Distribution of Per- and Polyfluoroalkyl Substances in the Rapidly Urbanizing Arroyo Colorado Watershed, Texas

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Abstract: This study presents the first report of per- and polyfluoroalkyl substances (PFAS) in water samples collected in the Arroyo Colorado (n = 15), irrigation canals (n = 6), stormwater and wastewater retention ponds (n = 7), as well as drinking waters (n = 2) across the Arroyo Colorado watershed. Of the 30 PFAS monitored in this study, 14 were detected in the samples in various combinations. Short-chain PFAS (less than 8 carbon atoms) were observed in most samples. Water collected from the Arroyo Colorado showed significant spatial variabilities, with high total PFAS concentrations observed near possible point sources - a municipal airport and wastewater treatment facilities. PFAS concentrations were generally higher in water samples collected in stormwater and wastewater retention ponds than in the Arroyo Colorado and irrigation canals. PFAS in stormwater retention ponds likely came from roadway runoff. Short-chain PFAS were observed in the two municipal water samples, but they were below the current U.S. EPA regulation limits or are not currently regulated. This study provides useful information for water quality in this region and provides insights into PFAS occurrence in a rapidly urbanizing area.

Keywords: *PFAS, urban water, agriculture*

Per- and polyfluoroalkyl substances (PFAS) are a diverse group of human-made chemicals with more than 10,000 chemicals found, to date, in the United States Environmental Protection Agency's CompTox Chemicals Dashboard (U.S. EPA 2023). PFAS are broadly used in many industrial and consumer products due to their unique physical-chemical properties. PFAS are in items we use every day, such as non-stick cookware, food packaging, textiles, cosmetics, and beyond (Trier et al. 2011; Glüge et al. 2020; Whitehead et al. 2021; Schellenberger et al. 2022). Aqueous film-forming foam (AFFF), which has been used to extinguish hydrocarbon-fuel fires for several decades, contains various PFAS compounds (Backe et al. 2013; Ruyle et al. 2021). Many PFAS are bioaccumulative and toxic to animals and humans (Giesy and Kannan 2001; Fenton et al. 2021; George et al. 2023).

PFAS are chemically diverse. Perfluorinated PFAS have fully fluorinated carbon chains, while polyfluorinated PFAS contain multiple carbon-fluorine bonds, but not all carbon atoms are bonded to fluorine. Additionally, PFAS are grouped based on the polar functional groups they contain, e.g., carboxylic, sulfonic, sulfonamide, etc. (Table 1). These chemical characteristics affect their fate and transport in the environment. PFAS with fully fluorinated carbon chains, i.e., perfluorinated, are extremely resistant to degradation and, thus, are persistent in the environment after release (Kwiatkowski et al. 2020). While polyfluorinated PFAS may be degraded in the environment, they are precursors to the perfluorinated compounds (Houtz

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Research Implications

- This is the first report on PFAS concentrations in the rapidly urbanizing Arroyo Colorado watershed, and it provides critical information on water quality in this region.

- PFAS were found in almost all water samples in this study, particularly short-chain PFAS. Short-chain PFAS may be taken up by plants, such as crops.

- This survey showed significant spatial heterogeneity of PFAS concentrations across the Arroyo Colorado watershed, with more PFAS types closer to possible sources. Concentrations and type distributions are both critical for understanding PFAS fate and transport within a watershed. Future studies should also consider temporal distributions.

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et al. 2013). PFAS are more mobile in the aqueous phase than non-polar legacy contaminants, such as dioxins, polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs), due to their amphiphilic properties. Therefore, PFAS are ubiquitously distributed in groundwater, surface waters, sediments, soil, air, and even our drinking water (Jahnke et al. 2009; Houtz et al. 2013;

Domingo and Nadal 2019; Aly et al. 2020; Strivens et al. 2021; Teymoorian et al. 2023).

There are numerous sources of PFAS with various combinations of compounds within this chemical class. Therefore, it is critical to understand which PFAS and at what concentrations are found in the environment to better assess possible exposure risks. In the past decade, researchers have investigated PFAS occurrence in different waterbodies worldwide because water can transport PFAS for long distances and is closely related to human exposure through water supplies and fish (Scott et al. 2009; Moller et al. 2010; Lam et al. 2014; D'Agostino and Mabury 2017; Gebbink et al. 2017; Groffen et al. 2018; Aly et al. 2020; Goodrow et al. 2020; Guillette et al. 2020; Ruyle et al. 2021). However, the diverse chemical characteristics and sources of PFAS likely mean that data from other waterbodies may not be extrapolated in certain regions. To date, information on the occurrence of PFAS in Texas rivers is scarce. This study investigates the distribution of 30 PFAS in the Arroyo Colorado watershed (Figure 1).

The Arroyo Colorado Watershed

The Arroyo Colorado watershed is located in the Lower Rio Grande Valley of South Texas,
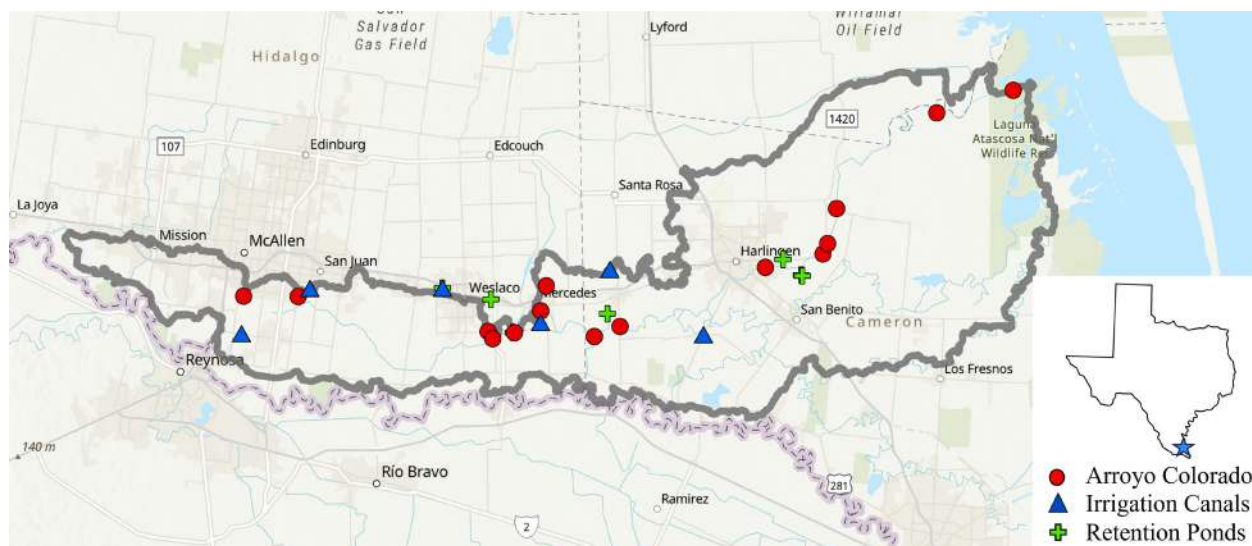

Figure 1. Sampling sites of this study. Red circles mark the locations of water samples collected in the Arroyo Colorado. Blue triangles mark the locations of water samples collected in irrigation canals. Green crosses mark the locations of water samples collected in stormwater or wastewater treatment plant retention ponds. The grey outline marks the boundary of the Arroyo Colorado watershed.

and includes portions of Cameron, Hidalgo, and Willacy counties. McAllen (Hidalgo County) and Harlingen (Cameron County), TX, are both considered urban areas in the 2020 U.S. Census. Smaller cities partly within the watershed include Mission, Pharr, San Juan, Alamo, Donna, Weslaco, Mercedes, La Feria, San Benito, and Rio Hondo. The entire area is undergoing urbanization, and many historically farmed lands are being converted to urban uses.

The Arroyo Colorado (~ 90 miles long), which flows eastward into the Lower Laguna Madre from its headwaters near Mission, is a historic distributary of the Rio Grande and lies within the Rio Grande delta. The Arroyo Colorado watershed is served by multiple irrigation districts that supply Rio Grande water across the Lower Rio Grande Valley for agricultural irrigation water and raw drinking water. Irrigation canals are hydrologically disconnected from the Arroyo Colorado, but irrigation return flows from these sources do flow into the Arroyo Colorado in many cases. In normal flow conditions, the Arroyo Colorado consists primarily of treated municipal wastewater effluent, agricultural irrigation return flows, and stormwater from the watershed. The lower 25 miles of the Arroyo Colorado are tidally influenced. This section has been dredged and is maintained as a ship and barge channel for the Port of Harlingen. In flood conditions, the Arroyo Colorado hydrologically connects to the Rio Grande and the North Floodway.

Approximately 706 square miles of land drains into the Arroyo Colorado. Primary land cover includes croplands (53%), rangelands/forests (14%), pastures (6%), mixed intensity developed spaces (19%), wetlands (8%), and waterbodies (Flores et al. 2017). Soils in the region range from sandy to silty loams across the larger Rio Grande delta and support large agricultural enterprises. Originally, cattle ranching dominated the region due to limited water resources. Large-scale irrigation changed this in the early 1900s, and the arrival of the railroad in 1904 allowed cultivated agriculture to expand rapidly (Vigness and Odintz 1952). This region is still agriculturally dominated, but has experienced rapid land use changes. Between 2001 and 2021, approximately 16,532 acres of agricultural working lands were converted into other uses, while developed space has increased by 14,268 acres representing a roughly 4% loss of open space across the watershed (Dewitz 2023). This rapid conversion continues today as importing goods and produce from Mexico has led to considerable industrial development. Agriculture and municipalities represent the largest scale water users in the watershed, and the return flows from these sources largely sustain flows in the Arroyo Colorado. These return flows carry nutrients, sediment, bacteria, and many pollutants (e.g., PCBs) into the water body, leading to various water quality impairments and concerns. However, PFAS concentrations have never been assessed in the Arroyo Colorado watershed. Therefore, this study will provide critical information on water resource quality in the Arroyo Colorado.

Methods

Sampling

All supplies, such as sample containers, laboratory consumables, solvents (Optima LC-grade), etc., were screened for PFAS to ensure the supplies were free of PFAS contamination before the study. Both field and laboratory blanks were ultrahigh-purity water (Milli-Q 18.2 MΩ·cm) contained in the same type of high-density polyethylene (HDPE) 250 mL bottles used for sample collection.

Sampling occurred on January 31st and February 1st, 2023, to cover areas across the Arroyo Colorado watershed. We collected samples in different sections of the Arroyo Colorado and irrigation canals to assess whether areas undergoing rapid urbanization experienced PFAS contamination and, if so, which PFAS. We collected 15 water samples in the Arroyo Colorado and 6 samples in irrigation channels. We also collected 7 samples from stormwater and wastewater treatment facility (WWTF) retention ponds in the region. To provide context to possible exposure to PFAS through drinking water, we also collected 2 drinking waters in the region.

Environmental water samples were collected via a HDPE bucket and rope. Prior to each sample collection, the bucket was triple rinsed with ambient water from the sampling site. Rinse water was deposited on the bank to minimize instream disturbance. Water samples were drawn as near

to the middle of the waterway as possible, poured into 250 mL HDPE bottles, and kept cold (on ice) until they arrived in the Halo-Carbon Laboratory on the Texas A&M University Campus in College Station, TX. Water samples were stored at ~4°C in the laboratory until extraction. All water samples were extracted within 14 days of collection.

PFAS Quantification

Thirty PFAS were quantified based on established analytical methods (Aly et al. 2020; Strivens et al. 2021; Hayman et al. 2023) (Table 1). PFAS samples, spiked with isotopically labeled extraction standard, were extracted with Water's Oasis weak anion exchange (WAX) solid phase extraction. PFAS concentrations were analyzed by High-Performance Liquid Chromatography (HPLC, Agilent 1290 Infinity II) / Triple Quadrupole Mass Spectrometer (QqQ-MS, Agilent 6470) equipped with a Jet Stream electrospray ionization (ESI) source. Twenty µL of samples in 96% methanol were injected and then separated by an Agilent ZORBAX Eclipse Plus C-18 narrow bore (2.1 mm × 50 mm, 1.8 µm) HPLC column maintained at 50°C. The flow rate was 0.4 mL min^{-1}. Chromatographic separation was achieved on Solvent A (5 mM ammonium acetate in water) and Solvent B (95% MeOH and 5% water with 5 mM ammonium acetate). The separation gradient method used was 0 - 0.5 min (holding at 10% B), 0.6 - 2 min (10% B to 30% B), 2.1 - 14 min (30% B to 95% B), 14.1 - 14.5 min (95 % B to 100 % B), 14.6 to 16.5 min (holding at 100% B), and then stabilize the column at 10% B for 6 min before the next injection. Mass spectrometer parameters were optimized for PFAS compounds under direct infusion at 0.4 mL min^{-1} to identify the MRM transitions (precursor/product fragment ion pair). Sample acquisition and analysis were performed with MassHunter B.08.02 (Agilent). Limits of quantifications, which were determined by serial dilution of PFAS standards, were 0.313 ng mL^{-1} for the perfluoroalkyl carboxylic acids and perfluoroalkyl sulfonic acids, and 3.13 ng mL^{-1} for the fluorotelomer sulfonic acids, perfluoroalkane sulfonamides, perfluorooctane sulfonamidoacetic acids, per- and polyfluoroether carboxylic acids, and fluorotelomer carboxylic acids. Recoveries for all PFAS monitored in this study were 102

± 17%. Sample triplicates were collected in a randomly selected location; one served as the regular sample, one served as a matrix spike, and one served as a matrix spike duplicate. Based on these samples, we confirmed that sampling and detection of PFAS were reproducible (< 5.1% variability).

Results and Discussion

PFAS in the Arroyo Colorado and Irrigation Canals

Of the 30 PFAS we monitored, 14 of them, namely, PFBA (C4), PFBS (C4), PFPeA (C5), PFPeS (C5), PFHxA (C6), PFHxS (C6), PFHpA (C7), PFHpS (C7), PFOA (C8), PFOS (C8), PFNA (C9), PFDA (C10), 6:2 FTS (C8), N-MeFOSAA (C11), were detected in various combinations in the samples (Table 1 and Table 2). Twenty of the 21 water samples (95%) collected in the Arroyo Colorado and irrigation canals have detectable amounts of PFAS. Most samples in the Arroyo Colorado and irrigation canals only contain shorter chain PFAS (less than 8 carbon atoms), besides a few isolated cases (Table 1 and Table 2). The total amounts of PFAS detected in these samples were spatially heterogeneous, with several locations having significantly higher concentrations than others (Figure 2). These samples were collected near sources known to release PFAS, such as WWTFs and airports (Clara et al. 2008; Houtz et al. 2018; Milley et al. 2018; Lenka et al. 2021; Carey et al. 2022; Helmer et al. 2022; Liu et al. 2022).

The highest total PFAS concentration (1259.88 ng L^{-1}) in the Arroyo Colorado was detected in AC13, which was collected south of the McAllen airport (Table 2 and Figure 2). This sample also contains a diverse number of PFAS with a wide range of carbon chain lengths (C4 to C8), namely PFBA, PFBS, PFPeA, PFPeS, PFHxA, PFHxS, PFHpA, PFHpS, PFOA, PFOS, and 6:2 FTS. AC13 is also the only site where 6:2 FTS was detected (698.06 ng L^{-1}). 6:2 FTS is found in AFFF formulations and AFFF-impacted sites (Houtz et al. 2013; Houtz et al. 2016; Méndez et al. 2022). 6:2 FTS concentration in AC13 was comparable to that found in certain locations in the Houston

Table 1. List of PFAS analytes with their abbreviations, number of carbon atoms per molecule, and number of total samples they were observed in.

Target Analyte Name	Abbreviation	Carbon Number	Number of Samples Observed In (Total = 30)
Perfluoroalkyl carboxylic acids			
Perfluorobutanoic acid	PFBA	4	24
Perfluoropentanoic acid	PFPeA	5	26
Perfluorohexanoic acid	PFHxA	6	27
Perfluoroheptanoic acid	PFHpA	7	3
Perfluorooctanoic acid	PFOA	8	4
Perfluorononanoic acid	PFNA	9	1
Perfluorodecanoic acid	PFDA	10	1
Perfluoroundecanoic acid	PFUdA	11	0
Perfluorododecanoic acid	PFDoA	12	0
Perfluorotridecanoic acid	PFTrDA	13	0
Perfluorotetradecanoic acid	PFTeDA	14	0
Perfluorohexadecanoic acid	PFHxDA	15	0
Perfluoroalkyl sulfonic acids			
Perfluorobutanesulfonic acid	PFBS	4	20
Perfluoropentansulfonic acid	PFPeS	5	2
Perfluorohexanesulfonic acid	PFHxS	6	2
Perfluoroheptanesulfonic acid	PFHpS	7	2
Perfluorooctanesulfonic acid	PFOS	8	5
Perfluorononanesulfonic acid	PFNS	9	0
Perfluorodecanesulfonic acid	PFDS	10	0
Perfluorododecanesulfonic acid	PFDoS	12	0
Fluorotelomer sulfonic acids			
1H,1H, 2H, 2H-Perfluorohexane sulfonic acid	4:2 FTS	6	0
1H,1H, 2H, 2H-Perfluorooctane sulfonic acid	6:2 FTS	8	1
1H,1H, 2H, 2H-Perfluorodecane sulfonic acid	8:2 FTS	10	0
Perfluoroalkane sulfonamides			
Perfluoro-1-octanesulfonamide	FOSA-I	8	0
Perfluorooctane sulfonamidoacetic acids			
N-methyl perfluorooctanesulfonamidoacetic acid	N-MeFOSAA	11	1
N-ethyl perfluorooctanesulfonamidoacetic acid	N-EtFOSAA	12	0
Per- and Polyfluoroether carboxylic acids			
Hexafluoropropylene oxide dimer acid	HFPO-DA (Gen-X)	6	0
Fluorotelomer carboxylic acids			
2-Perfluorohexyl ethanoic acid	FHEA	8	0
2-Perfluorooctyl ethanoic acid	FOEA	10	0
2-Perfluorodecyl ethanoic acid	FDEA	12	0

Table 2. PFAS concentrations (ng L^{-1}) in water samples collected from the Arroyo Colorado (AC), irrigation canals (IC), stormwater and wastewater treatment plant (WWTF) retention ponds (RP), and drinking water (municipal water supply and private well water) (PW).

| Sample ID	PFBA	PFBS	PFPeA	PFPeS	PFHxA	PFHxS	PFHpA	PFHpS	PFOA	PFOS	PFNA	PFDA	6:2 FTS	N-MeFOSAA	Total PFAS
Arroyo Colorado															
AC01	5.48	4.41	11.65		8.23										29.77
AC02	5.43	3.40	5.93		5.28										20.04
AC03	4.05	3.51	10.61		7.11										25.28
AC04	5.99	4.06	13.71		8.07										31.83
AC05	4.57	3.20	4.49		4.83										17.09
AC06	4.50	3.38	9.55		7.89										25.32
AC07	4.29	3.67	12.19		8.88										29.03
AC08		3.67	10.61		10.64										24.92
AC09		6.14	18.26		15.95					5.76					46.11
AC10	4.01	3.99	11.96		9.19										29.15
AC11	4.05	3.85	11.80		8.94										28.64
AC12			5.80		4.31										10.11
AC13	33.92	50.01	113.56	32.01	125.08	140.17	22.92	3.42	12.13	28.60			698.06		1259.88
AC14	4.97	8.23	28.87		15.47										57.54
AC15															
Irrigation Canals															
IC01	5.11		4.50		4.85										14.46
IC02	4.09		5.83		4.51					3.59					18.02
IC03	5.38		5.68		3.66										14.72
IC04	4.71		3.27		3.71										11.69
IC05	4.20		3.50		3.42										11.12
IC06	4.57		5.44		5.23										15.24
Retention Ponds															
IP01 — WWTP 1 Retention Pond	104.55	157.82	299.20	34.70	330.98	145.61	412.64	31.52	1391.30	553.54	198.96	110.05		39.47	3810.34
IP02 — WWTP 1 Retention Pond	12.74	20.73	65.73		30.34		3.65		5.57						138.76
IP03 — Stormwater 1	10.11	6.67	46.14		36.17				7.76						106.85
IP04 — Stormwater 2	5.22	3.36	4.53		5.94					3.80					22.85
IP05 — Stormwater 3															
IP06 — Stormwater 4	8.92	7.83			3.85										20.60
IP07 — WWTP 2 Effluent Pond	5.96	10.45	29.89		17.28										63.58
Private Water															
PW01 — Tap Water	24.57		5.34		5.16										35.07
PW02 — Groundwater		4.89													4.89
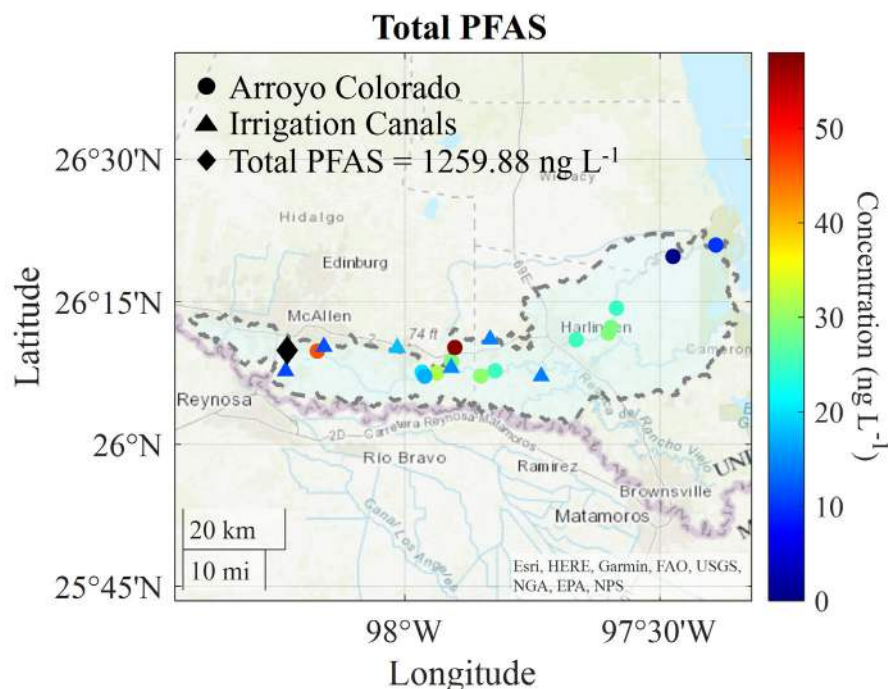
Total PFAS

Figure 2. Total PFAS concentrations (ng L⁻¹) in samples collected in the Arroyo Colorado (circles) and irrigation canals (triangles). The black diamond marked the location of water sample collected in the Arroyo Colorado with total PFAS significantly higher than the other samples.

ship channel during the Intercontinental Terminals Company (ITC) fire in March 2019, during which AFFF was actively used (Aly et al. 2020). 6:2 FTS (C8) can be microbially degraded into other PFAS, such as shorter chain PFPeA (C5) and PFHxA (C6) (Méndez et al. 2022), which were also detected in this sample. In surface water, we expect 6:2 FTS concentrations to decrease drastically away from the source due to dilution and degradation, as observed during the ITC fire (Aly et al. 2020). Therefore, site AC13 was likely impacted by AFFF applications at the time of sampling.

Relatively high total PFAS concentrations were also found in samples AC09 (46.11 ng L⁻¹) and AC14 (57.54 ng L⁻¹) (Table 2 and Figure 2). These samples were collected downstream of WWTFs. It should be noted that these samples contain different types of PFAS. AC09 contained PFBS (C4), PFPeA (C5), PFHxA (C6), and PFOS (C8), while AC14 contained shorter chain PFAS, namely, PFBA (C4), PFBS (C4), PFPeA (C5), and PFHxA (C6). PFPeA and PFHxA were the dominant PFAS compounds in both samples (Table 2 and Figure 3). PFPeA accounted for 40% and 50% of the total PFAS detected in AC09 and AC14, respectively.

PFHxA accounts for 35% and 27% of the total PFAS detected in AC09 and AC14, respectively. While it is not possible to deduce the sources for PFPeA and PFHxA in these two samples, it would be reasonable to assume they might, in part, be derived from precursor PFAS in WWTFs, such as fluorotelomers like 6:2 FTS. AC09 and AC14 also have elevated PFBS concentrations compared to other samples collected in the Arroyo Colorado, except for A13, which was collected near an airport.

PFBA, PFBS, PFPeA, and PFHxA were the most frequently detected PFAS in samples collected in the Arroyo Colorado and irrigation canals. This is to be expected because short-chain PFAS (less than 8 carbon atoms) are likely to be more mobile in water. PFBS, PFPeA, and PFHxA showed similar spatial heterogeneity (Figure 3), with significantly higher concentrations in sites near an airport or a WWTF. However, PFBA appeared more spatially homogeneous, with higher concentrations in the upper Arroyo Colorado. PFBA may be released directly from its point source or derived from the degradation of higher-chain PFAS in the environment. PFBA was found in Arctic ice cores

along with other ultrashort-chain PFAS (less than 4 carbon atoms), suggesting it is highly mobile in water and possibly in the atmosphere. The high environmental mobility of PFBA likely explains the spatial homogeneity observed in this study. PFBA and other PFAS concentrations were lower in the lower Arroyo Colorado (Figures 2 and 3). The only sample (AC15) in the watershed that does not have any detectable PFAS was collected in this region. These findings suggest possible dilution due to tidal movements.

All samples collected in irrigation canals contained short-chain PFAS (C4 to C6). IC02 also contained PFOS (C8). PFAS-containing irrigation water can contaminate soil and plants (Brown et al. 2020). Gen-X and PFOA have been found to cause phototoxicity and bioaccumulation in plants (Chen et al. 2020). Additionally, short-chain PFAS, such as PFBA, PFPeA, and PFHxA, have been found in crop tissues (Mroczko et al. 2022). PFBA, PFPeA, and PFHxA were observed in most of the samples in this study, as well. This suggests that future studies on the occurrence of PFAS in crops in this area are necessary.

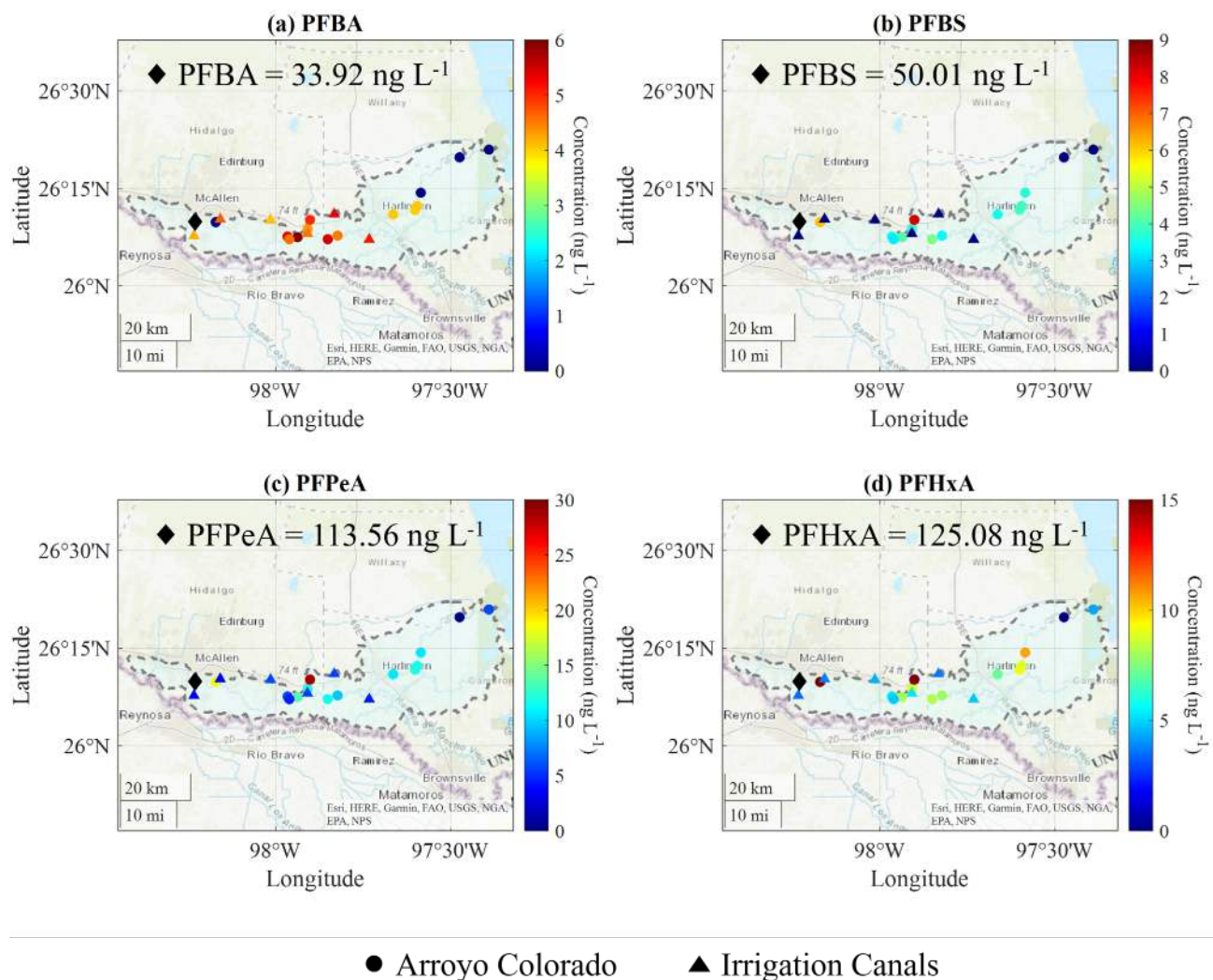Studies of PFAS concentrations across a watershed are rather limited at this time, but the

Figure 3. Concentration (ng L^{-1}) distributions of (a) PFBA, (b) PFBS, (c) PFPeA, and (d) PFHxA. Circles mark the locations of samples collected in the Arroyo Colorado. Triangles mark the locations of samples collected in irrigation canals. Black diamonds mark the location of samples collected in the Arroyo Colorado with PFAS significantly higher than the other samples, PFBA = 33.92 ng L^{-1}, PFBS = 50.01 ng L^{-1}, PFPeA = 113.56 ng L^{-1}, and PFHxA = 125.08 ng L^{-1}.

body of literature is rapidly growing. However, it is still difficult to make reasonable comparisons due to various geographical, hydrological, and environmental differences, e.g., the size of watersheds, the level of development, seasonality, river flow rates, or whether known manufacturing sources are present, etc. Here, we compared PFAS concentrations with other survey studies with one-time sample collection (i.e., no temporal coverage) across one or more watersheds. In general, PFAS concentrations in the Arroyo Colorado watershed were higher than in rivers and creeks in Canada and the Truckee River, which is a relatively pristine environment in Nevada, U.S. (Scott et al. 2009; Bai and Son 2021) (Table 3). However, comparisons with other urbanized or industrialized systems with known PFAS manufacturers or point sources are not as straightforward. For example, while total perfluorinated carboxylic acids (ΣPFCA) in the Arroyo Colorado was lower than in the Las Vagas Wash, total perfluorinated sulfonic acids (ΣPFSA) was higher in the Arroyo Colorado (Table 3). These two regions have different developments and, thus, likely have different sources/types of PFAS. Most of the compounds detected in this study were higher than those reported by Gebbink et al. (2017) from a river with a known PFAS production source (Table 3). However, Gebbink et al. (2017) reported elevated Gen-X downstream of the source, while Gen-X was below the detection limit for all samples in this study. ΣPFCA was generally lower than those observed in the Rhine River watershed, but ΣPFSA observed in this study was higher (Moller et al. 2010). It should be noted that even though ΣPFSA reported in this study appeared to be higher than other studies listed in Table 3, it is likely biased due to the fact that data for several PFSA compounds were not available in the other studies. However, besides PFBS, concentrations of the other individual PFSA compounds reported in this study were still higher (Table 3). PFAS concentrations in these studies all showed significant spatial heterogeneities, and the types of PFAS found in different surface waters also varied depending on the distance to the sources and source type. Within this study, we observed substantial spatial heterogeneity and variation of PFAS types closer to a source.

PFAS in Stormwater and WWTF Retention Ponds

Six water samples were collected from stormwater and WWTF retention ponds in the study area. Water from the WWTF retention ponds had been through primary (coagulation, flocculation, and sedimentation) and secondary (biodegradable matter removal) treatments. These ponds do not receive water directly from the Arroyo Colorado or irrigation channels, but some have permits to discharge to the Arroyo Colorado. In other words, we expect less dilution effect in PFAS concentrations. Indeed, PFAS concentrations observed in these samples were generally higher than in samples collected in the Arroyo Colorado and irrigation canals (Table 2). The highest total PFAS of all the samples collected in this study was found in a retention pond of a WWTF (IP01) at 3810.34 ng L^{-1}. IP01 also contains the most diverse PFAS, including long-chain PFAS (more than 8 carbon atoms), namely, PFBA (C4), PFBS (C4), PFPeA (C5), PFPeS (C5), PFHxA (C6), PFHxS (C6), PFHpA (C7), PFHpS (C7), PFOA (C8), PFOS (C8), PFNA (C9), PFDA (C9), and N-MeFOSAA (C11). PFAS were found in three of the four stormwater retention ponds (IP03, IP04, and IP05). It should be noted that it was rainy at the time of sample collection. Therefore, the elevated PFAS concentrations compared to samples collected in the Arroyo Colorado and irrigation canals may have come from road runoff.

PFAS in Drinking Water

We collected two drinking water samples, one from a municipal supply and one from a private well, to assess possible PFAS exposure in this region. While the number of samples was rather limited, it provided an opportunity to compare samples collected from the Arroyo Colorado watershed and retention ponds in the region (Table 2). PFBA (24.57 ng L^{-1}), PFPeA (5.34 ng L^{-1}), and PFHxA (5.16 ng L^{-1}) were found in the municipal water sample, while only PFBS (4.89 ng L^{-1}) was found in the private well sample. It should be noted that PFBA, PFPeA, and PFHxA are not currently regulated by the U.S. EPA for drinking water, while PFBS is proposed to be regulated based on a hazard index (unitless) considering the combination effects of PFNA, PFHxS, PFBS, and Gen-X.

Table 3. Mean PFAS concentrations (ng L⁻¹) in water samples collected from the Arroyo Colorado and irrigation canals in this study compared to other studies with one-time sampling across different watersheds. Number of samples (n) are presented if available. Red shades highlight relatively high values of a PFAS compound compared between the studies. Blue shades highlight relatively low values of a PFAS compound compared between the studies. "N.A." notes data are not available. "N.D." notes a PFAS compound was monitored but not detected.

	PFCA								PFSA					
	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	ΣPFCA	PFBS	PFPeS	PFHxS	PFHpS	PFOS	ΣPFSA
This study														
Arroyo Colorado (n = 15)	7.39	19.21	17.13	22.92	12.13	N.D.	N.D.	78.78	7.81	32.01	140.17	3.42	17.18	200.59
Irrigation Canals (n = 6)	4.68	4.70	4.23	N.D.	N.D.	N.D.	N.D.	13.61	N.D.	N.D.	N.D.	N.D.	3.59	3.59
Scott et al. 2009														
Canadian Rivers and Creeks	N.A.	N.A.	1.03	1.08	1.65	0.51	0.13	4.39	0.21	N.A.	0.72	0.13	2.15	3.21
Gebbink et al. 2017 (n = 18)														
Downstream of a fluorochemical production plant (n = 13)	7.78	4.82	5.34	1.85	4.62	0.67	0.41	25.50	21.00	N.A.	1.97	0.14	3.40	26.51
Upstream of a fluorochemical production plant (n = 3)	6.37	6.17	6.17	1.90	3.00	0.75	0.56	24.91	19.67	N.A.	2.10	0.16	4.77	26.70
Moller et al. 2010														
Rhine upstream Leverkusen (n = 27)	1.44	3.65	2.00	0.43	2.13	N.A.	N.A.	9.65	3.19	N.A.	3.04	N.A.	3.70	9.93
Rhine downstream Leverkusen (n = 9)	117.00	4.28	2.86	0.49	3.11	N.A.	N.A.	127.74	45.40	N.A.	1.93	N.A.	4.13	51.46
River Ruhr (n = 3)	16.60	21.35	8.74	0.99	14.30	N.A.	N.A.	61.98	7.08	N.A.	0.18	N.A.	4.21	11.47
River Moehne (n = 1)	115.00	59.30	49.90	5.78	42.10	N.A.	N.A.	272.08	31.10	N.A.	1.03	N.A.	3.11	35.24
Bai and Son 2021														
Truckee River (n = 8)	N.D.	5.80	18.00	1.70	6.90	N.D.	N.D.	32.40	5.20	0.70	6.40	N.D.	2.20	14.50
Las Vagas Wash (n = 10)	2.60	52.30	80.70	11.60	27.30	N.D.	N.D.	174.50	17.70	2.30	11.20	N.D.	12.90	44.10

Conclusions

This study presents the first report of PFAS in water samples collected in the Arroyo Colorado, irrigation canals, stormwater and WWTF retention ponds in the region, as well as a limited number of drinking waters. PFAS concentrations in water samples collected in the Arroyo Colorado watershed provide useful information for water quality in this region and provide insights into PFAS occurrence in a rapidly urbanizing area. When we compared our data with surveys in other watersheds, we noted many complicating factors, such as the size of watersheds, the level of development, seasonality, river flow rates, and the distance to known sources, making it challenging to systematically compare PFAS occurrence in different waterbodies. However, given that surface waters are one of the key factors for determining PFAS fate and transport and are closely connected to human and environmental health, it highlights the need for more data in different watersheds regardless of basin size. Long-term studies are necessary to capture temporal and spatial variabilities of PFAS types and concentrations to better understand whether different climatological and hydrological conditions affect PFAS distributions, fate, and transport across different watersheds. Additionally, water in the Arroyo Colorado as well as in many watersheds globally is used for agricultural irrigation. Therefore, long-term data on PFAS occurrence in crops should be collected.

Acknowledgments

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