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TECHNICAL REPORT

Emerging Contaminants

Spatiotemporal patterns of PFAS in water and crop tissue at a beneficial wastewater reuse site in central Pennsylvania

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Abstract

Per- and polyfluoroalkyl substances (PFAS) are a collective name for thousands of synthetic compounds produced to enhance consumer and industrial products since the 1940s. They do not easily degrade, and some are known to pose serious ecological and human health concerns at trace concentrations (ng L^{-1} levels). Per- and polyfluoroalkyl substances persist in treated wastewater and are inadvertently introduced into the environment when treated wastewater is reused as an irrigation source. The Pennsylvania State University (PSU) has been spray-irrigating its wastewater at a 2.45 km^2 mixed-use agricultural and forested site known as the "Living Filter" since the 1960s. To understand the spatiotemporal patterns of 20 PFAS at the Living Filter, water samples were collected bimonthly from fall 2019 through winter 2021 from the PSU's wastewater effluent and from each of the site's 13 monitoring wells. Crop tissue was collected at the time of harvest to assess PFAS presence in corn silage and tall fescue grown at the study site. Total measured PFAS concentrations in the monitoring wells ranged from nondetectable to 155 ng L^{-1}, with concentrations increasing with the direction of groundwater flow. Concentrations within each well exhibited little temporal variability across sampling events, with mixed relationships between PFAS and groundwater elevation observed between wells. Further, >84% of the PFAS present

Abbreviations: BTF, biotransfer factor; dw, dry weight; HDPE, high-density polyethylene; HFPO-DA, hexafluoropropylene oxide dimer acid; LOD, limit of detection; PFAS, per- and polyfluoroalkyl substances; PFBA, perfluorobutanoic acid; PFBS, perfluorobutane sulfonic acid; PFCAs, perfluoroalkyl carboxylic acids; PFDA, perfluorodecanoic acid; PFDoDA, perflurododecanoic acid; PFHpA, perfluoroheptanic acid; PFHxA, perfluorohexanoic acid; PFHxS, perfluorohexanesulfonic acid; PFOA, perfluorooctanoic acid; PFOS, perfluorooctane sulfonate; PFPeA, perfluoropentanoic acid; PFSAs, perfluoroalkane sulfonic acids; PSU, The Pennsylvania State University; WRF, water reclamation facility; WWTP, wastewater treatment plant.

in livestock feed crops were short-chain compounds, with PFAS consumed annually by livestock fed crops harvested from the site estimated to be 2.46–7.67 mg animal^{-1} yr^{-1}. This research provides insight into the potential impacts of long-term beneficial reuse of treated wastewater on groundwater and crop tissue quality.

1 | INTRODUCTION

The presence of per- and polyfluoroalkyl substances (PFAS) has become a topic of urgent emerging concern as the public becomes increasingly aware of the near-ubiquitous presence of these compounds in water utilized for drinking and agricultural operations. "Per- and polyfluoroalkyl substances" is a collective name for more than 4,700 compounds that are fully synthetic and have been historically produced by electrochemical fluorination and telomerization (Buck et al., 2011; Cousins et al., 2020) since the 1940s (Interstate Technology & Regulator Council, 2018). Because these compounds have surfactant and thermal resistance properties, they are widely used in industrial and manufacturing processes. Their properties also make them highly desirable in consumer products, such as water- and stain-resistant clothing, textiles, cleaning products, and nonstick cookware. Other products containing PFAS include food packaging. Because of their wide variety of uses, PFAS enter wastewater treatment plants (WWTPs) from both domestic and industrial sources. The chemical structures of PFAS are difficult to degrade, causing PFAS to persist in wastewater residuals and to become introduced into the environment when treated effluent is discharged to surface water bodies, spray-irrigated in beneficial reuse systems, or land-applied as biosolids.

Per- and polyfluoroalkyl substances have been found in environmental matrices ranging from the atmosphere to groundwater, surface water, and the ocean (Guelfo & Adamson, 2018; Hamid & Li, 2016; Vedagiri et al., 2018; Zareitalabad et al., 2013). Additionally, detectable concentrations of PFAS were found in soil samples taken in remote locations with no proximate anthropogenic activities (Rankin et al., 2016). The knowledge base regarding the health effects of PFAS observed in humans is evolving, with most health-effect studies focusing on perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) and a recent interest in the toxicity of perfluorobutane sulfonic acid (PFBS). Documented effects of PFAS on human health include endocrine disruptive and hepatotoxic properties that can affect development in children, increase risk of cancer, contribute to elevated cholesterol levels, interfere with women's fertility, and weaken immune systems (Agency for Toxic Substances & Disease Registry, 2018).

In response to recent concern over the presence of PFAS in the environment, the USEPA recommended drinking water health advisories for two compounds that are known carcinogens: PFOS and PFOA (USEPA, 2020). A national Lifetime Health Advisory of 70 ng L^{-1} was established by the USEPA in 2016 (USEPA, 2016), and ~28 states have established guidance values for PFAS concentrations (USEPA, 2020). However, in June 2022, the USEPA published new health advisories for PFOA, PFOS, PFBS, and GenX, hexafluoropropylene oxide dimer acid (HFPO-DA). The new interim health advisories for PFOA and PFOS are 0.004 and 0.02 ng L^{-1}, respectively, and the final health advisories released for GenX chemicals and PFBS are 10 and 2,000 ng L^{-1}, respectively (USEPA, 2022). These updated health recommendations are nonregulatory but represent a necessary step toward establishing appropriate drinking water standards. Additionally, the Pennsylvania Department of Environmental Protection has proposed maximum contaminant levels of 14 and 18 ng L^{-1}, respectively, for PFOA and PFOS in drinking water, which are far stricter than the federal guidelines (Pennsylvania Department of Environmental Protection, 2021), and more than 20 other states have established guidance values for PFAS concentrations (USEPA, 2020).

Wastewater reuse and spray-irrigation of treated wastewater inadvertently introduces PFAS into the environment because they are typically present in domestic wastewater effluent at concentrations ranging from 62 to 418 ng L^{-1} in the United States and Canada (Arvaniti & Stasinakis, 2015; Hamid & Li, 2016). Additionally, the spray-irrigation of treated wastewater likely affects the presence of PFAS in crops. Perfluorooctane sulfonate and PFOA are more mobile and available for crop uptake when introduced to agricultural fields through wastewater irrigation versus through biosolids application (Blaine et al., 2013, 2014). Field and greenhouse studies have investigated the presence of PFAS in various crops and have shown that accumulation differs by plant compartment, with concentrations generally greater in roots, lower in straw and grain, and lowest in the husk for corn (*Zea mays* L.) (Ghisi et al., 2019). Ryegrass (*Lolium perenne* L.) stalks tend to have higher concentrations during the second cutting (Ghisi et al., 2019), reflecting the impact of the roots having been largely developed by the first cutting and of plant uptake energizing stalk growth for the second cutting. Additionally, corn generally has much lower PFAS than wheat (*Triticum aestivum* L.) (Ghisi et al., 2019). Perfluoroalkyl carbon chain length and functional groups influence how plant tissues

concentrate various PFAS, with PFOA, which has a carboxylic functional group, generally concentrated more than PFOS, which has a sulfonic functional group. Of all measured PFAS, perfluorobutanoic acid (PFBA), which has three carbons in its perfluoroalkyl carbon chain, has the highest bioaccumulation factor in corn and wheat straw. Perfluorobutanoic acid has been found in garden produce at homes with PFAS contamination (Scher et al., 2018). Clearly, PFAS have the potential to enter and accumulate up the food chain, beginning with plant uptake and drinking water. Per- and polyfluoroalkyl substances have also been found in dairy and beef products, such as milk and meat (Kowalcyzk et al., 2013; Lupton et al., 2012; Van Asselt et al., 2013; Vestergren et al., 2013).

Here, we present the findings of a 14-mo study conducted at a beneficial reuse system in central Pennsylvania that has been spray-irrigated with treated wastewater since the 1960s. The goal of the study was to assess long-term impacts of these spray-irrigation activities on groundwater quality and crop tissues used as livestock feed. The objectives were to (a) quantify total measured PFAS in effluent leaving the WWTP; (b) characterize PFAS spatial and temporal patterns across the site's 13 groundwater monitoring wells and compare the results to USEPA Lifetime Health Advisory values; and (c) determine the presence PFAS in corn and tall fescue [*Schedonorus arundinaceus* (Schreb.) Dumort., nom. cons.] entering the food chain. 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.

2 | MATERIALS AND METHODS

2.1 | Study site description

The WWTP at The Pennsylvania State University (PSU) was installed in 1913, well in advance of national requirements for treating wastewater in the United States. The current design is a water reclamation facility (WRF) with a maximum capacity of 18.2 million L d^{-1} treating all wastewater generated by PSU's main campus. With students only on campus for portions of the year, the flow rates to the treatment plant vary. Flow is low in the summer months and over winter break and higher during the fall and spring semesters. The specific treatment processes included primary settling followed by activated sludge and secondary settling with chlorination prior to the effluent being pumped to the Living Filter for spray irrigation. More details about the treatment facility are provided in Kibuye et al. (2019).

The Living Filter is a 2.45-km^2 mixed-use area located ~4 km from the PSU WRF. It is approximately half forested

Core ideas

- Twenty PFAS were tracked in wastewater, groundwater, and crops at a beneficial reuse site.
- Groundwater concentrations ranged from nondetectable to 155 ng L^{-1} and increased with groundwater flow direction.
- PFOS and PFOA were as high as 22 and 30 ng L^{-1}, respectively, in all samples from 13 groundwater wells.
- PFAS in corn silage and fescue tissue were 0.97 and 11.3 µg kg^{-1} dw, respectively.
- More than 84% of PFAS in cattle feed crops were short-chain compounds (PFBA, PFPeA, PFHxA).

and half agricultural land use and is divided into two sections: the State Game Lands site and the Astronomy site. The Living Filter is operated under a permit from the Pennsylvania Department of Environmental Protection, with 13 monitoring wells across the site (seven wells on the State Game Lands site and six wells on the Astronomy site) that are sampled at least quarterly for nitrate as part of the permitting requirements. In general, the Living Filter is operated to maintain nitrate concentrations below 9 mg NO$_3$–N L^{-1}, ensuring that the aquifer remains below the primary drinking water standard of 10 mg NO$_3$–N L^{-1} (USEPA, 2009). Effluent irrigation occurs at the site such that several of the 177 irrigation laterals are on for 12 h d^{-1}, 7 d wk^{-1}, on a rotating schedule that allows individual fields within the Living Filter to be irrigated no more than once per week. The maximum permitted irrigation rate is 5 cm ha^{-1} wk^{-1}. Irrigation activities are preferentially selected such that forested portions of the site receive more irrigation in the winter months, whereas the laterals in cropped fields are used more in the spring and summer months within the permitting requirements of no more than 12 h of irrigation for any given field over the course of 1 wk.

Soils are primarily deep, well-drained Hublersburg silt loams (clayey, illitic, mesic Typic Hapludults) bracketed by Morrison sand loams (fine-loamy, mixed, active, mesic Ultic Halpudalfs) at the western end of the State Game Lands site and Hagerstown silt and silty clay loams (fine, mixed, semiactive, mesic Typic Halpudalfs) at the eastern end of the Astronomy site (USDA-NRCS, 2019). The irregular surface topography, resulting from nonuniform weathering of the parent carbonate bedrock, and a deep groundwater table of 30–90 m promote infiltration and filtering of both effluent and precipitation (Parizek, 2007). Full hydrogeological characteristics of the site are provided in Parizek et al. (1967).

2.2 | Sampling and analysis methods

2.2.1 | Water samples

Effluent wastewater 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. Flow-paced composite samples (24 h) were collected into 19-L glass jugs using automated (Teledyne ISCO) samplers equipped with flow sensors. Thus, smaller percentages of each composite sample were collected during low-flow periods of the day and higher percentages were collected during periods of high-flow at the treatment plant. All tubing used for sampling was replaced with PFAS-free high-density polyethylene (HDPE) to minimize potential contamination during sampling. Each 24-h composite was subsampled into a 1-L HDPE bottle with HDPE-lined cap using nitrile gloves. The 1-L sample was refrigerated at 4 °C for <6 h until it was picked up from the treatment plant and shipped on ice overnight to Eurofins Lancaster Laboratories, Inc., in Lancaster, PA, for PFAS analysis.

During sampling at each of the 13 monitoring wells, a field blank was collected by transferring deionized water into a blank HDPE bottle in the field to account for any atmospheric PFAS at the field location that could affect PFAS concentrations in the well water samples at the time of collection. Each well was pumped for ∼20 min prior to sample collection, following the standard permitting required protocols for nitrate sampling. Samples were held in coolers on ice during collection and then 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. All samples were extracted well within the maximum hold time of 90 d for aqueous samples (Shoemaker & Tettenhorst, 2018) and typically within 15–30 d of collection. Samples were analyzed for 20 PFAS (Supplemental Table S1) at Eurofins based on a modification of EPA Method 537.1 (Shoemaker & Tettenhorst, 2018) to accommodate non-potable water samples. Hereafter, we refer to "total measured PFAS" as including these 20 compounds, which excludes many precursors and some terminal perfluoroalkyl acids not included in this analysis.

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 bath 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: one method blank, one laboratory control sample, one laboratory control sample duplicate, one matrix spike, and one matrix spike duplicate.

2.2.2 | Crop tissue samples

At the time of harvest (22 Sept. 2020), farm services staff collected about 500 g (at harvest moisture) of corn silage into a large PFAS-free HDPE container to be subsampled into five replicates. Per- and polyfluoroalkyl substances present in the corn silage could originate from either direct foliar application during spray-irrigation activities or root uptake by the corn while it was growing. Corn silage samples were also collected from a portion of the site that was not directly spray-irrigated for comparison. No biosolids are applied at the Living Filter. However, there was still potential for PFAS to be present in the corn silage from background levels of PFAS in the atmosphere, rain, and/or soil; from application drift known to occur at the Living Filter (Woodward et al., 2014); and from PFAS that may be present in hydrologically upgradient groundwater at the site. The concentrations at which different PFAS were present in the corn silage were quantified to determine the range of PFAS that could enter the food chain through direct and indirect effects of spray-irrigation activities of treated wastewater.

Similarly, farm services staff collected ∼500 g (at harvest moisture) of endophyte-free tall fescue into a large PFAS-free HDPE container to be subsampled into five replicates and extracted for PFAS. The fescue was used for haylage and could only be collected from areas of the Living Filter that were directly spray-irrigated because fescue is not grown in the nonirrigated portions. Previous research has suggested that PFAS concentrations may be greater in the second cutting than the first (Ghisi et al., 2019). Therefore, we collected samples ($n = 5$) from the first and third cuttings (16 June and 23 Oct. 2020) of fescue used for haylage that had been directly spray-irrigated. The second cutting was not included in our sampling because it was harvested for baled hay instead of haylage.

Crop tissue subsamples were shipped in 500-mL, wide-mouthed HDPE bottles to Eurofins for PFAS analysis. Samples were analyzed for 20 target PFAS (Supplemental Table S1) at Eurofins based on a modification of USEPA 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–tandem 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.

Based on current sampling methods, we are unable to 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 measured PFAS present in and on the plant tissue at the time of harvest. However, we believe that these samples were 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 are therefore irrigated at the same times and rates, such that differences in irrigation management of the laterals would not be a factor in this study.

3 | RESULTS AND DISCUSSION

3.1 | Wastewater samples

A total of seven 24-h composite samples from the PSU WRF effluent were collected between October 2019 and February 2021. Ten of the 20 PFAS analyzed were found at concentrations above the limit of detection (LOD) in at least one sample, with detectable PFAS concentrations in 100% of the samples collected, including four short-chain perfluoroalkyl carboxylic acids (PFCAs) (PFBA, perfluoropentanoic acid [PFPeA], perfluorohexanoic acid [PFHxA], and perfluoroheptanic acid [PFHpA]), three long-chain PFCAs (PFOA, perfluorononanoic acid, and perfluorodecanoic acid [PFDA]), one short-chain perfluoroalkane sulfonic acid (PFSA) (PFBS), and two long-chain PFSAs (perfluorohexanesulfonic acid [PFHxS] and PFOS) (Figure 1). Total measured PFAS concentrations ranged from 32.4 to 87.8 ng L^{-1} (Figure 1a; Supplemental Table S2). These concentration ranges are similar to those observed in effluent sampled from WWTPs around the world: 30–200 ng L^{-1} for six WWTPs sampled in New Hampshire (Tavasoli et al., 2021), an average of 110 ng L^{-1} for 19 WWTPs in Australia (Coggan et al., 2019), up to 107 ng L^{-1} in effluent for municipal WWTPs

in China (Zhang et al., 2013), and typical PFAS concentration ranges of 30–150 ng L^{-1} for WWTPs in Europe and the United States (as reviewed by Margot et al. [2015]).

The nearly threefold difference in concentration observed for the PSU WRF 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. Per- and polyfluoroalkyl substances loads entering the PSU WRF were lowest in May 2020 when campus was not holding in-person classes and highest again in spring 2021, when students were returning to campus for in-person instruction to resume (Figure 1b).

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 during the study period remained similar (Figure 1c). 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% (Figure 1c). 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.

3.2 | Monitoring wells

Seven samples from each monitoring well were collected between October 2019 and February 2021, for a total of 91 well water samples. Of the 20 PFAS analyzed, the following were not found at detectable concentrations in any of the samples collected: 11-chloroeicosafluoro-3oxaundecane-1-sulfonic acid, 9-chlorohexadecafluoro-3oxanonane-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 1 (all data are available in Supplemental Tables S3–S15).

The total measured PFAS concentrations in the monitoring wells ranged from below the LOD to 155 ng L^{-1}. With the
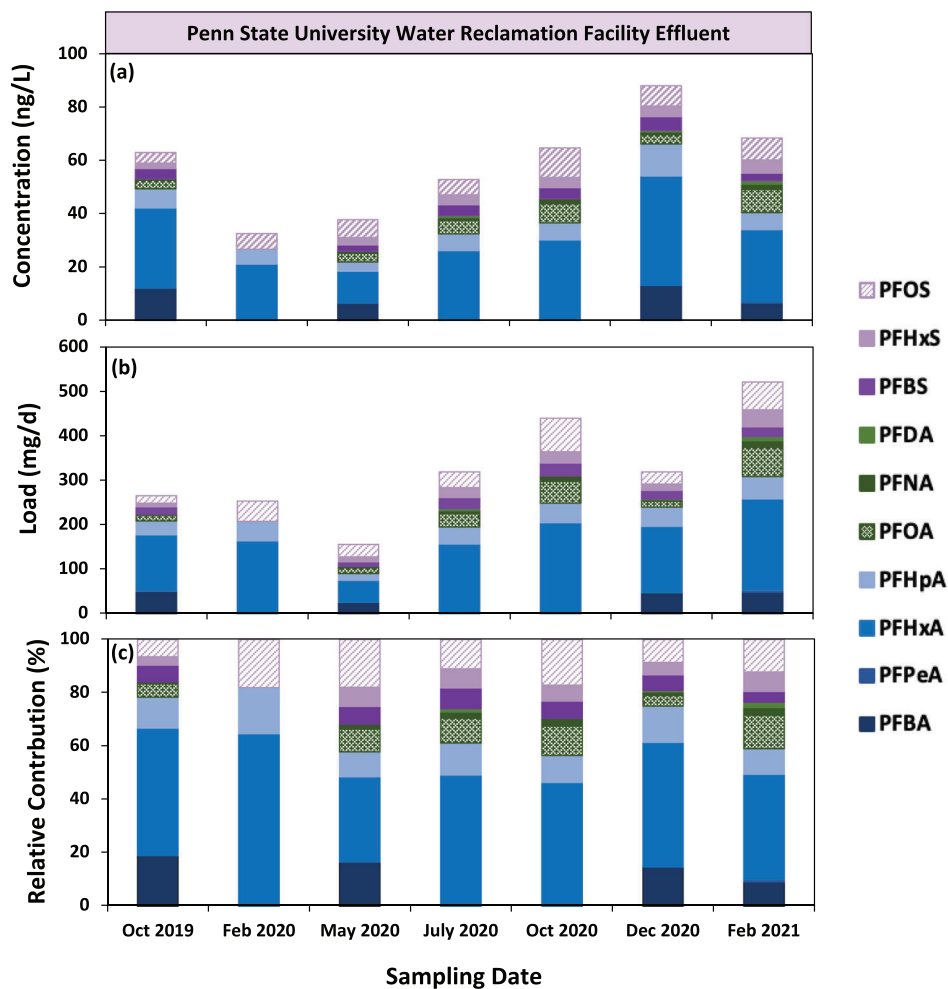
FIGURE 1 (a) Per- and polyfluoroalkyl substance (PFAS) concentrations (ng L⁻¹), (b) mass loadings (mg d⁻¹), and (c) relative contribution (%) of each PFAS to total measured PFAS for each sampling date in the effluent of The Pennsylvania State University Water Reclamation Facility. Concentrations are from 24-h composite samples collected from the final effluent prior to being pumped to the Living Filter spray-irrigation site. Compounds are shown in order of increasing chain length for short-chain perfluoroalkyl carboxylic acids (PFCAs) (blue), long-chain PFCAs (green), short-chain perfluoroalkane sulfonic acids (PFSAs) (dark purple), and long-chain PFSAs (light purple); perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) are shown with patterns. PFBA, perfluorobutanoic acid; PFBS, perfluorobutane sulfonic acid; PFDA, perfluorodecanoic acid; PFHpA, perfluoroheptanic acid; PFHxA, perfluorohexanoic acid; PFHxS, perfluorohexanesulfonic acid; PFNA, perfluorononanoic acid; PFPeA, perfluoropentanoic acid

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.

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 (Supplemental Table S16).

Low temporal variability in the total measured PFAS concentrations throughout the study period is likely a function of several factors. Although usage of pharmaceuticals, especially antibiotics, is known to follow seasonal patterns, with lower usage in warmer months compared with 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 to less than 5 years (Monteiro & Boxall, 2010; Walters et al., 2010; Wu et al., 2012), whereas 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

TABLE 1 Summary of per- and polyfluoroalkyl substance (PFAS) concentrations for seven monitoring wells at the State Game Lands site and the Astronomy site

State Game Lands[a]	W7	W2	G12	G10	W6	W5	W1
Short-chain PFCAs							
PFBA							
n > LOD, %	0	0	100	100	100	100	29
Range, ng L^{-1}	<LOD	<LOD	4.2–6.0	10.0–13.0	14.0–19.0	10.0–13.0	<LOD–2.0
Avg. n > LOD, ng L^{-1}	NA	NA	5.1	11.1	16.3	11.1	NA
PFPeA							
n > LOD, %	0	0	57	100	100	86	29
Range, ng L^{-1}	<LOD	<LOD	<LOD–9.4	0.72–21.0	0.80–31.0	<LOD–21.0	<LOD–3.1
Avg. n > LOD, ng L^{-1}	NA	NA	5.3	6.6	9.2	7.2	NA
PFHxA							
n > LOD, %	14.3	0	100	100	100	100	100
Range, ng L^{-1}	<LOD–1.1	<LOD	6.0–7.5	15.0–19.0	19.0–28.0	15.0–19.0	1.7–2.4
Avg. n > LOD, ng L^{-1}	NA	NA	6.73	17.7	24.3	17.14	2.1
PFHpA							
n > LOD, %	0	0	100	100	100	100	100
Range, ng L^{-1}	<LOD	<LOD	2.4–2.6	6.2–7.8	9.1–12.0	5.9–8.3	1.1–1.5
Avg. n > LOD, ng L^{-1}	NA	NA	2.5	7.3	10.3	7.3	1.3
Long-chain PFCAs							
PFOA							
n > LOD, %	14.3	0	100	100	100	100	100
Range, ng L^{-1}	<LOD–0.96	<LOD	5.3–7.6	18.0–22.0	24.0–30.0	17.0–24.0	2.4–3.6
Avg. n > LOD, ng L^{-1}	NA	NA	6.17	18.9	26.9	21.3	3.0
PFNA							
n > LOD, %	0	0	0	100	100	100	0
Range, ng L^{-1}	<LOD	<LOD	<LOD	0.63–1.0	0.6–1.2	2.6–3.5	<LOD
Avg. n > LOD, ng L^{-1}	NA	NA	NA	0.84	1.0	3.0	NA
Short-chain PFSA							
PFBS							
n > LOD, %	0	0	100	100	100	100	100
Range, ng L^{-1}	<LOD	<LOD	1.1–1.4	3.4–4.0	4.7–5.6	2.7–3.3	2.3–4.5
Avg. n > LOD, ng L^{-1}	NA	NA	1.3	3.7	5.1	2.9	3.2
Long-chain PFSAs							
PFHxS							
n > LOD, %	14.3	0	100	100	100	100	100
Range, ng L^{-1}	<LOD–0.69	<LOD	3.1–4.6	11.0–15.0	17.0–25.0	7.0–9.1	1.5–1.8
Avg. n > LOD, ng L^{-1}	NA	NA	4.0	13.4	10.1	8.1	1.7
PFOS							
n > LOD, %	0	0	100	100	100	100	100
Range, ng L^{-1}	<LOD	<LOD	1.0–2.0	5.0–7.2	5.0–7.7	16.0–21.0	3.4–8.0
Avg. n > LOD, ng L^{-1}	NA	NA	1.6	6.5	6.4	18.1	5.4
Total measured PFAS							
n > LOD, %	14.3	0	100	100	100	100	100
Range, ng L^{-1}	<LOD–2.75	<LOD	41.8–41.1	72.2–108.8	102.6–155.3	79.2–118.4	13.6–22.5
Avg. n > LOD, ng L^{-1}	NA	NA	30.4	86.0	106.0	95.2	18.1

(Continues)

T A B L E 1   (Continued)

Astronomy site	P5	P4	P3	F3	P2	P1
Short-chain PFCAs						
PFBA						
n > LOD, %	100	43	100	100	100	100
Range, ng L^{-1}	6.9–9.0	<LOD–2.5	5.5–8.2	11.0–13.0	12.0–15.0	11.0–15.0
Avg. n > LOD, ng L^{-1}	7.9	2.3	6.5	11.7	14.0	12.9
PFPeA						
n > LOD, %	43	29	43	100	100	86
Range, ng L^{-1}	<LOD–15.0	<LOD–1.3	<LOD–13.0	0.46–23.0	0.48–0.70	<LOD–26.0
Avg. n > LOD, ng L^{-1}	9.8	NA	8.2	6.8	8.4	7.66
PFHxA						
n > LOD, %	100	100	100	100	100	100
Range, ng L^{-1}	9.9–16.0	1.1–1.6	9.5–16.0	16.0–22.0	20.0–25.0	20.0–22.0
Avg. n > LOD, ng L^{-1}	12.6	1.19	11.4	18.3	22.6	20.9
PFHpA						
n > LOD, %	100	100	100	100	100	100
Range, ng L^{-1}	4.1–6.1	0.54–0.65	4.7–6.1	6.2–9.0	9.0–11.0	7.9–9.1
Avg. n > LOD, ng L^{-1}	5.2	0.62	5.3	7.7	10.1	8.5
Long-chain PFCAs						
PFOA						
n > LOD, %	100	100	100	100	100	100
Range, ng L^{-1}	12.0–17.0	1.1–1.4	9.6–13.0	9.1–21.0	19.0–30.0	16.0–20.0
Avg. n > LOD, ng L^{-1}	13.7	1.3	11.5	17.4	24.3	19.3
PFNA						
n > LOD, %	100	0	0	71	100	100
Range, ng L^{-1}	0.80–1.2	<LOD	<LOD	<LOD–0.83	1.2–1.9	2.0–2.9
Avg. n > LOD, ng L^{-1}	1.1	NA	NA	0.71	1.5	2.4
Short-chain PFSA						
PFBS						
n > LOD, %	100	100	100	100	100	100
Range, ng L^{-1}	2.2–2.7	1.2–1.5	1.9–2.5	2.8–3.6	3.4–4.2	3.4–4.5
Avg. n > LOD, ng L^{-1}	2.4	1.3	2.1	3.2	3.8	3.9
Long-chain PFSAs						
PFHxS						
n > LOD, %	100	86	100	100	100	100
Range, ng L^{-1}	6.1–8.9	<LOD–0.55	4.0–6.2	7.5–9.5	10.0–12.0	9.3–12.0
Avg. n > LOD, ng L^{-1}	7.5	0.51	5.0	8.6	11.0	10.6
PFOS						
n > LOD, %	100	86	100	86	100	100
Range, ng L^{-1}	7.9–9.0	<LOD–0.53	1.3–1.8	<LOD–6.9	7.4–12.0	15.0–22.0
Avg. n > LOD, ng L^{-1}	8.3	0.51	1.6	5.2	9.7	18.3
Total measured PFAS						
n > LOD, %	100	100	100	100	100	100
Range, ng L^{-1}	50.6–77.8	4.7–7.8	40.6–58.0	61.7–100.0	82.5–135.6	84.6–126.2
Avg. n > LOD, ng L^{-1}	62.9	6.5	47.0	79.6	105.3	104.3

Note. Seven samples for each well (n = 7) collected in Oct. 2019; Feb., May, July, Oct., and Dec. 2020; and Feb. 2021. LOD, limit of detection (values given in Supplemental Table S1); NA, not applicable because fewer than three samples contained concentrations above the LOD.

[a]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.

during colder months and lower degradation rates once introduced to the Living Filter site through wastewater irrigation activities.

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 for total measured PFAS concentrations in each well over the study period were low, with values ranging from 0.06 (Well G10) to 0.23 (Well W1). Generally, the wells with the highest total measured PFAS concentrations exhibited the lowest coefficients of variation (Supplemental Figure S1), suggesting that the more affected a well is, the lower the variability in concentrations. During the study period, groundwater elevations remained relatively constant across the study site: 9 of the 13 wells varied by <5 m, with the greatest difference during the study period of ~13 m for Well W6.

No strong relationships between groundwater elevation and total measured PFAS concentrations were found (Figure 2); 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 in Wells P1, P2, and P3 on the Astronomy site (well locations shown in Figure 3). 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 3), with the groundwater direction primarily away from rather than toward them. Thus, the PFAS concentration increases for Wells 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.

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 3). The lowest concentrations were observed in wells on the outer boundaries of the Living Filter that were least influenced by irrigation activities, and the highest concentrations were toward the northeastern portions of the sites. Groundwater at the State Game Lands site generally flows from Wells W7 and W2 toward Wells G12 and G10 and from Well W1 toward Well W5. Spatial trends in total measured PFAS concentrations followed these general hydrologic trends, with the undetectable total measured PFAS concentrations in Wells W2 and W7 gradually increasing to the highest total measured PFAS concentrations in Wells W6 and W5. Similar
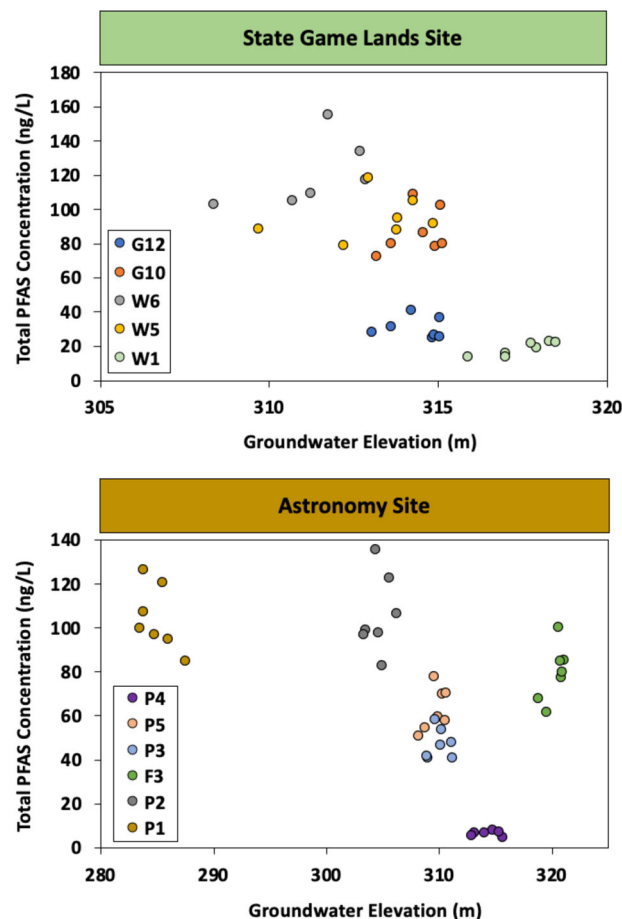

FIGURE 2 Total measured per- and polyfluoroalkyl substance (PFAS) concentrations as function of groundwater elevations for the State Game Lands site (left) and the Astronomy site (right). Data for Wells W2 and W7 are not shown in this figure because the number of samples with detected PFAS concentrations was 0 for W2 and only 1 for W7 (see Table 1)

patterns were observed on the Astronomy site, with concentrations increasing from Wells P4 and P3 to Wells F3 and P2, following the general groundwater direction (Figure 3).

Overall, the spatial pattern of PFAS at the Living Filter suggests 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 followed 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 Well W5 having the highest concentration of naproxen on the State Game Lands side. These wells, along with Wells 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 appear to be consistent with higher concentrations of other water quality parameters.
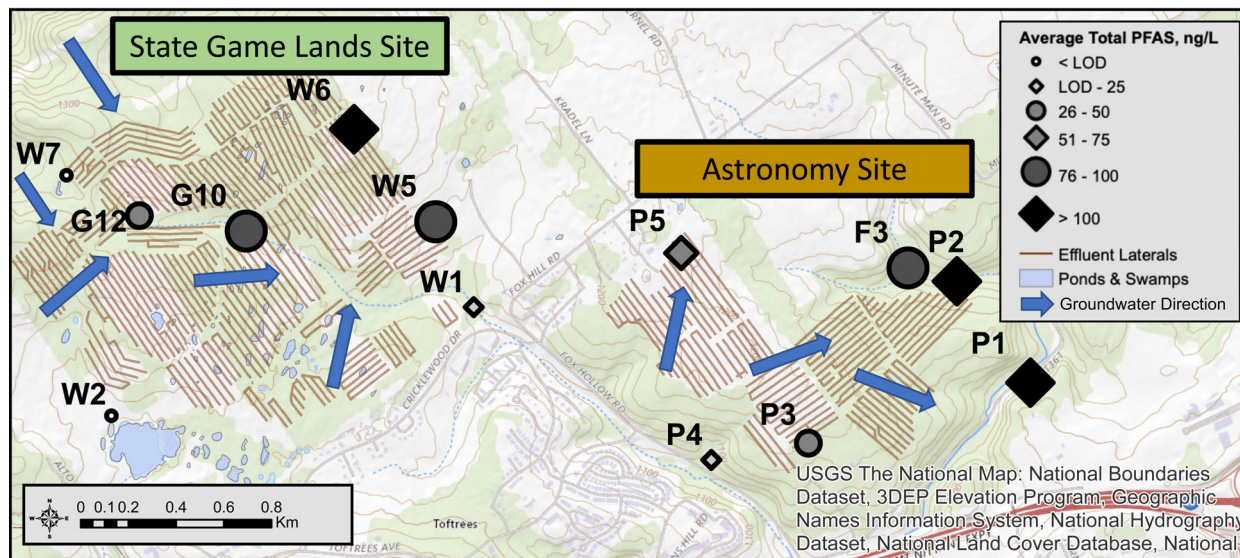
FIGURE 3 Average total measured per- and polyfluoroalkyl substance (PFAS) concentrations for each monitoring well location for the study period (October 2019–February 2021)

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 ~25% of the total measured PFAS concentrations observed, and PFHpA, PFBA, and PFHxS each contributed 10–15%. The contribution of PFOS to the total measured PFAS concentrations for each of Wells G10, G12, and W6 was <10%, but ~20% for Well W5. For Well W1, PFBS and PFOA each contributed ~20% of the total observed PFAS concentrations, whereas PFOS comprised ~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. Contributions of PFOS to the total measured PFAS concentrations varied from <5% for Well P3 to ~20% for Well P1.

3.3 | Wastewater and monitoring wells comparison

Average total measured PFAS concentrations were generally on the same order of magnitude for the effluent and monitoring wells from the State Game Lands and the Astronomy sites (Figures 1 and 4). Concentrations of PFAS 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. Per- and polyfluoroalkyl substances have been found to be persistent on the order of decades and longer (e.g., Washington et al., 2019) and thus would not exhibit the enhanced degradation rates during warmer months that have been observed for many pharmaceuticals. Given their ubiquitous use, PFAS are also less likely to exhibit seasonal variability in effluent, unlike some pharmaceuticals for which 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. Although 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, 2021). Jahn (2021) also found PFOA and PFOS storage in the soil to be significantly greater than the mass applied via annual effluent irrigation, suggesting a trade-off between
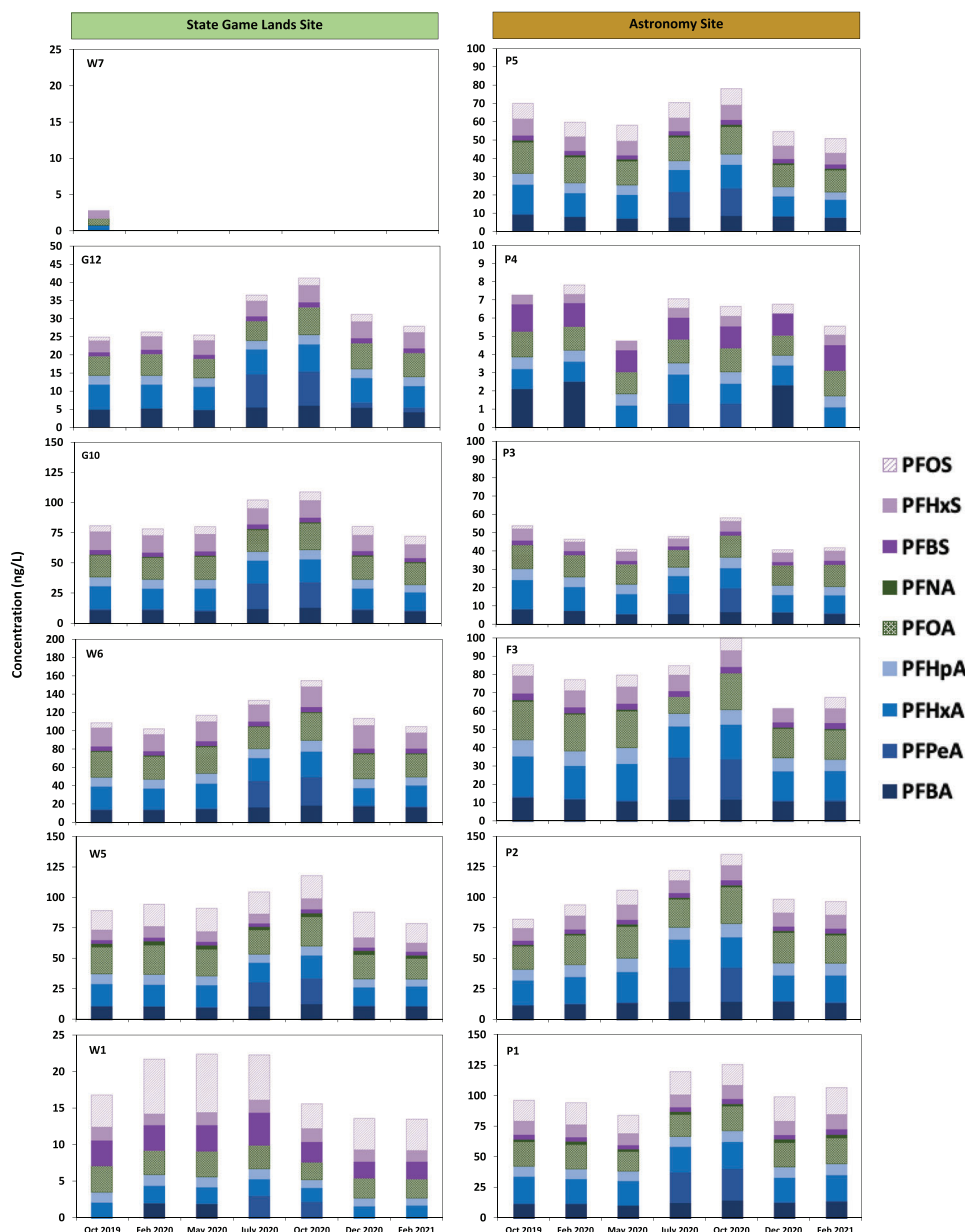
FIGURE 4 Per- and polyfluoroalkyl substance concentrations observed for each sampling date for each of the monitoring wells at the State Game Lands site (left) and the Astronomy site (right). Please note the differences in y-axis ranges. Also note that W2 is not included on the figure because no measured 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

immediate PFAS release into surface water or beneficial reuse serving as a long-term source to groundwater.

3.4 | Crop tissue

3.4.1 | Corn samples

Fresh corn silage samples harvested in fall 2020 contained detectable concentrations of PFBA in both the irrigated and nonirrigated samples (Supplemental Table S17),

with irrigated replicates containing 0.83–0.95 µg kg^{-1} dry weight (dw) of PFBA. Only two nonirrigated replicates had detectable PFBA concentrations (0.56 and 0.83 µg kg^{-1} 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 nonirrigated corn silage and detectable concentrations of PFHxA in one of the five replicates for irrigated corn silage (Supplemental Table S17). The preferential uptake of PFBA, a short-chain PFCA, has been observed in other studies (Blaine et al., 2013, 2014; Liu et al., 2019). Muschket

et al. (2020) and Navarro et al. (2017) 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 nonirrigated samples could arise from atmospheric deposition because its high volatility is conducive to long-range atmospheric transport (Wang et al., 2022) in addition to drift at the site and/or uptake from groundwater.

3.4.2 | Fescue haylage

Per- and polyfluoroalkyl substances in fescue samples (Supplemental Table S18) 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^{-1} dw) in all five replicates and PFOS (0.29 ± 0.07 µg kg^{-1} dw) in four of the five replicates (Supplemental Table S18). Perfluorooctane sulfonate was also detected in one of the five replicate samples from the spring 2020 harvest. Perfluorooctane sulfonate and PFOA, both long-chain PFAS, were either below their LODs or were 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 (Supplemental Table S18).

The spring and fall cuttings contained average total measured PFAS concentrations of 11.3 ± 1.5 and 3.8 ± 0.88 µg kg^{-1} 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. Perfluorohexanoic acid was detected in 100% of the wastewater effluent samples at concentrations ranging from 12 to 41 ng L^{-1} (Supplemental Table S2), and therefore it is perhaps unsurprising that it was detected in the spring fescue tissue samples. Moreover, although many PFAS are strongly retained in plant roots, Navarro et al. (2017) found that PFHxA was easily translocated to aboveground plant parts.

For the fall cutting of fescue, PFHxA was near the LOD and detected in four of the five replicates (Supplemental Table S18), with PFBA being the dominant contributor (~56%) to the total measured PFAS concentrations, similar to the findings of Muschket et al. (2020). Perfluorobutanoic acid was present in the wastewater effluent in 86% of the samples collected (Figure 1; Supplemental Table S2) at concentrations up to 13 ng L^{-1}. 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 (two to three times higher) observed in the spring 2020 harvest of fescue compared with values observed in fall 2020.

3.4.3 | 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 nonresearch dairy cows includes 0.91 kg animal^{-1} d^{-1} of corn silage and 11.1 kg animal^{-1} d^{-1} 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 2.46–7.67 mg animal^{-1} yr^{-1} (dw) of total measured PFAS (Table 2). The difference in PFAS concentrations of feed comprised of irrigated versus nonirrigated corn silage was approximately a factor of 2 because corn silage comprised approximately 40% of the daily ration. The PFAS estimated to be in the livestock feed in this current study were two to three orders of magnitude less than those in the Kowalczyk et al. (2013) study (0.01–0.03 compared with 14.7 µg kg^{-1} body weight).

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, whereas 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 with 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 biotransfer factor (BTF) to milk was highest for PFOA (log BTF = −1.95) and lowest for PFDoDA (log BTF = −1.52). Zhao et al. (2012) and Conder et al. (2008) found that PFAS accumulation is greater for PFSAs compared with 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 the potential for milk from the dairy cattle consuming crops from the

TABLE 2 Per- and polyfluoroalkyl substance (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[a]	2020 irrigated corn + spring 2020 fescue	2020 nonirrigated corn + spring 2020 fescue	2020 irrigated corn + fall 2020 fescue	2020 nonirrigated corn + fall 2020 fescue
	—mg animal^{-1} yr^{-1}—			
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	0.2	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	0.1	0.1
Total measured PFAS	7.67	4.96	5.17	2

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

[a]HFPO-DA, hexafluoropropylene oxide dimer acid; PFBA, perfluorobutanoic acid; PFHpA, perfluoroheptanic acid; PFHxA, perfluorohexanoic acid; PFHxS, perfluorohexanesulfonic acid; PFOA, perfluorooctanoic acid; PFOS, perfluorooctane sulfonate; PFPeA, perfluoropentanoic acid.

irrigated site to contain PFAS. For corn harvested in fall 2020 and fescue harvested in spring 2020, ~3% of the total measured PFAS detected in the feed were long-chain compounds (PFOS and PFOA) (Table 2); 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; Table 2) comprised ~87% of the total measured PFAS detected in the feed; the remaining 13% was comprised of long-chain compounds (PFHxS, PFOS, and PFOA) (Table 2). 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, although 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 Services 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, and PFBS and PFOA were near the detection limit (Kowalczyk et al., 2013). Perfluorobutanoic acid was the dominant PFAS in the feed analyzed for this project (Table 2), 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, whereas PFOS was most frequently detected in milk, with PFBA, PFOA, and PFPeA also detected in >40% of the milk samples. Perfluorobutanoic acid has been found in trace concentrations ranging from 4.7 to 43 ng L^{-1} 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 | CONCLUSIONS

This study represents a comprehensive assessment of PFAS occurrence at a long-term beneficial reuse facility. Overall, 10 PFAS were found across the site, with average total measured PFAS concentrations of 88 ng L^{-1} in the wastewater effluent and concentrations as high as 155 ng L^{-1} in the monitoring wells, suggesting that occurrence of PFAS across the site is nearly ubiquitous. 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^{-1} (USEPA, 2009), strict regulations for PFAS in potable water may limit the long-term feasibility of beneficial reuse of treated wastewater because PFOS and/or PFOA were detected (and therefore exceeded 2022 interim

health advisories) in all 13 of the monitoring wells across the site. However, these wells do not serve as supply wells for potable water and therefore do not pose a direct risk to human health.

Concentrations of PFAS showed little seasonal variability, and spatial patterns of PFAS concentrations in the monitoring wells followed the general groundwater flow direction, with the lowest PFAS concentrations 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 nonirrigated portions of the site, suggesting that PFAS could enter the food chain when these crops are fed to livestock. The vast majority (>84%) of the PFAS present in the feed crops were short-chain compounds, including PFBA, PFPeA, and PFHxA; 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.

AUTHOR CONTRIBUTIONS

Olivia Mroczko: Data curation, Formal analysis, Investigation, Visualization, Writing – original draft, Heather E. Preisendanz: Conceptualization, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, Writing – original draft, Christopher Wilson: Data curation, Formal analysis, Validation, Writing – original draft, Michael L. Mashtare: Methodology, Supervision, Writing – review & editing, Herschel A. Elliott: Conceptualization, Funding acquisition, Supervision, Visualization, Writing – review & editing, Tamie L. Veith: Conceptualization, Funding acquisition, Supervision, Visualization, Writing – review & editing, Kathy J. Soder: Conceptualization, Methodology, Writing – review & editing, and John E. Watson: Conceptualization, Funding acquisition, Supervision, Writing – review & editing.

CONFLICT OF INTEREST

Authors H.E. Preisendanz and T.L. Veith reside in the same household. The authors declare no other conflict of interest.

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SUPPORTING INFORMATION

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