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Perfluoroalkyl substances (PFAS) in surface water and sediments from two urban watersheds in Nevada, USA



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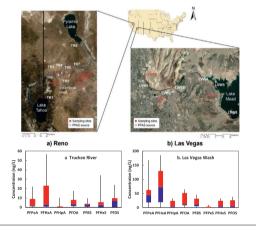
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HIGHLIGHTS

• Perfluoroalkyl substances (PFAS) pose human health and ecological risks.

- 17 PFAS were monitored in surface water and sediments from two urban watersheds.
- Short-chain PFAS (≤8 carbons) were predominant in water.
- Long-chain PFAS (>8 carbons) were predominant in sediments.
- PFCAs were more persistent in surface waters than PFSAs.

GRAPHICAL ABSTRACT



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ABSTRACT

This study measured 17 perfluoroalkyl substances (PFAS) in surface water and sediments collected from six locations along the Las Vegas Wash and Lake Mead and eight locations along the Truckee River, Lake Tahoe, and Pyramid Lake in Nevada, United States. Of the 17 PFAS analyzed, 12 were detected in the surface water (n = 18) and 14 were detected in the sediments (n = 21) of the two watersheds. The total concentration of PFAS in the Truckee River water was 441.7 ng/L and the PFAS detected in the Las Vegas Wash water was 2234.3 ng/L. The predominant PFAS species found in the water were perfluorohexanoic acid (PFHXA) (1.5–187.0 ng/L), followed by perfluoropentanoic acid (PFPA) (below detection limit [BDL] to 169.9 ng/L), perfluorooctanoic acid (PFOA) (BDL to 65.5 ng/L), and perfluorobutane sulfonic acid (PFBS) (BDL to 44.7 ng/L). The total PFAS in the sediments was 272.9 µg/kg (dry weight) for the Truckee River and 345.7 µg/kg for the Las Vegas Wash. The predominant species in the sediments were perfluorodecane sulfonic acid (PFDS) (BDL to 88.2 µg/kg), PFHxA (BDL to 20.3 µg/kg), PFBS (BDL to 29.1 µg/kg), and perfluoroundecanoic acid (PFUA) (BDL to 22.9 µg/kg). The results demonstrated that short-chain PFAS (C \leq 8) were more prevalent in water, whereas long-chain PFAS (C > 8) were more detectable in sediments. The Las Vegas Wash water had much higher PFAS levels compared with the Truckee River water. The PFAS concentrations and detection frequencies also significantly decreased in summer compared with winter along the Las Vegas Wash.

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Abbreviations: PFAS, perfluoroalkyl substances; PFCAs, perfluoroalkyl carboxylic acids; PFSAs, perfluoroalkyl sulfonic acids; PFBA, perfluorobutanoic acid; PFPA, perfluoropentanoic acid; PFHA, perfluorohexanoic acid; PFHA, perfluorohexanoic acid; PFDA, perfluorohexanoic acid; PFDA, perfluorodecanoic acid; PFDA, perfluoroundecanoic acid; PFDA, perfluorobutane sulfonic acid; PFDS, perfluoropentane sulfonic acid; PFHS, perfluorohexane sulfonic acid; PFDS, perfluorohexane sulfonic acid; PFDS

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1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are a class of more than 4000 synthetic chemicals that have been manufactured and released into the environment for over 50 years. Because of their long-term persistence, low biodegradability, and high bioaccumulation in wildlife and humans, the adverse effects of PFAS on humans are becoming a severe problem globally (Ahrens and Bundschuh, 2014; Giesy and Kannan, 2001; Tomy et al., 2004). The unique physical and chemical properties of PFAS-such as extreme thermal and chemical stability, and oil and water repellency—make them ideal for applications such as textile coatings, paper products, food packaging, nonstick cookware, and the aqueous film-forming foams used in firefighting (Brendel et al., 2018). Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) are the most extensively investigated PFAS because they have a wide variety of sources and they are the ultimate degradation products of many precursor compounds (Brusseau, 2018). In 2009, the EPA established provisional health advisory values of 0.4 µg/L for PFOA and 0.2 µg/L for PFOS (USEPA, 2009). In 2016, a lifetime health advisory of 0.07 µg/L was issued for long-term exposure to both PFOA and PFOS through drinking water (USEPA, 2016). The health effects of PFAS on wildlife and humans have recently been reported, but the adverse effects of a mixture of PFAS on humans and organisms are still unknown.

Numerous PFAS have been found ubiquitously in various environmental matrices, including wastewater, surface water, soils, sediments, groundwater, and landfill effluents (Banzhaf et al., 2017; Dalahmeh et al., 2018; Houtz et al., 2013). Both legacy and emerging PFAS have been detected in drinking water supplies in the Cape Fear River of North Carolina (Sun et al., 2016). Hu et al. (2016) investigated the occurrence of PFAS in drinking water for 4064 public water supplies in the Unites States, and found that drinking water supplies for six million U.S. residents exceeded the USEPA lifetime health advisory for PFOA/ PFOS (i.e., 0.07 µg/L). Wastewater treatment plants (WWTPs) are unable to remove most PFAS completely (Becker et al., 2010), and granular activated carbon and anion exchange are not effective in removing short-chain PFAS. Many PFAS are resistant to chemical and biological oxidation (Brendel et al., 2018), and the concentrations of some PFAS have increased in wastewater effluents because of the degradation of precursor compounds (Dickenson et al., 2015), Scientists and regulators are increasingly concerned about the occurrence, persistence, and fate of PFAS, and therefore better methods for identifying and quantifying PFAS in aquatic environments are urgently needed.

Of the numerous PFAS, perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs) are strong acids with pKa estimated to be near zero for PFCAs and -1 for PFSAs, which indicates that they are present in ionic form in most environmental conditions (Kjølholt et al., 2015). The perfluoroalkyl chain is highly hydrophobic and the anionic/acid functional groups are extremely hydrophilic. These acids are expected to be substantially mobile in the environment compared with other less soluble, more volatile PFAS, such as fluorotelomer alcohol (FTOH). Therefore, the fate and transport of PFCAs and PFSAs are of greater significance in aquatic environments.

The objective of this study was to fill the data gap on the occurrence of 17 PFAS in the Las Vegas and Reno watersheds in Nevada, as well as establish baseline data on the worldwide monitoring of PFAS in aquatic environments. Some of the 17 PFAS that were analyzed in this study have not been widely monitored in aquatic environments or reported on by others (e.g., perfluoroundecanoic acid [PFUA], perfluorododecanoic acid [PFDA], perfluorotridecanoic acid [PFTDA], and perfluorononane sulfonic acid [PFNS]). This study provides critical data on the identification of the selected PFAS in aquatic environments that will benefit research and regulation worldwide. It also provides much-needed information to solve regional water quality issues because no information is currently available on the occurrence and distribution of PFAS in the studied watersheds. The sampled watersheds are extensively affected by wastewater discharges, especially from Las

Table 1Target PFAS analytes.

Compound	Formula	MW (g/mol)		
Perfluoroalkyl carboxylic acids (PFCAs)				
Perfluorobutanoic acid (PFBA)	$C_4HF_7O_2$	214.04		
Perfluoropentanoic acid (PFPeA)	$C_5HF_9O_2$	264.05		
Perfluorohexanoic acid (PFHxA)	$C_6HF_{11}O_2$	314.05		
Perfluoroheptanoic acid (PFHpA)	$C_7HF_{13}O_2$	364.06		
Perfluorooctanoic acid (PFOA)	$C_8HF_{15}O_2$	414.07		
Perfluorononanoic acid (PFNA)	$C_9HF_{17}O_2$	464.08		
Perfluorodecanoic acid (PFDA)	$C_{10}HF_{19}O_2$	514.08		
Perfluoroundecanoic acid (PFUA)	$C_{11}HF_{21}O_2$	564.09		
Perfluorododecanoic acid (PFDoA)	$C_{12}HF_{23}O_2$	614.10		
Perfluorotridecanoic acid (PFTrDA)	$C_{13}HF_{25}O_2$	664.11		
Perfluoroalkyl sulfonic acids (PFSAs)				
Perfluorobutane sulfonic acid (PFBS)	$C_4HF_9O_3S$	300.10		
Perfluoropentane sulfonic acid (PFPeS)	$C_5HF_{11}O_3S$	350.10		
Perfluorohexane sulfonic acid (PFHxS)	$C_6HF_{13}O_3S$	400.11		
Perfluoroheptane sulfonic acid (PFHpS)	$C_7HF_{15}O_3S$	465.21		
Perfluorooctane sulfonic acid (PFOS)	$C_8HF_{17}O_3S$	500.13		
Perfluorononane sulfonic acid (PFNS)	$C_9HF_{19}O_3S$	549.12		
Perfluorodecane sulfonic acid (PFDS)	C ₁₀ HF ₂₁ O ₃ S	599.13		

Vegas. As the downstream water reservoir of the Las Vegas Wash, Lake Mead is likely to be exposed to PFAS. This is a concern because Lake Mead is the primary water supply for 30 million residents in the southwestern United States.

2. Materials and methods

2.1. Chemicals

The 17 PFAS (C_{4-13} PFCA and C_{4-10} PFSA) analyzed in this study include: PFBA (perfluorobutanoic acid), PFPeA (perfluoropentanoic acid), PFHxA (perfluorohexanoic acid), PFHpA (perfluoroheptanoic acid), PFOA, PFNA (perfluorononanoic acid), PFDA (perfluorodecanoic acid), PFUA, PFDOA, PFTrDA, PFBS (perfluorobutane sulfonic acid), PFPeS (perfluoropentane sulfonic acid), PFHxS (perfluorohexane sulfonic acid), PFHpS (perfluoroheptane sulfonic acid), PFOS, PFNS, and PFDS (perfluorodecane sulfonic acid) (Cambridge Isotope Laboratories, Inc., MA, USA). Tables 1 and 2 provide the general description, limit of detection (LOD), limit of quantification (LOQ), and analytical performance of the target PFAS. It is worth mentioning that the target PFAS were reported as anion forms instead of their acid forms because PFAS

Table 2Method detection limit, analytical variation, and recovery of 17 target PFAS.

Analyte	LOD	LOQ	RPD	Spiked sample recovery (water)		Spiked sample recovery (sediment)		
	ng/L	ng/L	%	10 ng/L	50 ng/L	50 ng/kg	100 ng/kg	
PFBA	1.04	2.42	3%	104%	101%	103%	83%	
PFPeA	1.24	2.90	2%	96%	101%	109%	91%	
PFHxA	1.21	2.83	2%	94%	104%	114%	96%	
PFHpA	3.59	8.38	2%	110%	94%	83%	90%	
PFOA	1.52	3.54	9%	111%	108%	84%	99%	
PFNA	20.98	48.95	22%	135%	119%	116%	113%	
PFDA	19.60	45.74	18%	118%	141%	109%	125%	
PFUA	4.56	10.64	18%	122%	121%	121%	118%	
PFDoA	15.54	36.26	5%	113%	108%	123%	99%	
PFTrDA	9.15	21.36	16%	116%	112%	123%	107%	
PFBS	2.22	5.19	1%	95%	78%	75%	66%	
PFPeS	3.33	7.77	2%	125%	121%	91%	104%	
PFHxS	3.37	7.87	1%	85%	82%	76%	74%	
PFHpS	5.35	12.49	29%	115%	142%	128%	106%	
PFOS	7.96	18.58	21%	115%	127%	90%	112%	
PFNS	5.90	13.77	7%	99%	98%	94%	97%	
PFDS	5.08	11.85	6%	88%	69%	66%	69%	

 $\label{eq:LOD} \mbox{LOD} = \mbox{limit of detection; LOQ} = \mbox{limit of qualification; RPD} = \mbox{relative percent difference} \ (\%) \mbox{ of duplicate samples.}$

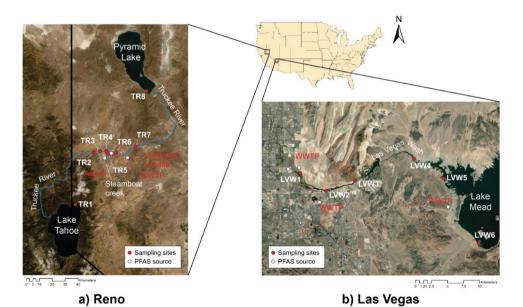
were usually present as anion forms in the environment (Shoemaker and Tettenhorst, 2018). Four ¹³C-labeled PFAS (i.e., ¹³C₆-PFHxA, ¹³C₈-PFOA, ¹³C₈-PFOS, and ¹³C₉-PFUA) were purchased from Cambridge Isotope Laboratories, Inc. (MA, USA) and used as internal standards.

2.2. Sample collection

Surface water and sediment samples were collected at multiple locations from Las Vegas (i.e., Las Vegas Wash and Lake Mead) in January and July of 2019. Water and sediment samples were collected from Reno (i.e., Truckee River, Pyramid Lake, and Lake Tahoe) in April of 2019. The two watersheds located in northern and southern Nevada to represent the growing Reno/Sparks and Las Vegas metropolitans, respectively. The source of the Truckee River is a nearly pristine alpine lake that receives degraded inputs along its course (through the major city of Reno) between Lake Tahoe and Pyramid Lake. The mean discharge of the Truckee River at Reno (USGS site 10348000) was about 3600 cubic feet per second (cfs) when the sampling took place in April of 2019. The source of the Las Vegas Wash includes urban runoff and treated wastewater, and is highly engineered. The mean discharge of the Las Vegas Wash was about 300 cfs (USGS sites 09419698, 09419747, 09419749) when the sampling took place there in January and July of 2019. Fig. 1 shows the detailed sampling locations. Onetime grab water samples and sediment samples were collected using 1 L polypropylene containers and ziplock bags, respectively. For the Las Vegas Wash, sediments were collected from two horizons at selected locations (i.e., upper [0–10 cm] versus lower [10–20 cm]). Research staff avoided using materials containing PFAS during sampling. Samples collected from Las Vegas were stored at $-20\,^{\circ}\mathrm{C}$ until they were shipped to Reno, Nevada, in a cooler with Blue Ice. All samples were kept frozen until extraction. Water chemistry parameters were measured on-site during winter and summer sampling events in Las Vegas (Table S1 in Supplementary Information).

2.3. PFAS analysis

On the day of extraction, water and sediment samples were thawed at room temperature (20 °C) and spiked with known amounts of the ¹³C-labeled PFAS internal standards. All water samples were filtered through a 47 mm polypropylene membrane filter unit (0.4 µm pore size, Pall Corporation, NY, USA). The empty sample bottles were then rinsed with methanol, which was added onto the filter unit to rinse the polypropylene membrane filter. The combined water samples (i.e., filtered water and methanol rinse) were then extracted using Oasis WAX solid phase extraction (SPE) cartridges (Waters, MA, USA). In brief, SPE cartridges were conditioned (at a rate of 2 drops per second) using 4 mL of 0.1% ammonia in methanol solution prepared with diluted 2 M ammonia in methanol solution (#341428, Sigma, MO,



Site	Latitude	Longitude							
Truckee Riv	Truckee River in Reno, NV								
TR1	39°14'9" N	120°1'30" W							
TR2	39°30'38" N	119°51'56" W							
TR3	39°31'17" N	119°46'14" W							
TR4	39°30'50" N	119°43'45" W							
TR5	39°31'2" N	119°42'20" W							
TR6	39°30'39" N	119°40'8" W							
TR7	39°33'53" N	119°29'12" W							
TR8	39°50'57" N	119°27'25" W							
Las Vegas V	Vash in Las Vegas, N	V							
LVW1	36°6'17" N	115°1'8.8" W							
LVW2	36°5'15" N	114°59'5" W							
LVW3	36°6'1" N	114°56'35" W							
LVW4	36°7'13" N	114°51'40.4" W							
LVW5	36°5'56" N	114°49'15" W							
LVW6	36°1'36" N	114°45'49" W							

Fig. 1. Map of sampling sites along the Truckee River and Las Vegas Wash watersheds in Nevada.

USA), 4 mL methanol (Fisher chemical, HPLC grade, PA, USA), followed by 4 mL HPLC grade water. The combined water samples were then loaded into the conditioned SPE cartridges at 1 drop per second rate. The SPE cartridges were then rinsed with 4 mL ammonium acetate buffer (20 mM, pH 4), followed by 8 mL tetrahydrofuran (Fisher chemical, HPLC grade, PA, USA): methanol (75:25, v/v) solution (at a rate of 2 drops per second). Then, PFAS on the SPE cartridges were eluted with 4 mL of the methanol with 0.1% ammonia solution at a rate of 1 drop per second. The elutes were concentrated under a gentle stream of ultra-high-purity nitrogen (99.999%, Airgas, NV, USA) to 200 µL. Final extracts were transferred into polypropylene autosampler vials (Waters, MA, USA) for PFAS analysis.

Sediment samples were spiked with known amounts of the ¹³Clabeled PFAS internal standards, air-dried overnight in the dark, and then homogenized. Two grams of the homogenized sediment samples were transferred into 15 mL polypropylene centrifuge tubes (Corning, NY, USA), and then were extracted using a series of acetic acid and methanol solutions. In brief, 10 mL of 1% acetic acid solution (#A35, Fisher chemical, HPLC grade, PA, USA) was added into the centrifuge vials, vortexed for 30 s, sonicated for 15 min at 60 °C, and then centrifuged for 10 min at 4500 RPM. The upper layers of the acetic acid solutions were decanted into secondary 50 mL polypropylene centrifuge tubes (Corning, NY, USA). After collecting the supernatants, a mixture of 2.5 mL of methanol and 1% acetic acid solution (9:1, v/v) was added into the tubes containing the sediment samples and the sample extraction steps (i.e., vortex, sonicate, centrifuge, and decant) were followed as described above. The above steps were repeated two times and followed by one more 1% acetic acid extraction. The final sample extract volumes were approximately 35 mL. The extracts were cleaned with the SPE procedure described above, concentrated, and then transferred into the polypropylene autosampler vials for analysis.

For PFAS analysis, the 5 μ L samples were injected into an ultraperformance liquid chromatography tandem mass spectrometer (Waters Acquity UPLC with Quattro micro API Tandem Quadrupole System [MS/MS]; Waters, MA, USA). Target PFAS and internal standards were separated using a Waters Acquity UPLC BEH C18 column (1.7 μ m, 2.1 × 50 mm; Waters, MA, USA) with the mobile phase consisting of solvent A: ammonium acetate buffer (20 mM, pH 4):acetonitrile (Fisher chemical, HPLC grade, PA, USA) = 9:1; solvent B: methanol:acetonitrile = 6:4. The mobile phase gradient used was as follows: hold 15% B at 0.0 min until 0.5 min, increase to 95% B until 10.0 min, decrease to 15% B until 11.0 min and hold until 13 min. The column and

autosampler temperatures were 40 °C and 20 °C, respectively. The target PFAS were analyzed using multiple reaction monitoring (MRM) with negative electron ionization mode, and then quantified using the six-point external calibration curves, followed by recovery corrections using the internal standards (Table 2).

3. Results and discussion

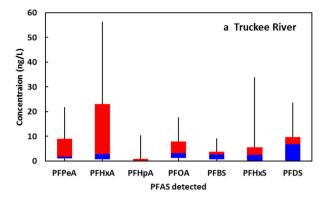
3.1. PFAS in water

The results show that PFAS concentrations in the surface waters measured in this study are in the high range relative similar studies. Table 3 summarizes statistics of PFAS concentrations in the Truckee River and Las Vegas Wash watersheds. All measured PFAS concentrations in water from each sampling site are available in Table S2. Of the 17 PFAS species measured, there were 10 and 11 PFAS species detected in the Truckee River and Las Vegas Wash water, respectively. In the Truckee River, the total concentration of PFAS was 441.7 ng/L, of which PFCAs were 259.0 ng/L and PFSAs were 182.7 ng/L. The median concentration of PFAS ranged from below the detection limit (BDL) to 6.9 ng/L. In the Las Vegas Wash, the total concentration of PFAS was 2234.3 ng/L, of which PFCAs were 1750.6 ng/L and PFSAs were 483.7 ng/L. The median concentration of PFAS ranged from BDL to 74.7 ng/L. Dalahmeh et al. (2018) measured 26 PFAS, including PFCAs and PFSAs, in surface waters and found that the total PFAS concentrations were 8.5 to 14 ng/L in the Nakivubo channel and wetland and 1.0 to 2.4 ng/L in Lake Victoria in Kampala, Uganda. Li et al. (2011) reported that the concentrations of nine PFAS were 40 to 174 ng/L in the Dagu Drainage Canal and 12 to 74 ng/L in the Haihe River in China.

Fig. 2 shows boxplots of the most dominant PFAS species found in the water from the two watersheds: PFHxA (C6) (median concentration at 6.2 and 74.7 ng/L for the Truckee River and Las Vegas Wash, respectively), followed by PFPeA (C5) (median concentration at 1.8 and 46.9 ng/L for the Truckee River and Las Vegas Wash, respectively), and PFOA (C8) (median concentration at 4.8 and 11.7 ng/L for the Truckee River and Las Vegas Wash, respectively). For PFSAs, the most dominant species was PFDS and PFBS in the Truckee River (median at 6.9 ng/L) and Las Vegas Wash (median at 11.4 ng/L), respectively. These PFAS species accounted for 68.7% and 79.7% of the total PFAS concentrations in the Truckee River and Las Vegas Wash, respectively. It is noteworthy that the shorter-chain (≤8 carbons) PFAS were the dominant PFAS, and the long-chain PFAS were found at much lower levels and frequencies in

Table 3Statistics of PFAS concentrations (ng/L) in water collected from the Truckee River and Las Vegas Wash.

Analyte	Truckee Ri	Truckee River $(n = 8)$					Las Vegas Wash ($n=10$)				
	Min	Max	Mean	Median	DF	Min	Max	Mean	Median	DF	
PFBA	ND	ND	ND	ND	0.0%	ND	21.8	2.6	ND	20.0%	
PFPeA	ND	21.8	5.8	1.8	75.0%	2.3	170.0	52.3	46.9	100.0%	
PFHxA	3.2	59.6	18.0	6.2	100.0%	1.5	187.0	80.7	74.7	100.0%	
PFHpA	ND	10.4	1.7	ND	25.0%	ND	32.5	11.6	3.7	60.0%	
PFOA	1.6	19.2	6.9	4.8	100.0%	ND	65.5	27.3	11.7	90.0%	
PFNA	ND	ND	ND	ND	0.0%	ND	ND	ND	ND	0.0%	
PFDA	ND	ND	ND	ND	0.0%	ND	ND	ND	ND	0.0%	
PFUA	ND	ND	ND	ND	0.0%	ND	5.2	0.5	ND	10.0%	
PFDoA	ND	ND	ND	ND	0.0%	ND	ND	ND	ND	0.0%	
PFTrDA	ND	ND	ND	ND	0.0%	ND	ND	ND	ND	0.0%	
PFBS	2.3	11.4	5.2	4.9	100.0%	ND	44.7	17.7	11.4	80.0%	
PFPeS	ND	5.6	0.7	ND	12.5%	ND	9.3	2.3	ND	30.0%	
PFHxS	ND	33.9	6.4	2.4	50.0%	ND	31.8	11.2	4.4	60.0%	
PFHpS	ND	ND	ND	ND	0.0%	ND	ND	ND	ND	0.0%	
PFOS	ND	17.4	2.2	ND	12.5%	ND	38.0	12.9	4.6	50.0%	
PFNS	ND	9.0	1.1	ND	12.5%	ND	ND	ND	ND	0.0%	
PFDS	ND	23.7	7.3	6.9	62.5%	ND	16.2	4.3	ND	40.0%	
ΣPFCA	259.0					1750.6					
ΣPFSA	182.7					483.7					
ΣPFAS	441.7					2234.3					



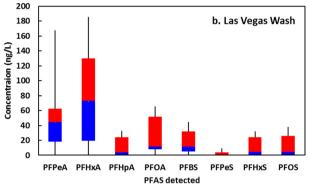


Fig. 2. Boxplots of the most dominant PFAS species detected in water from the (a) Truckee River (n = 8) and (b) Las Vegas Wash (n = 10).

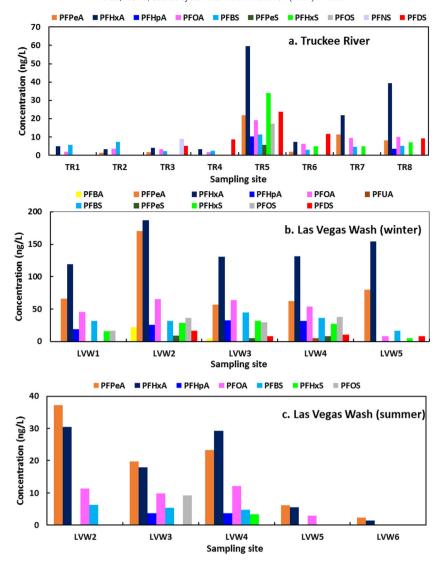
both watersheds (Table 3). Similarly, Clara et al. (2009) reported that long-chain PFAS (PFUA, PFDoA, and PFDS) were not detected in Austrian rivers, but PFOA (<1.1 to 1.9 ng/L) and PFOS (<4 to 35 ng/L) were the most relevant PFAS measured. Wang et al. (2019) measured eight PFCAs and three PFSAs in urban surface waters in Beijing, China, and found that the most abundant PFAS was PFBA (BDL to 75.5 ng/L), followed by PFPeA (BDL to 111.0 ng/L) and PFBS (BDL to 151.6 ng/L).

Short-chain PFAS have been found ubiquitously in aquatic environments across the globe. For example, in the United States, PFHxA was detected at 5.14 ng/L in Cape Fear drainage basin in North Carolina (Nakayama et al., 2007), 1.7 ng/L in Rhode Island and New York surface water sources (Zhang et al., 2016), 1.59 ng/L in the Upper Mississippi River (Nakayama et al., 2010), and <5 ng/L in a New Jersey public drinking water system (Post et al., 2013). In addition, PFHxA was found at 0.13-2.2 ng/L in the Pearl River (So et al., 2007), 0.16-5.3 ng/L in the Yangtze River (So et al., 2007), 8.04-47.3 ng/L in the Yellow River (Zhao et al., 2016), and 27.8-462 ng/L in Tangxun Lake in China (Zhou et al., 2013); and 0.62-49.6 ng/L in the River Rhine watershed in Europe (Moller et al., 2010). Perfluoropentanoic acid has been reported at BDL to 63.9 ng/L in the Yellow River (Zhao et al., 2016) and 26.4–254 ng/L in Tangxun Lake (Zhou et al., 2013) in China, and 0.66–69.5 ng/L in the River Rhine watershed in Europe (Moller et al., 2010). Perfluorobutane sulfonic acid, a C-4 PFAS that was developed as a replacement to PFOS, has been found at BDL to 6.67 ng/L in the Yellow River (Zhao et al., 2016) and 0.03-3.4 ng/L in the Pearl River in China (So et al., 2007), and 0.22-153 ng/L in the River Rhine watershed in Europe (Moller et al., 2010). Short-chain PFAS are frequently detected in surface water maybe because they are extensively used in manufacturing processes as alternatives to long-chain PFAS and are resistant to natural (e.g., biodegradation, hydrolysis, and photolysis) and engineered (e.g., adsorption and oxidation) treatment processes. Studies have also shown that short-chain PFAS are equally persistent and bioaccumulative as their long-chain counterparts (Gomis et al., 2018; Wilkinson et al., 2017a, 2017b), which also attributes to the frequent detection in aquatic environments. The present study reported relatively high levels of PFAS in the urban watersheds in Nevada compared with many other surface waters worldwide, which may be because of the unique hydrological characteristics and climate in this semiarid region, such as low surface flow.

The total PFAS concentrations measured at different locations ranged from 12.4 to 203.0 ng/L in the Truckee River and from 271.9 to 591.9 ng/L in the Las Vegas Wash during the winter/spring sampling events (Fig. 3, Table S2). The Las Vegas Wash water sampled in winter had much higher levels of PFAS compared with the Truckee River in all sites, which suggests that the wetland ecosystem and the downstream water supply reservoir (i.e., Lake Mead) are exposed to high levels of PFAS in the southern Nevada watershed. Potentially, the 30 million residents that use Lake Mead water on a daily basis are exposed to PFAS as well. The predominant PFAS species found in the Truckee River and Las Vegas Wash were similar (e.g., PFHxA, PFPeA, PFOA, and PFBS) (Fig. S1, Table S2). The total PFCA concentrations ranged from 5.0 to 111.0 ng/L and 242.2 to 470.1 ng/L in the Truckee River and Las Vegas Wash, respectively. The total PFSA concentrations ranged from 5.6 to 92.0 ng/L and 29.8 to 121.8 ng/L in the Truckee River and Las Vegas Wash, respectively. The results showed that PFCAs were at much higher levels in both watersheds compared with PFSAs.

In both watersheds, there are no known nearby manufacture facilities for PFAS production, but source water, municipal wastewater, runoff, land use, military bases (in Las Vegas only), and snowmelt (in Reno only) may affect the total PFAS loads in the watersheds. For the Truckee River, site TR5 had the highest levels of PFAS (i.e., 203.0 ng/L), which were a few magnitudes greater than other sites (Fig. 3a, Table S2). This sampling site is downstream of an airport and a WWTP, which could be point sources of PFAS. The second and third highest PFAS were detected farther downstream along the Truckee River at Pyramid Lake (TR8), with total PFAS of 82.3 ng/L, and the outlet of an industrial complex (TR7), with total PFAS of 52.2 ng/L (Table S2). Pyramid Lake (TR8) is an endorheic lake that facilitates PFAS accumulation. Although specific sources of PFAS were not identified at site TR7, a waste disposal site located in the upstream Truckee River (Lockwood, NV) and/or plastic- and rubber-handling companies within the industrial complex could be the potential sources of the high PFAS concentrations detected. Lake Tahoe water (TR1) contained the lowest levels of PFAS (i.e., 12.4 ng/L) (Table S2). Site TR5 had the most PFAS species (9 PFAS) detected in the Truckee River, and PFHxA, PFPeA, and PFOA were the predominant species found in this watershed (Fig. 4a).

The Las Vegas Wash sampling sites, in order from highest to lowest PFAS concentrations, are LVW2, LVW3, LVW4, LVW1, and LVW5 in winter and LVW2, LVW4, LVW3, LVW5, and LVW6 in summer (Fig. 3b and c). Overall, LVW2 had the highest levels of PFAS (i.e., 591.9 ng/L in winter and 85.4 ng/L in summer) (Table S2), which is likely because this site is immediately downstream of a WWTP and the wastewater effluents contribute to the PFAS load in the river. Sites LVW5 (Las Vegas Bay, entry into Lake Mead, 271.9 and 14.8 ng/L of PFAS measured in winter and summer, respectively) and LVW6 (Lake Mead Marina, 3.8 ng/L of PFAS measured), which are the farthest downstream, had the lowest PFAS levels because of dilution and natural attenuation during water flow. As reported in other studies, organic contaminants (e.g., pharmaceuticals and personal care products) exhibited the same pattern, with higher levels detected in the Las Vegas Wash and much lower levels detected in Las Vegas Bay and Lake Mead (Bai and Acharya, 2017, 2019b). In addition, 10 PFAS species were detected in LVW2 and LVW3, which is the greatest number of species detected among all the sampling sites, with similar dominant species to the Truckee River (i.e., PFHxA, PFPeA, and PFOA) (Fig. 4a and b). To the best of our knowledge, there are no other studies available on monitoring PFAS levels in the Nevada watersheds to use as a comparison. This study provided much-needed information to fill this data gap and demonstrated the prevalence of PFAS in the two urban watersheds.



 $\textbf{Fig. 3.} \ Spatial \ variation \ of PFAS \ concentrations \ in \ water \ from \ the \ (a) \ Truckee \ River \ (n=8), \ (b) \ Las \ Vegas \ Wash \ (sampled \ in \ winter) \ (n=5), \ and \ (c) \ Las \ Vegas \ Wash \ (sampled \ in \ summer) \ (n=5).$

3.2. PFAS in sediments

The PFAS composition in sediment samples differed from those of surface water samples. Table 4 summarizes the PFAS concentrations in the sediments from the two watersheds. Measured PFAS concentrations

in sediments from each sampling site can be found in Table S3. Of the 17 PFAS analyzed, 13 and 12 PFAS species were detected in the Truckee River and Las Vegas Wash sediments, respectively. The total PFAS found in sediments of the Truckee River were 272.9 μ g/kg (dry weight hereafter), of which PFCAs were 143.1 μ g/kg and PFSAs were

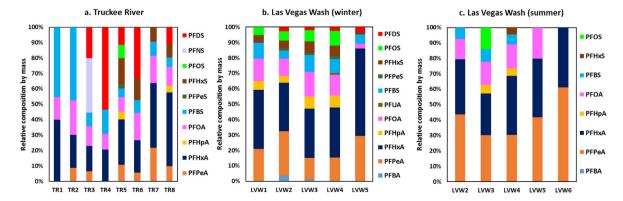


Fig. 4. Relative composition of PFAS species in water from the (a) Truckee River (n = 8), (b) Las Vegas Wash (sampled in winter) (n = 5), and (c) Las Vegas Wash (sampled in summer) (n = 5).

 $\begin{tabular}{ll} \textbf{Table 4} \\ \textbf{Statistics of PFAS concentrations } (\mu g/kg) \ in sediments collected from the Truckee River and Las Vegas Wash. \\ \end{tabular}$

Analyte	Truckee Ri	Truckee River $(n = 8)$					Las Vegas Wash ($n=13$)				
	Min	Max	Mean	Median	DF	Min	Max	Mean	Median	DF	
PFBA	ND	ND	ND	ND	0.0%	ND	2.2	0.3	ND	15.4%	
PFPeA	ND	ND	ND	ND	12.5%	ND	2.1	0.2	ND	7.7%	
PFHxA	1.8	20.3	4.9	2.8	100.0%	ND	18.7	2.8	ND	30.8%	
PFHpA	ND	21.8	2.7	ND	12.5%	ND	7.2	0.6	ND	7.7%	
PFOA	ND	10.0	1.3	ND	12.5%	ND	6.3	0.9	ND	15.4%	
PFNA	ND	ND	ND	ND	0.0%	ND	ND	ND	ND	0.0%	
PFDA	ND	ND	ND	ND	0.0%	ND	ND	ND	ND	0.0%	
PFUA	ND	22.9	4.6	ND	25.0%	ND	9.8	2.1	ND	30.8%	
PFDoA	ND	18.6	2.3	ND	12.5%	ND	ND	ND	ND	0.0%	
PFTrDA	ND	14.0	1.7	ND	12.5%	ND	ND	ND	ND	0.0%	
PFBS	ND	29.1	5.2	ND	25.0%	ND	10.0	2.6	ND	38.5%	
PFPeS	ND	3.9	0.5	ND	12.5%	ND	4.0	0.6	ND	15.4%	
PFHxS	ND	21.3	3.3	ND	25.0%	ND	12.1	1.8	ND	23.1%	
PFHpS	ND	15.5	3.3	ND	25.0%	ND	6.9	1.0	ND	15.4%	
PFOS	ND	ND	ND	ND	0.0%	ND	ND	ND	ND	0.0%	
PFNS	ND	7.8	1.0	ND	12.5%	ND	8.9	1.7	ND	23.1%	
PFDS	ND	12.5	3.0	ND	25.0%	ND	88.2	12.2	ND	46.2%	
ΣΡΓCΑ	143.1					88.6					
ΣPFSA	129.8					257.0					
ΣPFAS	272.9					345.7					

DF: detection frequency. ND: not detected. All data presented after subtract limit of detection for each analyte.

129.8 μ g/kg. The median concentration of PFAS ranged from BDL to 2.8 μ g/kg. For the Las Vegas Wash, the total PFAS were detected at 345.7 μ g/kg, of which PFCAs were 88.6 μ g/kg and PFSAs were 257.0 μ g/kg. Unlike in the water samples—for which the most abundant species were PFHxA, PFPeA, PFOA, and PFBS—the predominant species in the sediment samples were found to be PFDS (C10) (BDL to 12.5 μ g/kg in the Truckee River and BDL to 88.2 μ g/kg in the Las Vegas

Wash), PFHxA (C6) (1.8 to 20.3 µg/kg in the Truckee River and BDL to 18.7 µg/kg in the Las Vegas Wash), PFBS (C4) (BDL to 29.1 µg/kg in the Truckee River and BDL to 10.1 µg/kg in the Las Vegas Wash), and PFUA (C11) (BDL to 22.9 µg/kg in the Truckee River and BDL to 9.8 µg/kg in the Las Vegas Wash). These predominant species accounted for 52.0% and 74.0% of the total PFAS concentrations in the sediments of the Truckee River and Las Vegas Wash, respectively. Comparing the

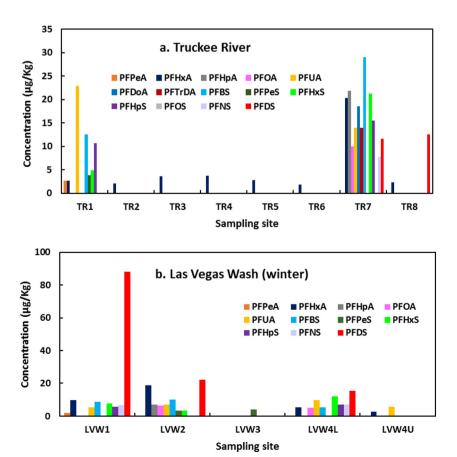


Fig. 5. Spatial variation of PFAS concentrations in sediments from the (a) Truckee River (n = 8) and (b) Las Vegas Wash (sampled in winter) (n = 5).

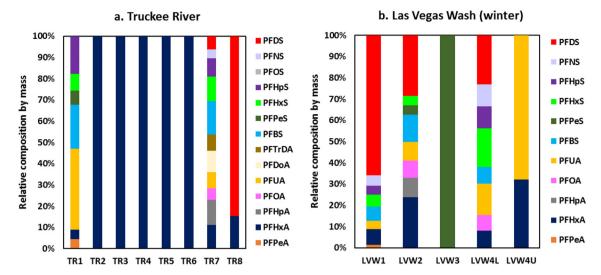


Fig. 6. Relative composition of PFAS species in sediments from the (a) Truckee River (n = 8) and (b) Las Vegas Wash (sampled in winter) (n = 5).

distribution of various PFAS species in the water and sediment samples from the two watersheds (Fig. S2), the short-chain carboxylic acids PFHxA and PFPeA were dominant in water, whereas the long-chain sulfonic acid PFDS was more prevalent in sediments. More PFAS species were detected in sediments than in water, such as the long-chain species PFDoA and PFTrDA (Tables 3 and 4). In other studies, PFHxA and PFPeA were detected at <0.5 to 1.7 ng/g and <0.5 to 2.9 ng/g in sediments in France (Dauchy et al., 2017), and PFBS was detected at 21.1 to 114 ng/g in sediments at Tangxun Lake in China (Zhou et al., 2013). Furthermore, PFUA, PFBS, and PFHxA were found at BDL to 3.8 ng/g, BDL to 0.22 ng/g, and BDL to 0.4 ng/g, respectively, in sediments from watershed in northwest Georgia, United States (Lasier et al., 2011). In sediments from Haihe River in China, PFHxA was also detected at 0.6 to 3.2 ng/g (Li et al., 2011). The PFAS levels measured in the Nevada watershed sediments were higher than the previously reported concentrations in other watersheds worldwide, which indicates that the Nevada watersheds are highly exposed to PFAS.

The long-chain PFAS species PFUA (C11), PFDoA (C12), PFTrDA (C13), and PFNS (C9) had higher detection frequencies in the sediments than in the surface waters (Tables 3 and 4). This is likely because of the higher hydrophobicity and sorption affinity of the long-chain compounds to the organic matter in sediments. The estimated log Koc value was 3.4 for PFHxA and 4.4 for PFUA in river sediments in China (Li et al., 2011). The log Koc values ranged from 2.54 to 3.57 for C8-C12 PFCAs in sediments from Dianchi Lake in China (Zhang et al., 2012). The results from this study showed that short-chain PFAS (C \leq 8) were more prominent in water, whereas long-chain PFAS (C > 8) were more detectable in sediments. Lasier et al. (2011) reported similar results, which showed that PFCAs with eight or less carbons were the most prominent in surface waters, and PFCAs with more than 10 carbons were predominate in sediment and tissue samples from watersheds in northwest Georgia.

The total PFAS concentrations measured in the sediments at different locations ranged from 3.9 to 134.2 $\mu g/kg$ in the Las Vegas Wash and from 1.8 to 183.8 $\mu g/kg$ in the Truckee River during winter/spring sampling (Fig. 5, Table S3). The PFAS concentrations were slightly greater in the Truckee River sediments compared with the Las Vegas Wash. The dominant species found in the Las Vegas Wash were PFDS and PFHxA, which accounted for 55.7% of the total PFAS detected. In the Truckee River, many PFAS species were detected at equivalent levels and the most abundant species were PFBS, PFHxA, and PFUA, which accounted for 43.2% of the total PFAS detected (Fig. S3). The PFCA concentrations were at 1.8 to 98.6 $\mu g/kg$ and the PFSA concentrations ranged from BDL to 85.2 $\mu g/kg$ in the Truckee River sediments. For the Las Vegas Wash sediments, PFCAs were detected at BDL to 39.2 $\mu g/kg$

and PFSAs were detected at BDL to $117.0~\mu g/kg$. In contrast to the findings for surface water, PFSAs were found to be more prevalent in the sediments of the two watersheds compared with PFCAs.

In the Truckee River sediments, TR7 had the highest PFAS levels detected (183.8 µg/kg) (Fig. 5a, Table S3). This site is located near the outlet of an industrial complex and 11 out of 17 PFAS species were detected at this location. Sediments at Lake Tahoe (TR1) had the second highest PFAS level detected (60.3 µg/kg) and the second most PFAS species identified (7 out of 17 PFAS analyzed) of the eight sampling sites, with PFUA being the predominant species (Fig. 5a, Table S3). In contrast, Lake Tahoe water contained the lowest PFAS compared with the other sampling sites (12.4 ng/L of total PFAS detected), and PFUA was not detected in the water sample (Fig. 3, Table S2). Based on the observations, although PFAS levels are low in Lake Tahoe water because of dilution, more PFAS species can be present in sediments, especially long-chain compounds, and bioaccumulation in sediments may result in ecological risks to aquatic organisms. The third highest PFAS concentrations were found in Pyramid Lake (TR8) (14.8 µg/kg), but only two PFAS species were found (i.e., PFDS and PFHxA). For all other sites along the Truckee River, PFHxA was the only species detected (Figs. 5a and 6a). The results indicated that the presence and types of PFAS in the Truckee River sediments varied greatly depending on the sampling locations, and that the sources of PFAS at each location need to be identified. In the Las Vegas Wash sediments (winter), LVW1 had the highest PFAS concentrations (134.2 µg/kg), followed by LVW2 (78.5 µg/kg) and LVW4L (67.2 μg/kg) (Fig. 5b, Table S3). The three sites also had more PFAS species detected, with PFDS being the dominant species. At site LVW4, more PFAS species and higher PFAS concentrations were detected from the lower (i.e., LVW4L) compared with the upper sediments (i.e., LVW4U) (Figs. 5b and 6b). As reported previously, PFAS tend to be associated with organic matter and absorb strongly onto sediments (Powley et al., 2005; Voogt and Sáez, 2006; Zhang et al., 2012). In the Las Vegas Wash, the sediments from the lower horizon has higher organic matter content compared with the upper horizon due to lower microbial activities (LaBounty and Burns, 2005; Zhou et al., 2004); therefore, more PFAS can be accumulated.

3.3. Seasonal effects

The Las Vegas Wash sites 2 to 5 were sampled in both winter and summer to evaluate seasonal effects on PFAS occurrence. For the water samples, the total PFAS concentrations in the four duplicated sites were 1676 ng/L in winter compared with 242.8 ng/L in summer (Fig. 3b and c, Table S2). The composition of PFAS showed the same pattern in both seasons, with PFHxA, PFPeA, and PFOA being the dominant

species (Fig. 4 and S1). For the sediment samples, less PFAS species were detected and they were at much lower levels during summer than winter (Table S3). The total PFAS found in sediments from the Las Vegas Wash in summer was $53.5~\mu g/Kg~(n=8)$ versus $292.1~\mu g/kg$ in winter (n=5). In addition to lower concentrations, only PFBA, PFBS, PFDS, and PFNS were detected in the sediment samples collected in summer. The decreased PFAS levels in summer may be caused by dilution from higher water flow, lower organic matter resulting in less sorption to sediments, and increased uptake by phytoplankton during algal blooms. Algae can play a role in removing organic contaminants from aquatic environments (Bai and Acharya, 2016, 2019a). A previous study also reported that concentrations of organic contaminants were much higher in winter (baseflow season) compared with summer (runoff season) in the watersheds in Denver, Colorado (Bai et al., 2018).

4. Conclusions

This study sampled surface water and sediments from six locations in the Las Vegas Wash and eight locations in the Truckee River in Nevada. The results filled the data gap on PFAS occurrence and distribution in two important urban watersheds in the western United States. Of the 17 target PFAS analyzed, 12 were detected in surface waters and 14 were detected in sediments. The predominant PFAS species found were PFHxA, PFPeA, PFOA, and PFBS in water and PFDS, PFHxA, PFBS, and PFUA in sediments. Overall, PFCAs were more frequently detected than PFSAs. In addition, short-chain PFAS (≤8 carbons) were more abundant in water and long-chain PFAS (>8 carbons) were more prevalent in sediments. The PFAS concentrations in the Las Vegas Wash water were much higher than in the Truckee River. The PFAS levels also decreased significantly in summer compared with winter in the Las Vegas Wash. Although some long-chain PFAS species may not be detected in water, aquatic organisms may still accumulate PFAS from sediments. The presence and distribution of different PFAS species depend on the chain length and functional moieties. Hydrophilic short-chain PFAS have greater impacts on surface waters and hydrophobic long-chain PFAS may accumulate in sediments and present risks to aquatic organisms.

CRediT authorship contribution statement

Xuelian Bai: Conceptualization, Methodology, Formal analysis, Investigation, Writing - original draft, Supervision, Project administration. **Yeongkwon Son:** Methodology, Validation, Resources, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary Information

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