOD – 6.9 5.2	100% 7.4 – 12.0 97	100% 15.0 – 22.0 18.3
Total PFAS	100% 50.6 – 77.8 62.9	100% 4.7 – 7.8 6.5	100% 40.6 – 58.0 47.0	100% 61.7 – 100.0 79.6	100% 82.5 – 135.6 105.3	100% 84.6 – 126.2 104.3

n = 7, with seven samples for each well collected in: Oct 2019, Feb, May, July, Oct, Dec 2020, and Feb 2021.
LOD = Limit of detection; Note that averages were calculated using a value of 0 when the concentration was less than the LOD NA = not applicable because fewer than three samples contained concentrations above the LOD.

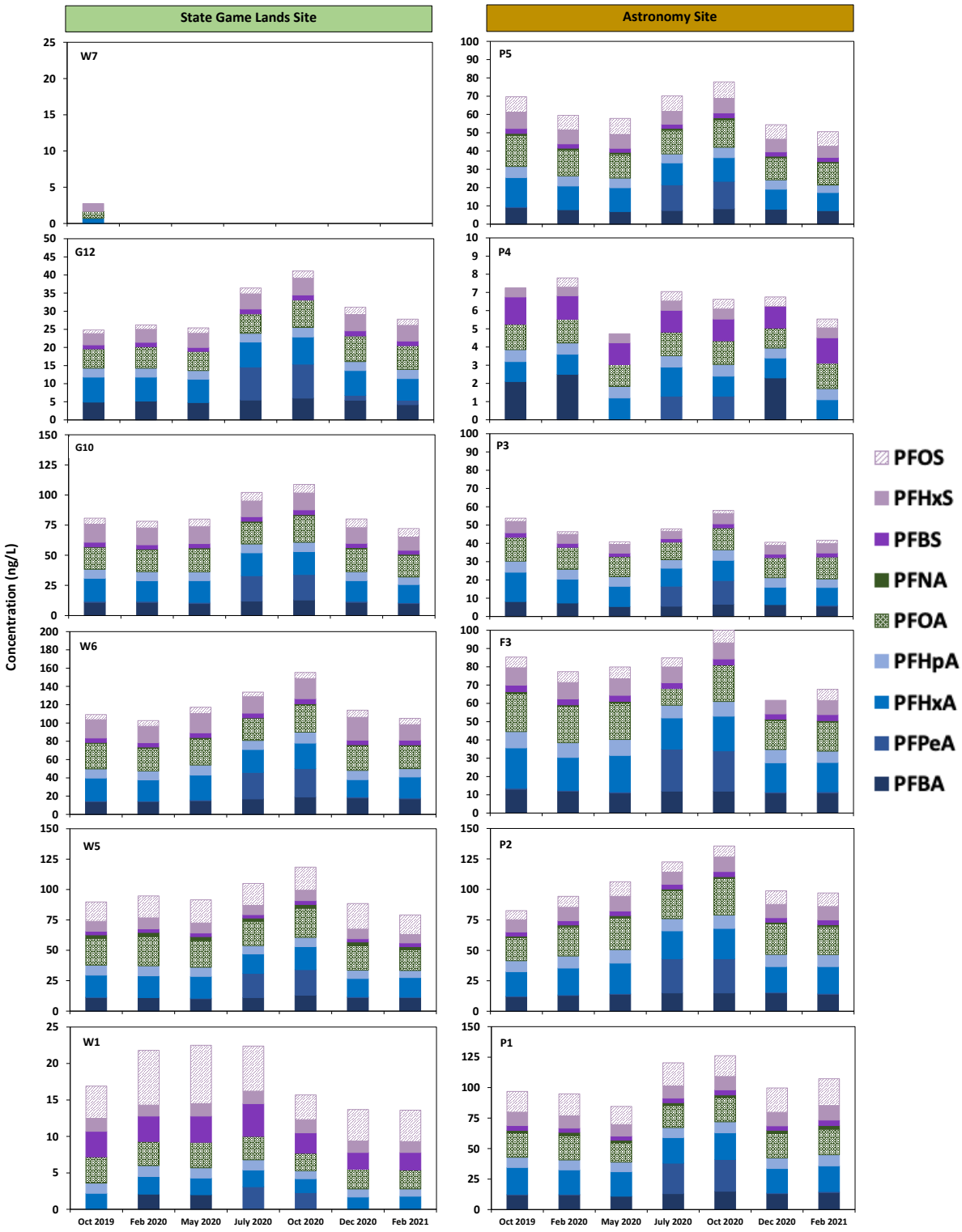


Figure 4. Per- and polyfluoroalkyl substance concentrations observed for each sampling date for each of the monitoring wells at the State Game Lands site (left) and the Astronomy site (right). Please note the differences in y-axis ranges. Also note that W2 is not included on the figure because no measured PFAS were present at detectable levels. PFBA, perfluorobutanoic acid; PFBS, perfluorobutane sulfonic acid; PFHpA, perfluoroheptanic acid; PFHxA, perfluorohexanoic acid; PFHxS, perfluorohexanesulfonic acid; PFNA, perfluorononanoic acid; PFOA, perfluorooctanoic acid; PFOS, perfluorooctane sulfonate; PFPeA, perfluoropentanoic acid

Previous research on the presence of pharmaceuticals in the monitoring wells at the Living Filter showed strong temporal variations in concentrations, with pharmaceutical concentrations higher in the colder months and lower in the warmer months (Kibuye et al., 2019). In contrast, PFAS observed in the monitoring wells exhibited no strong temporal patterns and very low variability overall (Table 10).

Low temporal variability in the total measured PFAS concentrations throughout the study period is likely a function of several factors. While usage of pharmaceuticals, especially antibiotics, are known to follow seasonal patterns, with lower usage in warmer months compared to higher usage in colder months, sources of PFAS to wastewater effluent are likely more constant over time. Further, the degradation rates of most pharmaceuticals previously studied at the Living Filter site (see Kibuye et al., 2019) are on the order of days (Monteiro and Boxall, 2010; Walters et al., 2010; Wu et al., 2012) while the half-lives of PFAS are estimated to be on the order of decades and longer (Washington et al., 2019). Therefore, higher concentrations of pharmaceuticals in the colder months are likely due to both increased usage during colder months and lower degradation rates once introduced to the Living Filter site through wastewater irrigation activities.

Table 10. Coefficient of variation (CV) of total PFAS concentrations (ng/L) for monitoring wells throughout the Living Filter

State Game Lands Site							
Well ID	W7	W2	G12	G10	W6	W5	W1
CV	N/A	N/A	0.11	0.06	0.09	0.09	0.23
Astronomy Site							
Well ID	P5	P4	P3	F3	P2	P1	
CV	0.20	0.19	0.17	0.17	0.10	0.10	

Additionally, the total measured PFAS concentrations were comprised largely of terminal degradation products, with PFBA, PFPeA, PFHxA, PFHpA, PFOA, and PFOS contributing to 72-85% of the total measured PFAS observed at each well throughout the study period, such that they would not be affected by the biological, physical, and chemical processes driving degradation of the pharmaceutical compounds. Therefore, the coefficients of variation (CV) for total measured PFAS concentrations in each well over the study period was low, with values ranging from 0.06 (G10) to 0.23 (W1). Generally, the wells with the highest total measured PFAS concentrations

exhibited the lowest CV values (Figure 5), suggesting that the more impacted a well is, the lower the variability in concentrations. During the study period, groundwater elevations remained relatively constant across the study site: nine of the 13 wells varied less than 5 m, with the greatest difference during the study period ~ 13 m for well W6. No strong relationships between groundwater elevation and total measured PFAS concentrations were found (Figure 6); however; weak inverse relationships between total measured PFAS concentrations and groundwater elevation were observed in wells G10 and G12 on the State Game Lands Site and P1, P2, and P3 on the Astronomy Site (well locations shown in Figure 7). This suggests that, for several of the wells, PFAS concentrations were diluted when groundwater elevation was higher. Wells that had a weak positive relationship between groundwater elevation and PFAS concentrations (W1, P5, and F3) were generally positioned on the outer portions of the site (Figure 7), with the groundwater direction primarily away from rather than towards them. Thus, PFAS concentration increases for W1, P5, and F3 were likely due to vertical transport through the soil profile during infiltration events. In these cases, PFAS concentrations had to travel shorter distances through the soil profile to reach the groundwater table when the groundwater elevations were higher.

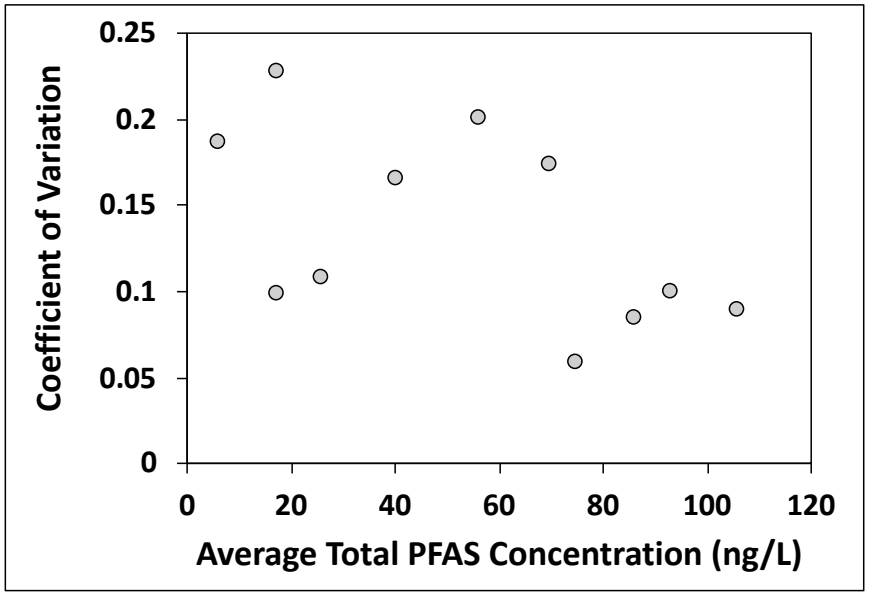


Figure 5. Coefficient of variation (CV) of total PFAS concentrations as a function of average PFAS concentrations for each monitoring well throughout the Living Filter over the period of the study (Fall 2019- Winter 2021)

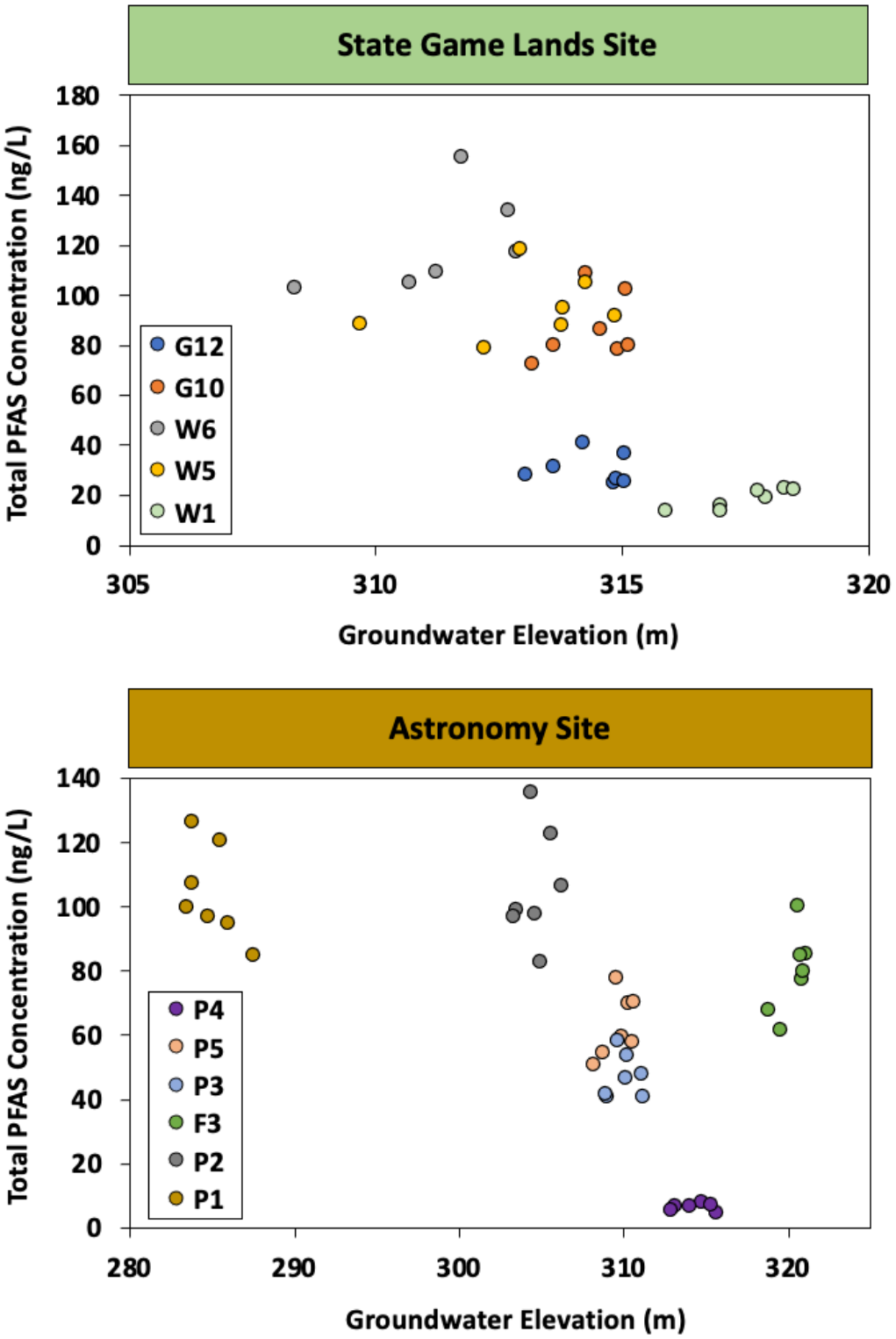


Figure 6. Total measured PFAS concentrations as function of groundwater elevations for the State Game Lands Site (left) and Astronomy Site (right). Data for W2 and W7 are not shown in this figure since the number of samples with detected PFAS concentrations was zero for W2 and only one for W7.

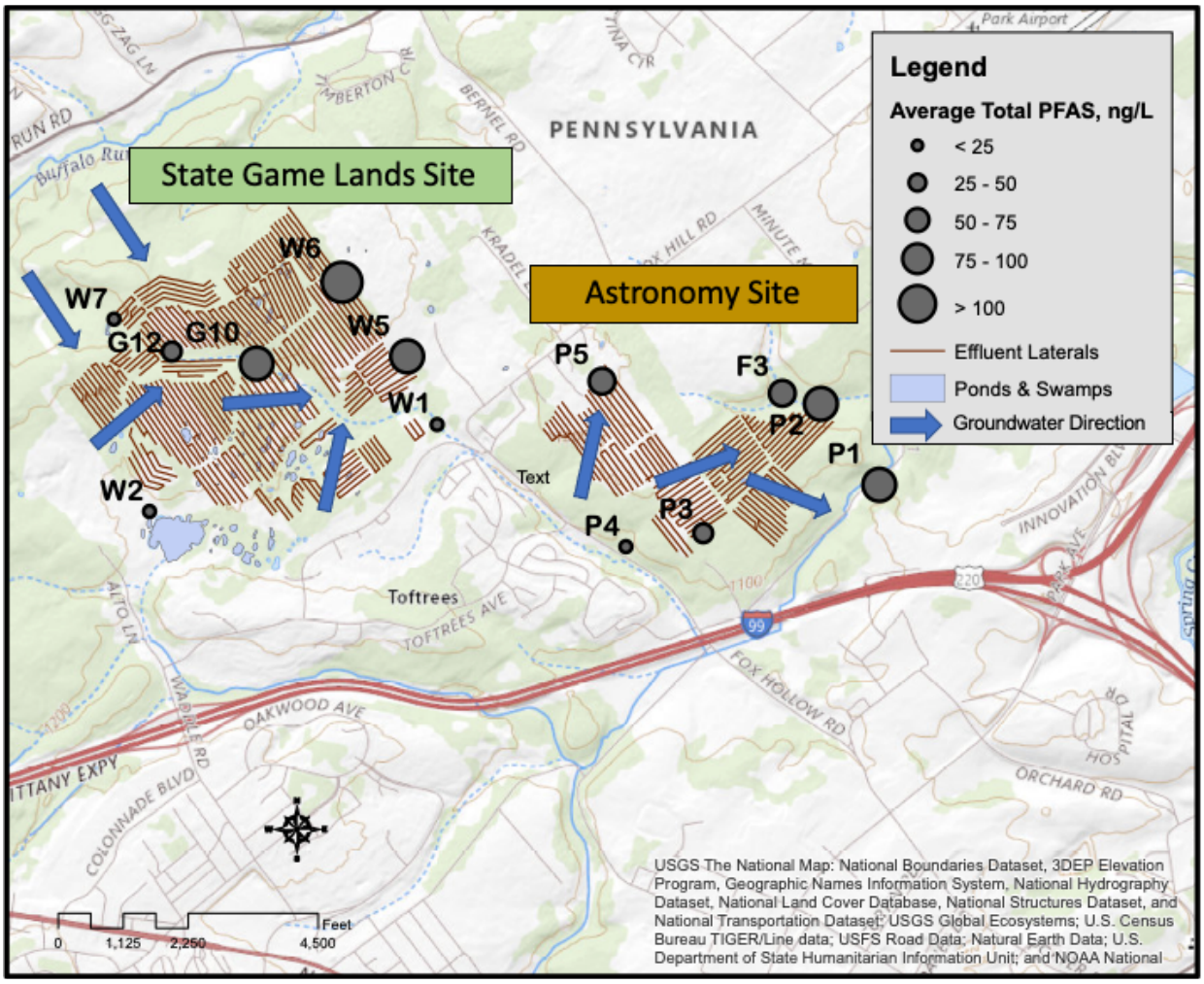


Figure 7. Average total PFAS concentrations at each of the monitoring wells throughout the Living Filter for the study period (October 2019 through February 2021)

A spatial assessment of the total measured PFAS concentrations revealed that the concentrations generally followed the groundwater flow direction across the Living Filter on both the State Game Lands and Astronomy Sites (Figure 7). The lowest concentrations were observed in wells on the outer boundaries of the Living Filter that were least influenced by irrigation activities, while highest concentrations were towards the northeastern portions of the sites. Groundwater at the State Game Lands Site generally flows from W7 and W2 toward G12 and G10; and from W1 toward W5. Spatial trends in total measured PFAS concentrations followed these general hydrologic trends, with the undetectable total measured PFAS concentrations in W2 and W7 gradually increasing to the highest total measured PFAS concentrations in W6 and W5. Similar patterns were observed on the Astronomy Site, with concentrations increasing from P4 and P3 to F3 and P2, following the general groundwater direction (Figure 7).

Overall, the spatial pattern of PFAS at the Living Filter suggest a PFAS gradient across the site, with increasing concentration in the groundwater due to infiltration and aquifer recharge of surface-applied effluent at various points along the groundwater flow path. The spatial patterns of PFAS at the Living Filter site follow similar patterns to those observed by Kibuye et al. (2019) for some pharmaceuticals, with well P2 having the highest concentrations of acetaminophen, ampicillin, ofloxacin, and trimethoprim on the Astronomy site and W5 having the highest concentration of naproxen on the State Game Lands side. These wells, along with W6, G10, P1, and P5, have also been observed to have elevated nitrate concentrations in comparison to other wells at the Living Filter. Therefore, wells with higher PFAS concentrations across the Living Filter appears to be consistent with higher concentrations of some pharmaceuticals and nitrate.

For each monitoring well, the relative contribution of each of the 20 PFAS analyzed remained relatively constant over time and the results were generally similar between monitoring wells on the State Game Lands and Astronomy Sites of the Living Filter (Figure 4). For wells G10, G12, W6, and W5, PFHxA and PFOA each contributed approximately 25% of the total measured PFAS concentrations observed, while PFHpA, PFBA, and perfluorohexanesulfonic acid (PFHxS) each contributed 10 to 15%. PFOS contribution to the total measured PFAS concentrations for each of wells G10, G12, and W6 was less than 10%, but approximately 20% for W5. For well W1, PFBS and PFOA each contributed approximately 20% of the total observed PFAS concentrations, whereas PFOS comprised approximately 30% throughout the study period.

At the Astronomy Site, PFOS and PFHxA also contributed between 20 and 30% of the total measured PFAS concentrations observed throughout the period of study for each of the monitoring wells. These results were similar to percent contributions of PFOS and PFHxA to the total observed PFAS concentrations on the State Game Lands Site. That is, PFBA, PHFpA, and PFHxS contributed to between 10 and 15% of the total measured PFAS concentrations observed for each monitoring well. PFOS contributions to the total measured PFAS concentrations varied from < 5% for P3 to approximately 20% for P1.

4.3 Wastewater and Monitoring Wells Comparison

Average total measured PFAS concentrations were generally on the same order of magnitude for the influent, effluent, and monitoring wells from the State Game Lands and the Astronomy Sites (Tables 7, Table 8). PFAS concentrations across the PSU WRF remained relatively constant across all sampling locations and times. This contrasts with observations for pharmaceuticals at the site, where Kibuye et al. (2019) found that average concentrations were as much as two orders of magnitude smaller in the monitoring wells relative to effluent, and the PSU WRF treatment processes could remove some pharmaceuticals by more than 90%. PFAS have been found to be persistent on the order of decades and longer (e.g., Washington et al., 2019) and thus would not exhibit enhanced degradation rates during warmer months that has been observed for many pharmaceuticals. Given their ubiquitous use, PFAS are also less likely to exhibit seasonal variability in effluent, unlike some pharmaceuticals where use is often tied to seasonal events (e.g., flu season, allergy season). Thus, given constant input and the recalcitrant nature of PFAS, PFAS concentrations at this study site exhibiting low variability in wastewater and groundwater is consistent with expectations.

Previous studies have shown that some PFAS have an affinity for soil organic carbon, with higher concentrations typically found near the soil surface and decreasing with increasing depths in the profile of soil and streambed sediment (Fabregat-Palau et al., 2021; Li et al., 2019; Navarro et al., 2022), which is consistent with observations at the Living Filter for hormones (Woodward et al., 2014) and carbamazepine (Filipović et al., 2020). Thus, we would anticipate that effluent-irrigated soil would reduce or slow down the transport of these chemicals to groundwater, serving as a sink for PFAS storage. While effluent irrigation would reduce the immediate release of PFAS to surface water, the sink-source dynamics of the soil may lead to a long-term source to groundwater. A soil core study at the Living Filter found significantly higher mass storage of PFAS at the soil surface than the mass applied via effluent irrigation on an annual basis (Jahn et al., 2021). Jahn et al. (2021) also found PFOA and PFOA storage to be significantly greater than the mass applied via annual effluent irrigation, suggesting a trade-off between immediate PFAS release into surface water, or beneficial reuse serving as a long-term source to groundwater.

4.4 Crop Samples

Fresh corn silage samples harvested in Fall 2020 contained detectable concentrations of PFBA in both the irrigated and non-irrigated samples (Table 11), with irrigated replicates containing 0.83 – 0.95 μg/kg dry weight (dw) of PFBA. Only two non-irrigated replicates had detectable PFBA concentrations (0.56 and 0.83 μg/kg dw). The remainder of the 20 PFAS analyzed for in this project were largely below the method detection limits, with detectable concentrations of HFPO-DA in one of the five replicates for non-irrigated corn silage and detectable concentrations of PFHxA in one of the five replicates for irrigated corn silage (Table 11). The preferential uptake of PFBA, a short-chain PFCA, has been observed in other studies (Blaine et al., 2013, 2014; Navarro et al., 2017; Liu et al., 2019). Muschket et al. (2020) found that PFBA was detected at the highest concentrations in maize leaves. For corn silage harvested from the Living Filter, the presence of PFBA in non-irrigated samples could arise from atmospheric deposition, since its high volatility is conducive to long-range atmospheric transport (Wang et al., 2022), in addition to drift at the site and/or groundwater.

Table 11. PFAS concentrations (μg/kg wet weight) of irrigated and non-irrigated corn samples harvested for silage on September 22, 2020. Each sample is a replicate. LOD = Limit of Detection (see LOD values in Table 6). Moisture content ranged from 28.5 – 45.2% (36.5 ± 6.8%) for the irrigated corn silage and from 30.5 – 50.5% (42.1 ± 8.5%) for the non-irrigated corn silage.)

Irrigated Corn, Fall 2020					
PFAS Compound	Replicate #1	Replicate #2	Replicate #3	Replicate #4	Replicate #5
HFPO-DA	< LOD	< LOD	< LOD	< LOD	< LOD
PFBA	1.3	1.5	1.4	1.4	1.3
PFHxA	< LOD	0.72	< LOD	< LOD	< LOD
Non-Irrigated Corn, Fall 2020					
PFAS Compound	Replicate #1	Replicate #2	Replicate #3	Replicate #4	Replicate #5
HFPO-DA	< LOD	< LOD	< LOD	< LOD	0.4
PFBA	1.3	< LOD	< LOD	0.89	< LOD
PFHxA	< LOD	< LOD	< LOD	< LOD	< LOD

4.4.2. Fescue Haylage

PFAS in fescue samples (Table 12) also showed the preferential uptake of shorter-chain PFCAs (PFBA, PFPeA, and PFHxA) which has been documented for grasses previously (García-Valcárcel et al. 2014). Fresh fescue tissue samples harvested in Spring 2020 contained detectable

concentrations of PFBA (5.4 ± 3.0 μg/kg, dw) in all five replicates and PFOS (0.29 ± 0.07 μg/kg, dw) in four of the five replicates (Table 12). PFOA was also detected in one of the five replicate samples from the Spring 2020 harvest. PFOA and PFOS, both long-chain PFAS, were either below their LODs or detected at levels below the shorter-chain PFAS, consistent with previous literature (Ghisi et al., 2019). The remainder of the 20 PFAS analyzed were below their respective LODs. However, data collected from the Fall 2020 harvest showed a wider range of PFAS present at detectable concentrations, with HFPO-DA, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFHxS, and PFOS observed at detectable concentrations in at least one of the five replicates (Table 12).

Table 12. PFAS concentrations (μg/kg wet weight) in fescue samples harvested for haylage on June 16, 2020, and November 4, 2020. Each sample is a replicate. LOD = Limit of Detection (see LOD values in Table 6). Moisture content ranged from 22.8 – 42% (33.1 ± 7.1%).

Spring 2020 Cutting of Fescue Samples					
PFAS Compound	Replicate #1	Replicate #2	Replicate #3	Replicate #4	Replicate #5
HFPO-DA	< LOD	< LOD	< LOD	< LOD	< LOD
PFBA	< LOD	< LOD	< LOD	< LOD	< LOD
PFPeA	0.95	1.1	0.71	0.78	0.91
PFHxA	15.0	17.0	12.0	17.0	15.0
PFHpA	< LOD	< LOD	< LOD	< LOD	0.19
PFOA	0.24	0.28	0.25	0.37	< LOD
PFHxS	< LOD	< LOD	< LOD	< LOD	< LOD
PFOS	0.51	0.65	0.48	0.56	0.52
Total measured PFAS	16.70	19.03	13.44	18.71	16.62
Fall 2020 Cutting of Fescue Samples					
PFAS Compound	Replicate #1	Replicate #2	Replicate #3	Replicate #4	Replicate #5
HFPO-DA	0.94	< LOD	< LOD	< LOD	< LOD
PFBA	2.4	2.7	4.8	2.6	3.1
PFPeA	0.88	1.2	1.4	1.1	1.1
PFHxA	0.59	0.41	0.56	< LOD	< LOD
PFHpA	< LOD	< LOD	< LOD	< LOD	< LOD
PFOA	0.24	< LOD	< LOD	0.23	0.22
PFHxS	< LOD	< LOD	0.2	< LOD	< LOD
PFOS	0.59	0.41	0.56	0.38	0.51
Total measured PFAS	5.64	4.72	7.52	4.31	4.93

*Note that to provide conservative estimates, any PFAS concentration present below the limit of detection (Table 6) was considered to be zero for purposes of these calculations.

The Spring and Fall cuttings contained an average total measured PFAS concentrations of 11.3 ± 1.5 and 3.8 ± 0.88 μg/kg dw, respectively. The largest contributor to total measured PFAS concentrations in the Spring cutting was PFHxA, which comprised 90% of the total measured

PFAS concentration. PFHxA was detected in 100% of the wastewater effluent samples at concentrations ranging from 12 to 41 ng/L (Table 7), and therefore perhaps unsurprising that it was detected in the spring fescue tissue samples. Moreover, while many PFAS are strongly retained in plant roots, (Navarro et al. 2022) found that PFHxA was easily translocated to above-ground plant parts.

For the fall cutting of fescue, PFHxA was near the LOD and detected in 4 of the 5 replicates (Table 13), with PFBA the dominant contributor (~56%) to the total measured PFAS concentrations, similar to the findings of Muschket et al. 2020. PFBA was present in the wastewater effluent in 86% of the samples collected (Figure 4; Table 7) at concentrations up to 13 ng/L. Irrigation activities at the Living Filter are operated such that laterals associated with crop fields on the Astronomy Site are run more frequently in spring and summer, with forested land use irrigated more frequently in the fall and winter. This allows the facility to optimize usage of the wastewater to meet crop demands during the growing season while operating within the site's permit requirements. This emphasis on crop irrigation in the spring and summer may have led to the elevated concentrations (2-3 times higher) observed in the Spring 2020 harvest of fescue compared to values observed in Fall 2020.

4.4.3 Implications for Animal Feed

Fescue and corn harvested from the Living Filter are fed as haylage and silage, respectively, to livestock raised at PSU. The diet consumed by non-research dairy cows includes 2 kg/animal/d of corn silage and 24.5 kg/animal/d of fescue haylage (dw). Overall, these two products comprise ~42% of the feeding ration for these dairy cows. Based on this diet and the observed PFAS concentrations in the corn and fescue samples, these dairy cows consume an estimated 15.3 mg/animal/yr to 46.2 mg/animal/yr (dw) of total measured PFAS (Table 13). The difference in PFAS concentrations of feed comprised of irrigated versus non-irrigated corn silage was <2%, as corn silage comprised only ~3% of the daily ration. The PFAS estimated to be in the livestock feed in this current study were at least two orders of magnitude less than those in the Kowalczyk et al. (2013) study (0.06-0.19 μg/kg body weight compared to 14.7 μg/kg body weight).

Table 13. PFAS masses consumed annually by non-research dairy cows fed corn (irrigated and non-irrigated) and irrigated fescue harvested from the Living Filter spray-irrigation facility.

PFAS	2020 Irrigated Corn + Spring 2020 Fescue (mg/animal/yr)	2020 Non-Irrigated Corn + Spring 2020 Fescue (mg/animal/yr)	2020 Irrigated Corn + Fall 2020 Fescue (mg/animal/yr)	2020 Non-Irrigated Corn + Fall 2020 Fescue (mg/animal/yr)
HFPO-DA	0.00	0.19	0.04	0.23
Short-Chain PFCAs				
PFBA	3.55	1.03	4.24	1.72
PFPeA	0.01	0.20	0.25	0.25
PFHxA	3.74	3.37	0.48	0.11
PFHpA	0.01	0.01	0.00	0.00
Long-Chain PFCA				
PFOA	0.05	0.05	0.03	0.03
Long-Chain PFSAs				
PFHxS	0.00	0.00	0.01	0.01
PFOS	0.12	0.12	0.10	0.10
Total measured PFAS	7.67	4.96	6.17	2.46

*Note that any PFAS concentration present below the method detection limit (Table 1) was considered to be zero for purposes of these calculations; this approach may underestimate masses consumed.

Of specific concern for human health following PFAS consumption by dairy cattle is the potential for PFAS to enter the food chain by secretion into milk or accumulation in tissue. Kowalczyk et al. (2013) found that short-chain compounds were more likely to be present in milk of Holstein dairy cows, while long-chain compounds tended to accumulate in tissue. Houde et al. (2011) had previously reported increasing bioaccumulation rates with increasing perfluoroalkyl carbon chain lengths Although the specific processes controlling the biomagnification and biotransfer of PFAS in tissue and milk are unclear and appear to vary by compound and animal. Vestergen et al. (2013) reported high biomagnification factors (10-20) for PFOS and PFDA in dairy cattle liver tissue compared to muscle tissue (1.1-1.3) and low values (< 1) for PFOA in both types of tissue. Vestergen et al. (2013) also reported that the highest biotransfer factor (BTF) to milk was for PFOA (log BTF = -1.95) and lowest for PFDoDA (log BTF = -1.52). Zhao et al. (2012) and Conder et al. (2008) have found that PFAS accumulation is greater for PFSAs compared to PFCAs with the same perfluorinated carbon chain length due to differences in their functional groups.

Compounds detected in the feed in the current study were overwhelmingly short-chain PFCAs, suggesting potential for milk from the dairy cattle consuming crops from the irrigated site to contain PFAS. For corn harvested in fall 2020 and fescue harvested in spring 2020, approximately 3% of the total measured PFAS detected in the feed were long-chain compounds (PFOS and PFOA; see Table 13), while the remaining 97% was the short-chain compound PFBA. For the corn harvested in fall 2020 and fescue harvested in fall 2020, short-chain PFCAs (PFBA, PFPeA, and PFHxA; see Table 13) comprised ~87% of the total measured PFAS detected in the feed, while the remaining 13% was comprised of long-chain compounds (PFHxS, PFOS, and PFOA; see Table 13). However, the relationship between PFAS occurrence in feed and milk is unclear. Liu et al. (2022) collected 107 raw milk samples and 70 cow feed samples from nine provinces in China and found that while PFBA was the most commonly detected PFAS in feed, PFOS dominated in milk, and no correlations were found between PFAS in paired feed and milk samples. Further, it is unclear what specific levels of PFAS present in the feed may lead to unsafe levels of PFAS in milk, although there appears to be movement in some states (e.g., Maine) to reimburse dairy farmers for lost revenue due to PFAS contamination in milk (Farm Service Agency, 2021), and Liu et al. (2022) found the hazard risk quotients of PFAS in milk were higher for children than adults, with PFOS having the highest risk quotient.

Milk samples collected after a feeding study of Holstein dairy cows found accumulation of PFHxS and PFOS in the milk, while PFBS and PFOA were near the detection limit (Kowalczyk et al., 2013). PFBA was the dominant PFAS in the feed analyzed for this project (Table 13), contributing to 60-97% of the PFAS present in the feed. These observations are in line with the Liu et al. (2022) study that found PFBA to be the dominant PFAS in cattle feed, while PFOS was most frequently detected in milk, with PFBA, PFOA, and PFPeA also detected in more than 40% of the milk samples. PFBA has been found in trace concentrations ranging from 4.7 to 43 ng/L in retail dairy milk in South Africa (Macheka et al., 2021), China (Yu et al., 2015), Germany (Still et al., 2013), and The Netherlands (Noorlander et al., 2011). However, those studies did not include analysis of PFAS in the feed, and therefore it is unclear what the impacts of PFAS present in the feed for the current study might be to milk.

4.4 United Kingdom Policy and Levels Applied to the Living Filter

In fulfillment of the International Agriculture and Development (INTAD) Degree, comparison of PFAS levels between the United Kingdom and the United States, the system of interest being the Living Filter, are discussed below.

Groundwater contributes to a small amount of the raw water supply for most throughout the United Kingdom. Most of the potential raw water supply for potable water is sourced from surface waters, making groundwater an under-utilized resource. Due to the conflict of Northern Ireland leaving the European Union in 2016, status regarding the use of groundwater management and the boundaries of groundwater and surface waters throughout the United Kingdom are under debate and review. These are called the "Brexit" boundaries and is an agreement of the groundwater implications and transboundary of groundwater between the Republic of Ireland and Northern Ireland (Jahnke et al. 2009). All information that has been collected in reference to PFAS aligns with both the Republic of Ireland, still part of the European Union, and Northern Ireland's policies, as well as the United Kingdom's policy pertaining to PFAS. Within the EU Water Framework Directive (WFD), states are asked to align their water policies with that of EU standards. The United Kingdom falls under this directive and aligns their water policy to the EU Framework. This alignment directive is a direct parallel to how the United States handles their water policy and regulations. All the US states must meet the national requirement, with prerogative to choose their own, more restrictive, policies. Due to having transboundary aquifers as the main source of groundwater supply throughout Ireland and other parts of the United Kingdom, all information discussed will be in regulation to the EU framework and United Kingdom Policy as a whole.

Between 2016 and 2018, a study was done to determine how much PFOS and PFOA were in coastal and freshwater estuaries throughout the United Kingdom. Inland surface waters were measured throughout most of England, Scotland, Wales, and Ireland with a total of approximately 470 freshwater sites monitored. In this study, 55 sites were chosen, monitored, and sampled. An annual average (AA) environmental quality standard (EQS) for PFOS (measured in ppt) was used as an initial assessment for risk in EU surface waters, which was again revisited in 2018 and had been under deliberation for the change in values. PFOS was

found below the EQS in only 3% of the sites. Over 50% of the sampling sites had concentrations found at over 10 times the EQS. The highest samples were found to be approximately 50 times the EQS, in the upper Thames and Humber basins (Environment Agency, 2019). It can be hypothesized that due the immense pollution and industrial discharge into the rivers over the course of hundreds of years, that it can be a contributing factor on why there is such a high value of PFAS found, however, there is no determined cause for such a large magnitude of PFAS.

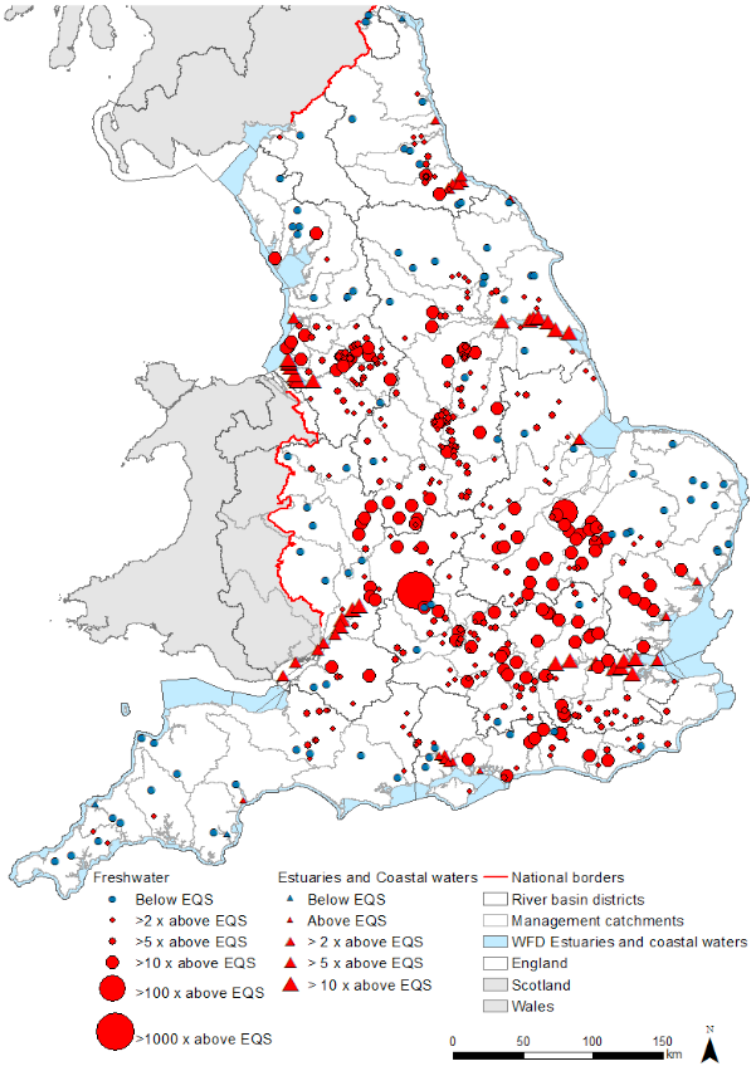


Figure 8. Mean measured PFOS concentrations at the sampling sites across the United Kingdom from the Environmental Agency water monitoring study with AA EQS values in England, 2016- 2018 (Environment Agency 2019)

As it stands, the AA EQS value for EU surface and coastal waters pertaining to PFOS was determined to be 6.5 x 10^{-4} μg/L or 0.65 ppt (European Environmenal Agency; European Union,

2008). In addition to this, the EU also established a proposed limit value of 0.1 μg/L for each individual PFAS that is found in the 2018 EU Drinking Water Directive (European Union, 2020). This directive holds 11 PFAS contaminants in review for this statute of limitation, including PFBS, PFHxS, PFOS, 6:2 FTSA, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA and PFDA. If the sum of all these is greater than 0.09 μg/L, or 90ppt, then the EU recommends measures to be taken to reduce the pollution and PFAS values (European Union, 2020). In January of 2022, a decision was released pertaining to the levels and monitoring of the PFAS analytes under debate and further elaborates concerns regarding PFAS. However, this update is outside of the timeframe this study is based upon, and as such, only information released prior to February 2021, will be discussed (European Union, 2020).

The World Health Organization recommended adopting parametric values for the two PFAS substances that dictate the toxicity reporting levels; PFOS and PFOA. PFOS should not exceed a value of 0.4 µg/L and PFOA should not exceed a value of 4 µg/L (WHO, 2016). The United Kingdom, and subsequently the EU, in addition to America, have a more regulated policy than the WHO guidelines and show that lower parametric values are achievable (European Union, 2020; Vierke et al., 2012).

From the 20 analytes that were measured throughout the research period at the Living Filter, 10 of them were found to be a part of this list. The 11th analyte in the 2018 EU Directive, 6:2 FTSA, was not measured in this study.

The 10 analytes that were listed in the EU Directive and reported in the study were summed together to create a Total Average PFAS amount. This amount was then compared to the EU regulation of a PFAS total of 0.09 μg/L (90 ng/L) to determine if the Living Filter well would be considered within the Statute of Limitation.

Table 14. Living Filter Monitoring Well Average PFAS Values compared to the EU Policy Restriction Value of 90 ng/L

Well	Average Total PFAS	Meets EU Restriction
G12	26.14	Yes
G10	74.86	Yes
W7	N.D.	Yes

W6	105.87	No
W5	85.95	Yes
W2	N.D.	Yes
W1	17.41	Yes
P5	56.44	Yes
P4	6.3	Yes
P3	40.15	Yes
F3	69.69	Yes
P2	92.99	No
P1	92.99	No

Of the 13 groundwater wells, only 3 do not meet the Statute of Limitation, wells W6, P2 and P1. Additionally, both the EU and the US proposed the limit of PFOA/PFOS being 0.07 μg/L, which is below the WHO value for PFAS in drinking water or potable water sources. With reporting values of the Living Filter (Table 15) being notably below the limit, the Living Filter would be an achievable system in the EU regulated environment, so long as monitoring and action, if need be, were available. Water from the Living Filter would be a beneficial utility, with levels already at a reasonable value, compared to that of the surface water values from the Environmental Agency study of 2016.

Conclusion

This study represents a comprehensive assessment of PFAS occurrence at a long-term beneficial reuse facility. Overall, ten PFAS were found across the site, with average total measured PFAS concentrations of 88 ng/L in the wastewater effluent and concentrations as high as 155 ng/L in the monitoring wells, suggesting that occurrence of PFAS across the site is nearly ubiquitous. Since the Living Filter is operated to maintain groundwater concentrations below the EPA's primary drinking water standard of nitrate of 10 mg NO_3-N/L (USEPA, 2009), strict regulations for PFAS in potable water may limit the long-term feasibility of beneficial reuse of treated wastewater, as PFOS and/or PFOA were detected (and therefore exceeded 2022 interim health advisories) in all 13 of the monitoring wells across the site. However, it should be noted that these wells do not serve as supply wells for potable water and therefore do not pose a direct risk to human health.

PFAS concentrations showed little seasonal variability, while spatial patterns of PFAS concentrations in the monitoring wells followed the general groundwater flow direction, with the lowest concentrations of PFAS on the periphery, upgradient portions of the field that were least influenced by irrigation activities and highest concentrations in the irrigated areas that receive the accumulated groundwater flow. Several PFAS were detected in crop tissue samples collected at both irrigation and non-irrigated portions of the site, suggesting that PFAS could enter the food chain when these crops are fed to livestock. The vast majority (>87%) of the PFAS present in the feed crops were short-chain compounds, including PFBA, PFPeA, and PFHxA, whereas long-chain compounds comprised the remainder. Future research is needed to determine potential risks to livestock health and the potential implications of PFAS presence in meat and dairy products, including milk.

Bibliography

Agency, European Environmental. "Emerging Chemical Risks in Europe — 'PFAS.'" *European Environmental Agency*. https://www.eea.europa.eu/publications/emerging-chemical-risks-in-europe.

Agency, United States Environmental Protection. 2019. "Basic Information on PFAS." *PFOA, PFOS, and Other PFAS*. https://www.epa.gov/pfas/basic-information-pfas.

American Water Works Association. 2019. "Per- and Polyfluoroalkyl Substance (PFAS) Overview and Prevalence." : 1–3. https://www.epa.gov/pfas/epas-pfas-action-plan.

Arvaniti, Olga S., and Athanasios S. Stasinakis. 2015. "Review on the Occurrence, Fate and Removal of Perfluorinated Compounds during Wastewater Treatment." *Science of the Total Environment* 524–525: 81–92.

van Asselt, E.D. et al. 2013. "Transfer of Perfluorooctane Sulfonic Acid (PFOS) from Contaminated Feed to Dairy Milk." *Food Chemistry* 141(2): 1489–95. https://www.sciencedirect.com/science/article/pii/S0308814613004810 (November 11, 2019).

ATSDR. 2021. "Toxicological Profile for Perfluoroalkyls - Release May 2021." *Agency for Toxic Substances and Disease Registry* (May): 1–993. https://www.atsdr.cdc.gov/toxprofiles/tp200.pdf.

Blaine, Andrea C. et al. 2013. "Uptake of Perfluoroalkyl Acids into Edible Crops via Land Applied Biosolids: Field and Greenhouse Studies." *Environmental Science and Technology* 47(24): 14062–69.

Blanks, Field. 2020. "Field Sampling Guidelines for PFAS Using EPA Method 537 or 537 . 1." (December): 1–4.

Buck, Robert C. et al. 2011. "Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins." *Integrated Environmental Assessment and Management* 7(4): 513–41.

"CompTox Chemicals Dashboard." 2023. *Reference Module in Biomedical Sciences*.

Conder, Jason M. et al. 2008. "Are PFCAs Bioaccumulative? A Critical Review and Comparison with Regulatory Criteria and Persistent Lipophilic Compounds." *Environmental Science and Technology* 42(4): 995–1003.

Costello, M. Christina Schilling, and Linda S. Lee. 2020. "Sources, Fate, and Plant Uptake in

Agricultural Systems of Per- and Polyfluoroalkyl Substances." *Current Pollution Reports*. https://link.springer.com/article/10.1007/s40726-020-00168-y.

Crook, James, David K Ammerman, Daniel A Okun, and Robert L Matthews. 1996. "Guidelines for Water Reuse." (September).

DEP, Florida. "Uses of Reclaimed Water | Florida Department of Environmental Protection."

Dery, Jessica L, Daniel Gerrity, and Channah M Rock. 2019. "Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS): What Consumers Need to Know." (April).

Energy, US Department of. "Reclaimed Wastewater Map How to Use the Map." *Federal Energy Management Program*.

Environment Agency. 2019. "Perfluorooctane Sulfonate (PFOS) and Related Substances: Sources, Pathways and Environmental Data." (October): 1–44. https://consult.environment-agency.gov.uk/environment-and-business/challenges-and-choices/user_uploads/perfluorooctane-sulfonate-and-related-substances-pressure-rbmp-2021.pdf.

EPA. 2018. "2018 Edition of the Drinking Water Standards and Health Advisories." *United States Environmental Protection Agency* (March): 2–6. http://pubs.rsc.org/en/content/articlepdf/1987/pc/pc9878400201.

European Chemicals Agency. 2021. "Per- and Poly-Fluoroalkyl Substances (PFAS)." *Ministry for the Environment*: 1–4. https://environment.govt.nz/what-government-is-doing/areas-of-work/land/per-and-poly-fluoroalkyl-substances-pfas/.

European Parliament. 2015. *Conflict and Cooperation over Water - The Role of the EU in Ensuring the Realisation of Human Rights*. http://www.europarl.europa.eu/RegData/etudes/STUD/2015/549056/EXPO_STU(2015)549056_EN.pdf.

European Union. 2020. *DIRECTIVE (EU) 2020/2184 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL*. The European Union. https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32020L2184.

Fidra. 2020. "UK Minister Agrees PFAS ' Need to Be Addressed as a Group ." *April 24, 2020*.

Fidra UK. 2018. "Types of PFAS Polymer PFAS Are Used on Our Non-Stick Pans and Clothing Are All PFAS Harmful ?" : 43895. https://www.pfasfree.org.uk/about-pfas/pfas-science-the-basics#:~:text=Poly- means %27many%27 and,shorter than those of polymers.

García-Valcárcel, A. I. et al. 2014. "Uptake of Perfluorinated Compounds by Plants Grown in Nutrient Solution." *Science of the Total Environment* 472: 20–26.

Gaskin, Julia W, and L Mark Risse. 2022. "Beneficial Reuse of Municipal Biosolids in Agriculture Biosolids Use — Advantages and Disadvantages What the Farmer Should Know Contact Your Local O Ffi Ce." *University of Georgia, Extension*: 2022.

Ghisi et. al. 2019. "Accumulation of Perfluorinated Alkyl Substances (PFAS) in Agricultural Plants: A Review." *Environmental Research* 169(June 2018): 326–41.

Gowdy, John, and Philippe Baveye. 2018. "An Evolutionary Perspective on Industrial and Sustainable Agriculture." *Agroecosystem Diversity: Reconciling Contemporary Agriculture and Environmental Quality*: 425–33. https://www.oecd.org/chemicalsafety/portal-perfluorinated-chemicals/aboutpfass/.

Hamid, Hanna, and Loretta Li. 2016. "Role of Wastewater Treatment Plant in Environmental Cycling of Poly- and Perfluoroalkyl Substances." *Ecocycles* 2(2 SE-): 43–53. https://www.ecocycles.net/ojs/index.php/ecocycles/article/view/62.

Hodgkins, Linda M., Ryan P. Mulligan, John M. McCallum, and Kela P. Weber. 2019. "Modelling the Transport of Shipborne Per- and Polyfluoroalkyl Substances (PFAS) in the Coastal Environment." *Science of the Total Environment* 658: 602–13. https://doi.org/10.1016/j.scitotenv.2018.12.230.

Hopkins, Zachary R., Mei Sun, Jamie C. DeWitt, and Detlef R.U. Knappe. 2018. "Recently Detected Drinking Water Contaminants: GenX and Other Per- and Polyfluoroalkyl Ether Acids." *Journal - American Water Works Association* 110(7): 13–28.

Houde, Magali, Amila O. De Silva, Derek C.G. Muir, and Robert J. Letcher. 2011. "Monitoring of Perfluorinated Compounds in Aquatic Biota: An Updated Review." *Environmental Science and Technology* 45(19): 7962–73.

Jahnke, Annika, Jonathan L. Barber, Kevin C. Jones, and Christian Temme. 2009. "Quantitative Trace Analysis of Polyfluorinated Alkyl Substances (PFAS) in Ambient Air Samples from Mace Head (Ireland): A Method Intercomparison." *Atmospheric Environment* 43(4): 844–50. https://www.sciencedirect.com/science/article/abs/pii/S135223100801008X (October 31, 2019).

Johnson, Gwynn R. 2022. "PFAS in Soil and Groundwater Following Historical Land Application of Biosolids." *Water Research* 211: 2023.

Kibuye, Faith A. et al. 2019. "Fate of Pharmaceuticals in a Spray-Irrigation System: From Wastewater to Groundwater." *Science of the Total Environment* 654: 197–208. https://doi.org/10.1016/j.scitotenv.2018.10.442.

Kowalczyk, Janine et al. 2013. "Absorption, Distribution, and Milk Secretion of the Perfluoroalkyl Acids PFBS, PFHxS, PFOS, and PFOA by Dairy Cows Fed Naturally Contaminated Feed." *Journal of Agricultural and Food Chemistry* 61(12): 2903–12.

Krafft, Marie Pierre, and Jean G. Riess. 2015. "Selected Physicochemical Aspects of Poly- and Perfluoroalkylated Substances Relevant to Performance, Environment and Sustainability-Part One." *Chemosphere* 129: 4–19. http://dx.doi.org/10.1016/j.chemosphere.2014.08.039.

Leeuwen, Van. 2023. "European Environmental Agency; Cross-Cutting Story 3 : PFAS." *European Environmental Agency*.

Liu, Yifei et al. 2022. "Occurrence of Per- and Polyfluoroalkyl Substances (PFASs) in Raw Milk and Feed from Nine Chinese Provinces and Human Exposure Risk Assessment." *Chemosphere* 300: 2023.

Macheka, Linda R., Joshua O. Olowoyo, Liziwe L. Mugivhisa, and Ovokeroye A. Abafe. 2021. "Determination and Assessment of Human Dietary Intake of per and Polyfluoroalkyl Substances in Retail Dairy Milk and Infant Formula from South Africa." *Science of the Total Environment* 755: 2023.

Manzetti, Sergio et. al. 2014. "Chemical Properties, Environmental Fate, and Degradation of Seven Classes of Pollutants." *Chemical Research in Toxicology* 27(5): 713–37.

Medicine, National Library of. "Perfluorotridecanoic Acid." (PubChem): 10–11. https://pubchem.ncbi.nlm.nih.gov.

Mueller, Robert (NJDEP), and Virginia (MNDoH) Yingling. 2017. "History and Use of Per- and Polyfluoroalkyl Substances (PFAS)." *Interstate Technology Regulatory Council Sheets* (KEMI 2015): 1–8. https://pfas-1.itrcweb.org/fact_sheets_page/PFAS_Fact_Sheet_History_and_Use_April2020.pdf.

Muschket, Matthias et al. 2020. "Determination of Transformation Products of Per- and Polyfluoroalkyl Substances at Trace Levels in Agricultural Plants." *Journal of Chromatography A* 1625: 2023.

Nassazzi, Winnie et al. 2023. "Phytoextraction of Per- and Polyfluoroalkyl Substances (PFAS) and the Influence of Supplements on the Performance of Short–Rotation Crops."

Environmental Pollution 333(June): 122038. https://doi.org/10.1016/j.envpol.2023.122038.

Navarro, Divina A., Danielle P. Oliver, Stuart L. Simpson, and Rai S. Kookana. 2022. "Organic Carbon and Salinity Affect Desorption of PFAS from Estuarine Sediments." *Journal of Soils and Sediments* 22(4): 1302–14.

Newland, Ashley, Mirza Mohammad Omar Khyum, Jan Halamek, and Seshadri Ramkumar. 2023. "Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) — Fibrous Substrates." *Tappi Journal* 22(9): 559–72. https://www.niehs.nih.gov/health/topics/agents/pfc/index.cfm.

Noorlander, Cornelle W et al. 2011. "Levels of Perfluorinated Compounds in Food and Dietary Intake of Terms & Conditions."

NRCS, Natural Resource Conservation Service. "Search Map Unit Legend Soil Map." (5): 414. https://websoilsurvey.nrcs.usda.gov/app/WebSoilSurvey.aspx.

NSW government. 2011. "PFOS and PFOA." *State of New South Wales*: 1–3. http://www.health.nsw.gov.au/environment/factsheets/Pages/pfos.aspx%0Ahttp://www.testingeducation.org/BBST/testdesign/HAZOP_Guidelines.pdf.

OECD. "Polymeric Per- and Polyfluoroalkyl Substances." *Portal on Per and Poly Fluorinated Chemicals*. https://www.oecd.org/chemicalsafety/portal-perfluorinated-chemicals/aboutpfass/.

Office of Research, Epa. 2019. *Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) Methods and Guidance for Sampling and Analyzing Water and Other Environmental Media Background*.

Priyantha Ranjan, S., So Kazama, and Masaki Sawamoto. 2006. "Effects of Climate and Land Use Changes on Groundwater Resources in Coastal Aquifers." *Journal of Environmental Management* 80(1): 25–35. https://www.sciencedirect.com/science/article/pii/S0301479705002616 (October 31, 2019).

Public Health of England. "PFOS and PFOA General Information." *Toxicology Department*: 1–3.

Richardson, D.C. 2010. "The Living Filter." *Water Efficiency* 5(4): 34–38.

Salvidge, Rachel. 2023. "Support the Guardian Revealed : Scale of ' Forever Chemical ' Pollution across UK and Europe Reimagine How Work Gets Done with IBM AI Assistants." *The Guardian*: 2023.

Sharma, Brij Mohan et al. 2016. "Perfluoroalkyl Substances (PFAS) in River and Ground/Drinking Water of the Ganges River Basin: Emissions and Implications for Human Exposure." *Environmental Pollution* 208: 704–13. https://www.sciencedirect.com/science/article/pii/S0269749115301500 (October 31, 2019).

Shoushtarian, Farshid, and Masoud Negahban-Azar. 2020. "World Wide Regulations and Guidelines for Agriculturalwater Reuse: A Critical Review." *Water (Switzerland)* 12(4).

Still, Mona et al. 2013. "Impact of Industrial Production and Packaging Processes on the Concentration of Per- and Polyfluorinated Compounds in Milk and Dairy Products." *Journal of Agricultural and Food Chemistry* 61(38): 9052–62.

Stockholm Convention. 2017. "National Phase out of PFOS Ratification of the Stockholm Convention Amendment on PFOS Regulation Impact Statement for Consultation October 2017." (October).

Sungur, Ş, Muaz Köro, and Faruk Turgut. 2023. "Determination of per Fl Uorooctanoic Acid (PFOA) and per Fl Uorooctane Sulfonic Acid (PFOS) in Food and Beverages." : 4.

Szabo, Drew et al. 2018. "Investigating Recycled Water Use as a Diffuse Source of Per- and Polyfluoroalkyl Substances (PFASs) to Groundwater in Melbourne, Australia." *Science of the Total Environment* 644: 1409–17.

Templeton, Jessica. 2020. "Stockholm Convention on Persistent Organic Pollutants." *Essential Concepts of Global Environmental Governance*: 242–44.

Thompson, Richard C., Charles J. Moore, Grederick S. vom Saal, and Shanna H. Swan. 2002. "Plastics, the Environment and Human Health: Current Consensus and Future Trends." *Nature* 416(6883): 808–9.

Treat, Sharon. 2021. "Forever Chemicals and Agriculture Case Study | IATP." *IATP, Institute for Agriculture and Trade Policy* (November). https://www.iatp.org/documents/forever-chemicals-and-agriculture-case-study.

Union, European. "European Chemicals Agency." *EU. Environmental Quality Standards (EQS) for Priority Substances: Annex I, Part A, Directive 2008/105/EC*. https://echa.europa.eu/environmental-quality-standards?p_p_id=eucleflegislationlist_WAR_euclefportlet&p_p_lifecycle=1&p_p_state=normal&p_p_mode=view&_eucleflegislationlist_WAR_euclefportlet_javax.portlet.action=searchLegislationLists.

United States Environmental Protection Agency. 2020. “Basic Information about Water Reuse.” *United States Environmental Protection Agency*: 2020.

US EPA. 2023. “Safe Drinking Water Act Per- and Polyfluoroalkyl Substances (PFAS) Proposed PFAS National Primary Drinking Water Regulation.”

US EPA. 2017. “Technical Fact Sheet - Perfluorooctane Sulfonate (PFOS) and Perfluorooctanoic Acid (PFOA). EPA 505-F-17-001, United States Environmental Protection Agency.” (May): 6. https://www.epa.gov/sites/production/files/2017-12/documents/ffrrofactsheet_contaminants_pfos_pfoa_11-20-17_508_0.pdf.

USDA, and Farm Service Agency. 2021. “Dairy Margin Coverage Program.” https://www.fsa.usda.gov/programs-and-services/dairy-margin-coverage-program/index.

USEPA. 2018. “Fact Sheet: Draft Toxicity Assessments for GenX Chemicals and PFBS.” (November): 1–6. https://www.epa.gov/risk/conducting-human-health-risk-assessment.%0Ahttps://www.epa.gov/risk/conducting-human-health-risk-assessment.%0Ahttps://www.epa.gov/sites/production/files/2018-11/documents/factsheet_pfbs-genx-toxicity_values_11.14.2018.pdf.

USEPA. 2020. “537.1 - 1.” 1(2009): 1–50.

USEPA. 2023a. “Biosolids Laws and Regulations How Biosolids Are Regulated Process for Regulating Pollutants in Biosolids Regulatory Determinations for Pollutants in Biosolids.” *503 Regulations*. https://www.epa.gov/biosolids/biosolids-laws-and-regulations#:~:text=40 CFR Part 503 applies,regulation was finalized in 1993.

USEPA. 2023b. “Per- and Polyfluoroalkyl Substances National Primary Drinking Water Regulation.” : 18638–754.

USEPA. 2023c. “Reusing Water for Agricultural Activities Resources.” *Water Reuse*. https://www.epa.gov/waterreuse/reusing-water-agricultural-activities-resources.

USFDA. 2020. “Testing Food for PFAS and Assessing Dietary Exposure.” *Food and Drug Administration*: 6332. https://www.fda.gov/food/chemicals/testing-food-pfas-and-assessing-dietary-exposure.

Vierke, Lena et al. 2012. “Perfluorooctanoic Acid (PFOA)-Main Concerns and Regulatory Developments in Europe from an Environmental Point of View.” *Environmental Sciences Europe* 24(5): 1–11.

Wang, Zhanyun, Ian T. Cousins, Martin Scheringer, and Konrad Hungerbuehler. 2015. “Hazard

Assessment of Fluorinated Alternatives to Long-Chain Perfluoroalkyl Acids (PFAAs) and Their Precursors: Status Quo, Ongoing Challenges and Possible Solutions." *Environment International* 75: 172–79. http://dx.doi.org/10.1016/j.envint.2014.11.013.

Weber, Andrea K. et al. 2017. "Geochemical and Hydrologic Factors Controlling Subsurface Transport of Poly- and Perfluoroalkyl Substances, Cape Cod, Massachusetts." *Environmental Science and Technology* 51(8): 4269–79.

WHO. 2016. "Keeping Our Water Clean: The Case of Water Contamination in the Veneto Region, Italy." *World Health Organization - Regional Office for Europe* Patrocinio: 72. https://www.euro.who.int/en/publications/abstracts/keeping-our-water-clean-the-case-of-water-contamination-in-the-veneto-region,-italy-2017.

World Health Organization, Drinking-water. 2022. "WHO/SDE/WSH/XXXXXX English Only PFOS and PFOA in Drinking-Water Background Document for Development of WHO Guidelines for Drinking-Water Quality." (September): 2023.

Xing, Zhenni et al. 2016. "Occurrence of Perfuorooctanoic Acid and Perfluorooctane Sulfonate in Milk and Yogurt and Their Risk Assessment." *International Journal of Environmental Research and Public Health* 13(10): 717–23.

Yu, Yucheng et al. 2015. "QuEChERs Combined with Online Interference Trapping LC-MS/MS Method for the Simultaneous Determination of 20 Polyfluoroalkane Substances in Dietary Milk." *Journal of Agricultural and Food Chemistry* 63(16): 4087–95.

Zeng, Lingke, and Steve Zemba. 2023. "Short or Long ? PFAS Chain Length Impacts on Regulation and Treatment for Landfill Leachate In Your Inbox PFAS Chain Length Impact on Contamination Landfill Leachate Composition PFAS Chain Length on Chemical and Physical Characteristics." : 2023.

Zhao, Y. G., C. K.C. Wong, and M. H. Wong. 2012. "Environmental Contamination, Human Exposure and Body Loadings of Perfluorooctane Sulfonate (PFOS), Focusing on Asian Countries." *Chemosphere* 89(4): 355–68.

Appendix A. Program of Study

Program of Study

Fall 2019	
Course/ Deliverable	Requirement Fulfilled
ABE 500 (3)	ABE M.S. Requirement
ABE 559 (3)	3 Credits of ABE 5XX
CE 570 (3)	3 Credits of Biological Engineering
Recommended Faulty Member to Serve on Committee	ABE M.S. Requirement
Submit These Proposal to Advisor	ABE M.S. Requirement
Submit Plan of Study and Proposal to Advisory Committee	ABE M.S. Requirement
Complete SARI Online Modules	ABE M.S. Requirement
Spring 2020	
Course/ Deliverable	Requirement Fulfilled
CE 573 (3)	3 Credits for 5XX class
Meet with Advisory Committee for Proposal Approval	ABE M.S. Requirement
Semi-Annual Progress Report	ABE M.S. Requirement
ABE 600 Research Work	ABE M.S. Requirement
Summer 2020	
STAT 500 (3)	Math/Statistics Requirement
ABE 600 Research Work	ABE M.S. Research Requirement
Semi-Annual Progress Report	ABE M.S. Requirement
Prepare First Draft of Thesis	ABE M.S. Requirement
Fall 2020	
AEE 525 (3)	INTAD Requirement
SOILS 502 (3)	3 Credits for 5XX Class/ INTAD Requirement
Submit Intent to Graduate	ABE M.S. Requirement

Pay Thesis Fee	ABE M.S. Requirement
Submit Draft Copy of Thesis to Advisor	ABE M.S. Requirement
Present Department Seminar	ABE M.S. Requirement
Schedule Thesis Defense	ABE M.S. Requirement
Spring 2021	
INTAD 820 (3)	INTAD Requirement
Defend Thesis	ABE M.S. Requirement
Finish Any Other Requirements Prior to Graduation	ABE M.S. Requirement

Appendix B. Concentrations Data

Table S1. Analytical results of the PFAS compounds analyzed throughout the study period in the Penn State Water Reclamation Facility (PSU WRF) influent. LOD = Limit of Detection

Date	Oct 2019	Feb 2020	May 2020	July 2020	Oct 2020	Dec 2020	Feb 2021
11Cl-PF3OUdS	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
9Cl-PF3ONS	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
DONA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
HFPODA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
NEtFOSAA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
NMeFOSAA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFBA	27	26	5.6	7.9	9.8	< LOD	4.9
PFBS	< LOD	< LOD	2.8	3.0	4.5	< LOD	3.7
PFDA	0.92*	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFDoA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFHpA	< LOD	< LOD	3.2	3.0	2.6	15	2.7
PFHxA	12	9.4	12	41	12	< LOD	11
PFHxS	< LOD	< LOD	3.3	3.5	3.9	< LOD	2.9
PFNA	< LOD	< LOD	0.68*	1.4*	7.0	< LOD	0.89*
PFOA	6.0	5.4	5.2	7.0	6.5	7.3	5.1
PFOS	11	< LOD	3.0	4.5	63	7.9	5.4
PFPeA	< LOD	< LOD	< LOD	71	10	< LOD	< LOD
PFTeDA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFTrDA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD

*Value is below the limit of quantification and is therefore estimated

Table S2. Analytical results of the PFAS compounds analyzed throughout the study period in the Penn State Water Reclamation Facility (PSU WRF) effluent. LOD = Limit of Detection

Date	Oct 2019	Feb 2020	May 2020	July 2020	Oct 2020	Dec 2020	Feb 2021
11Cl-PF3OUdS	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
9Cl-PF3ONS	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
DONA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
HFPODA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
NEtFOSAA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
NMeFOSAA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFBA	12	< LOD	6.3	< LOD	< LOD	13	6.3
PFBS	3.9	< LOD	2.5	4.1	4.2	5.2	2.8
PFDA	< LOD	< LOD	< LOD	0.71	< LOD	0.5	1.3
PFDoA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFHpA	7.3	5.6	3.5	6.3	6.5	12	6.5
PFHxA	2	< LOD	2.7	3.8	3.8	4	5
PFHxS	30	21	12	26	30	41	27
PFNA	0.56	< LOD	0.74	1.2	1.9	1.1	2
PFOA	4	5.8	6.7	5.7	11	7.5	8.2
PFOS	3.1	< LOD	3.2	4.9	7.1	3.5	8.6
PFPeA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.56
PFTA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFTrDA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD

Table S3. Analytical results of the PFAS compounds analyzed throughout the study period at Well W7. LOD = Limit of Detection

Date	Oct 2019	Feb 2020	May 2020	July 2020	Oct 2020	Dec 2020	Feb 2021
11Cl-PF3OUdS	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
9Cl-PF3ONS	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
DONA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
HFPODA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
NEtFOSAA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
NMeFOSAA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFBA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFBS	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFDA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFDoA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFHpA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFHxA	1.1	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFHxS	0.69	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFNA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFOA	0.96	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFOS	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFPeA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFTA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFTrDA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD

Table S4. Analytical results of the PFAS compounds analyzed throughout the study period at Well W2. LOD = Limit of Detection.

Date	Oct 2019	Feb 2020	May 2020	July 2020	Oct 2020	Dec 2020	Feb 2021
11Cl-PF3OUdS	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
9Cl-PF3ONS	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
DONA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
HFPODA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
NEtFOSAA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
NMeFOSAA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFBA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFBS	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFDA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFDoA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFHpA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFHxA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFHxS	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFNA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFOA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFOS	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFPeA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFTA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFTrDA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD

Table S5. Analytical results of the PFAS compounds analyzed throughout the study period at Well G12. LOD = Limit of Detection.

Date	Oct 2019	Feb 2020	May 2020	July 2020	Oct 2020	Dec 2020	Feb 2021
11Cl-PF3OUdS	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
9Cl-PF3ONS	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
DONA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
HFPODA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
NEtFOSAA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
NMeFOSAA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFBA	4.9	5.2	4.8	5.5	6	5.4	4.2
PFBS	1.1	1.2	1.1	1.3	1.4	1.4	1.3
PFDA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFDoA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFHpA	2.5	2.5	2.4	2.4	2.6	2.5	2.5
PFHxA	6.9	6.6	6.4	6.9	7.5	6.8	6
PFHxS	3.1	3.6	3.9	4.2	4.6	4.5	4.3
PFNA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFOA	5.3	5.9	5.3	5.4	7.6	7.1	6.6
PFOS	1	1.2	1.5	1.6	2	2	1.7
PFPeA	< LOD	< LOD	< LOD	9.1	9.4	1.4	1.2
PFTA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFTrDA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD

Table S6. Analytical results of the PFAS compounds analyzed throughout the study period at Well G10. LOD = Limit of Detection.

Date	Oct 2019	Feb 2020	May 2020	July 2020	Oct 2020	Dec 2020	Feb 2021
11Cl-PF3OUdS	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
9Cl-PF3ONS	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
DONA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
HFPODA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
NEtFOSAA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
NMeFOSAA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFBA	11	11	10	12	13	11	10
PFBS	3.8	3.5	3.6	3.8	4	3.5	3.4
PFDA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFDoA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFHpA	7.5	7.5	7.3	7.4	7.8	7.5	6.2
PFHxA	19	17	18	19	19	17	15
PFHxS	15	14	14	13	14	13	11
PFNA	0.63	0.82	0.88	0.84	0.85	1	0.87
PFOA	18	18	19	18	22	19	18
PFOS	5	5.6	6.3	7.1	7.1	7.2	7
PFPeA	0.84	0.83	0.95	21	21	0.89	0.72
PFTA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFTrDA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD

Table S7. Analytical results of the PFAS compounds analyzed throughout the study period at Well W6. LOD = Limit of Detection.

Date	Oct 2019	Feb 2020	May 2020	July 2020	Oct 2020	Dec 2020	Feb 2021
11Cl-PF3OUdS	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
9Cl-PF3ONS	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD

DONA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
HFPODA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
NEtFOSAA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
NMeFOSAA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFBA	14	14	15	17	19	18	17
PFBS	4.9	4.7	5.1	5.1	5.6	5.1	5.2
PFDA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFDoA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFHpA	9.9	9.8	11	10	12	10	9.1
PFHxA	25	23	27	25	28	19	23
PFHxS	20	18	21	18	22	25	17
PFNA	0.92	1.2	1.2	0.68	1	1.1	0.96
PFOA	28	25	29	24	30	27	25
PFOS	5.6	6.1	6.9	5	6.7	7.7	6.8
PFPeA	0.86	0.8	1	29	31	1.1	1
PFTA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFTrDA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD

Table S8. Analytical results of the PFAS compounds analyzed throughout the study period at Well W5. LOD = Limit of Detection.

Date	Oct 2019	Feb 2020	May 2020	July 2020	Oct 2020	Dec 2020	Feb 2021
11Cl-PF3OUdS	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
9Cl-PF3ONS	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
DONA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
HFPODA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
NEtFOSAA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
NMeFOSAA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFBA	11	11	10	11	13	11	11
PFBS	2.9	2.9	2.9	2.8	3.3	2.7	3
PFDA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFDoA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFHpA	8.3	8.2	7.4	6.9	7.6	6.8	5.9
PFHxA	18	18	18	16	19	15	16
PFHxS	8.2	9.1	8.3	7.6	8.5	7.9	7
PFNA	2.9	3.5	3.3	2.6	3	3.2	2.6
PFOA	22	24	22	20	24	20	17
PFOS	16	18	19	18	19	21	16
PFPeA	0.49	< LOD	0.58	20	21	0.79	0.52
PFTA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFTrDA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD

Table S9. Analytical results of the PFAS compounds analyzed throughout the study period at Well W1. LOD = Limit of Detection.

Date	Oct 2019	Feb 2020	May 2020	July 2020	Oct 2020	Dec 2020	Feb 2021
11Cl-PF3OUdS	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
9Cl-PF3ONS	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
DONA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
HFPODA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
NEtFOSAA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
NMeFOSAA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD

PFBA	< LOD	2.1	2	< LOD	< LOD	< LOD	< LOD
PFBS	3.5	3.5	3.6	4.5	2.8	2.3	2.4
PFDA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFDoA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFHpA	1.4	1.5	1.4	1.4	1.1	1.1	1
PFHxA	2.2	2.4	2.3	2.3	1.9	1.7	1.8
PFHxS	1.8	1.5	1.7	1.7	1.8	1.6	1.5
PFNA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFOA	3.6	3.3	3.5	3.2	2.4	2.7	2.6
PFOS	4.4	7.5	8	6.2	3.4	4.3	4.3
PFPeA	< LOD	< LOD	< LOD	3.1	2.3	< LOD	< LOD
PFTA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFTrDA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD

Table S10. Analytical results of the PFAS compounds analyzed throughout the study period at Well P5. LOD = Limit of Detection.

Date	Oct 2019	Feb 2020	May 2020	July 2020	Oct 2020	Dec 2020	Feb 2021
11Cl-PF3OUdS	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
9Cl-PF3ONS	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
DONA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
HFPODA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
NEtFOSAA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
NMeFOSAA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFBA	9	7.9	6.9	7.5	8.4	8.1	7.4
PFBS	2.7	2.3	2.2	2.3	2.6	2.3	2.3
PFDA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFDoA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFHpA	6.1	5.5	5.3	4.9	5.6	5.1	4.1
PFHxA	16	13	13	12	13	11	9.9
PFHxS	8.9	7.6	7.6	7.1	8	7	6.1
PFNA	1.1	1.2	1.1	0.99	1.2	1	0.8
PFOA	17	14	13	13	15	12	12
PFOS	8.4	8	8.7	8.4	9	7.9	8
PFPeA	0.46	< LOD	< LOD	14	15	< LOD	< LOD
PFTA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFTrDA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD

Table S11. Analytical results of the PFAS compounds analyzed throughout the study period at Well P4. LOD = Limit of Detection.

Date	Oct 2019	Feb 2020	May 2020	July 2020	Oct 2020	Dec 2020	Feb 2021
11Cl-PF3OUdS	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
9Cl-PF3ONS	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
DONA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
HFPODA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
NEtFOSAA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
NMeFOSAA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFBA	2.1	2.5	< LOD	< LOD	< LOD	2.3	< LOD
PFBS	1.5	1.3	1.2	1.2	1.2	1.2	1.4

PFDA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFDoA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFHpA	0.65	0.62	0.63	0.62	0.64	0.54	0.61
PFHxA	1.1	1.1	1.2	1.6	1.1	1.1	1.1
PFHxS	0.5	0.47	0.5	0.51	0.55	0	0.54
PFNA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFOA	1.4	1.3	1.2	1.3	1.3	1.1	1.4
PFOS	< LOD	0.51	< LOD	0.52	0.53	0.51	0.49
PFPeA	< LOD	< LOD	< LOD	1.3	1.3	< LOD	< LOD
PFTA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFTrDA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD

Table S12. Analytical results of the PFAS compounds analyzed throughout the study period at Well P3. LOD = Limit of Detection.

Date	Oct 2019	Feb 2020	May 2020	July 2020	Oct 2020	Dec 2020	Feb 2021
11Cl-PF3OUdS	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
9Cl-PF3ONS	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
DONA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
HFPODA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
NEtFOSAA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
NMeFOSAA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFBA	8.2	7.4	5.5	5.6	6.7	6.5	5.6
PFBS	2.5	2.2	1.9	1.9	2.2	1.9	2.2
PFDA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFDoA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFHpA	6.1	5.4	5.3	4.7	5.8	5.2	4.7
PFHxA	16	13	11	9.8	11	9.5	9.7
PFHxS	6.2	4.9	4.7	4	5.5	4.8	5.2
PFNA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFOA	13	12	11	9.6	12	11	12
PFOS	1.8	1.5	1.4	1.3	1.8	1.7	1.8
PFPeA	< LOD	< LOD	< LOD	11	13	0	0.54
PFTA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFTrDA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD

Table S13. Analytical results of the PFAS compounds analyzed throughout the study period at Well F3. LOD = Limit of Detection.

Date	Oct 2019	Feb 2020	May 2020	July 2020	Oct 2020	Dec 2020	Feb 2021
11Cl-PF3OUdS	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
9Cl-PF3ONS	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
DONA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
HFPODA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
NEtFOSAA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
NMeFOSAA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFBA	13	12	11	12	12	11	11
PFBS	3.6	3.2	3.3	3.2	3.3	2.8	3.3
PFDA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFDoA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFHpA	9	8	8.7	7	8	7.2	6.2
PFHxA	22	18	20	17	19	16	16

PFHxS	9.5	9	9.1	8.6	8.8	7.5	7.7
PFNA	0.75	0.76	0.83	< LOD	< LOD	0.66	0.71
PFOA	21	20	20	9.1	20	16	16
PFOS	5.9	5.9	6.4	5	6.9	< LOD	6.1
PFPeA	0.6	0.46	0.57	23	22	0.53	0.67
PFTA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFTrDA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD

Table S14. Analytical results of the PFAS compounds analyzed throughout the study period at Well P2. LOD = Limit of Detection.

Date	Oct 2019	Feb 2020	May 2020	July 2020	Oct 2020	Dec 2020	Feb 2021
11Cl-PF3OUdS	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
9Cl-PF3ONS	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
DONA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
HFPODA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
NEtFOSAA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
NMeFOSAA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFBA	12	13	14	15	15	15	14
PFBS	3.4	3.5	3.8	3.9	4.2	3.6	4
PFDA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFDoA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFHpA	9	9.9	11	10	11	10	9.8
PFHxA	20	22	25	23	25	21	22
PFHxS	10	11	12	10	12	11	11
PFNA	1.2	1.4	1.9	1.3	1.4	1.5	1.5
PFOA	19	24	26	23	30	25	23
PFOS	7.4	9	12	8.3	9	11	11
PFPeA	0.52	0.48	0.56	28	28	0.67	0.7
PFTA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFTrDA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD

Table S15. Analytical results of the PFAS compounds analyzed throughout the study period at Well P1. LOD = Limit of Detection.

Date	Oct 2019	Feb 2020	May 2020	July 2020	Oct 2020	Dec 2020	Feb 2021
11Cl-PF3OUdS	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
9Cl-PF3ONS	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
DONA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
HFPODA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
NEtFOSAA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
NMeFOSAA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFBA	12	12	11	13	15	13	14
PFBS	3.9	3.6	3.4	3.7	4.2	3.7	4.5
PFDA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFDoA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFHpA	8.3	8.1	7.9	8.2	9	8.6	9.1
PFHxA	22	20	20	21	22	20	21
PFHxS	11	10	9.3	10	11	11	12
PFNA	2.1	2.6	2	2.5	2	2.7	2.9
PFOA	20	20	16	18	20	20	21
PFOS	17	18	15	19	17	20	22

PFPeA	0.54	0.54	< LOD	25	26	0.7	0.84
PFTA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
PFTrDA	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD