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Per- and polyfluoroalkyl substances in source and treated drinking waters of the United States

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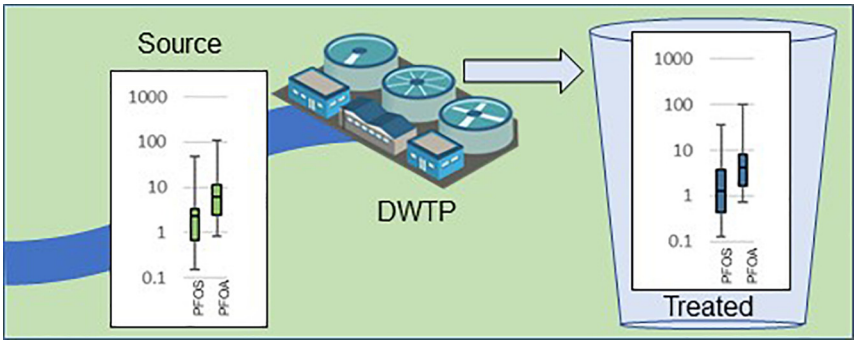
HIGHLIGHTS

- Seventeen per- and polyfluoroalkyl substances (PFAS) were monitored by LC/MS/MS.
- Twenty-five paired source and treated drinking waters were sampled.
- All 50 samples had detectable PFAS; one exceeded health advisory guidelines.
- Distinctive PFAS patterns were observed for two large river systems.
- Minimal removal during drinking water treatment; granular activated carbon recharge link

GRAPHICAL ABSTRACT



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ABSTRACT

Contaminants of emerging concern (CECs), including per- and polyfluoroalkyl substances (PFAS), are of interest to regulators, water treatment utilities, the general public and scientists. This study measured 17 PFAS in source and treated water from 25 drinking water treatment plants (DWTPs) as part of a broader study of CECs in drinking water across the United States. PFAS were quantitatively detected in all 50 samples, with summed concentrations of the 17 PFAS ranging from <1 ng/L to 1102 ng/L. The median total PFAS concentration was 21.4 ng/L in the source water and 19.5 ng/L in the treated drinking water. Comparing the total PFAS concentration in source and treated water at each location, only five locations demonstrated statistically significant differences (i.e. $P < 0.05$) between the source and treated water. When the perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) concentrations in the treated drinking water are compared to the existing US Environmental Protection Agency's PFOA and PFOS drinking water heath advisory of 70 ng/L for each chemical or their sum one DWTP

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Drinking water
Source water

exceeded the threshold. Six of the 25 DWTPs were along two large rivers. The DWTPs within each of the river systems had specific PFAS profiles, with the three DWTPs from one river being dominated by PFOA, while three DWTPs on the second river were dominated by perfluorobutyric acid (PFBA).

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are commonly used in many household and industrial products due to their unique chemical and physical properties (Kotthoff et al., 2015). PFAS are used as components in aqueous film-forming foams (AFFFs) used in firefighting (Baduel et al., 2017; Barzen-Hanson et al., 2017; Boone et al., 2014). One of the downsides of PFAS use is that they end up in the water cycle, either directly through nonpoint sources such as runoff and groundwater infiltration, or through point sources such as firefighting training grounds, industrial facilities, and municipal and industrial wastewater treatment plant effluent, or even through atmospheric deposition (Hu et al., 2016; Lu et al., 2017). PFAS are not readily biodegradable (Liou et al., 2010), so transport away from the sources of contamination is nearly inevitable. Humans can be exposed to PFAS through consumption of food and water. Elimination of PFAS from the body varies by compound, but can take several years for humans (Lau et al., 2007; Zhang et al., 2013). Determining the effects of environmental exposures to humans is difficult, given that animals do not model human toxicokinetics and that the exposures are typically to mixtures of PFAS (Post et al., 2017).

In the United States, the 1996 amendments to the Safe Drinking Water Act (SDWA; USEPA, 1996) outlines the requirement of the US Environmental Protection Agency (USEPA) to protect human health by establishing drinking water standards. Every five years, the USEPA is charged with developing the contaminant candidate list (CCL), which identifies unregulated chemicals and microorganisms of health interest that are known or anticipated to occur in public water systems. The fourth such list (CCL 4) was finalized in 2016 (USEPA, 2016a). Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) are two of the 97 chemicals on CCL 4. One of the criteria used to determine if an analyte should be regulated is if it frequently occurs in drinking water at levels which are a public health concern. An additional authority under the SDWA amendments (USEPA, 1996) is the option to gather nationwide occurrence data through the unregulated contaminant monitoring rule (UCMR). The UCMR allows the Agency to gather occurrence data for a maximum of 30 analytes in a five-year cycle for all utilities that serve >10,000 people, and a statistical sampling of those utilities serving <10,000 (USEPA, 2012). The USEPA's Office of Water conducted the third round of sampling (UCMR 3) between 2013 and 2015; UCMR 3 included six PFAS compounds, perfluorobutanesulfonic acid (PFBS), perfluoroheptanoic acid (PFHpA), perfluorohexanesulfonic acid (PFHxS), perfluorononanoic acid (PFNA), PFOS, and PFOA (USEPA, 2012). At the time of sampling, the USEPA provisional drinking water health advisories for PFOS and PFOA were 200 ng/L and 400 ng/L, respectively (USEPA, 2009). In 2016, EPA published national drinking water health advisories of 70 ng/L for either PFOS, PFOA, or their sum (USEPA, 2016b, 2016c). Some states and other countries have established lower regulatory or guidance levels for PFOS and PFOA, as well as levels for other PFAS (ITRC, 2017; Post et al., 2017). Given these lower human health thresholds, occurrence data with method reporting levels lower than those used in the UCMR (40 ng/L for PFOS, 20 ng/L for PFOA; USEPA, 2012) and which incorporate more than six PFAS will be useful for future regulatory and non-regulatory evaluations.

This paper is part of a series of papers describing a comprehensive study of the presence, concentrations, and persistence associated with chemical and microbial contaminants of emerging concern (CECs) in source and treated drinking waters of the United States (Glassmeyer et al., 2017; Batt et al., 2017; Benson et al., 2017; Conley et al., 2017; Furlong et al., 2017; King et al., 2016; Kostich et al., 2017; Varughese et al., 2018). This research was a joint effort between the USEPA and the U.S. Geological Survey (USGS), as part of a long-term interagency agreement. The study was conducted in two phases, sampling a total of 29 drinking water treatment plants (DWTPs). Phase I collected paired source and treated drinking water samples from nine DWTPs and analyzed the samples for 84 chemical CECs; Phase II collected paired samples from 25 DWTPs (including five from Phase I), which were analyzed for 247 chemical and microbial CECs. Three of these 25 used a groundwater source. A primary goal of the study was to provide data for assessing potential human exposure via drinking water to an extensive set of CECs. The interdisciplinary approach of this nationwide study included measurement of CECs in both source and treated waters, evaluation of the potential health effects of the contaminants in an in vitro estrogenic activity bioassay, and screening for human and ecological health impact assessments. This manuscript focuses on the occurrence of PFAS in the source and treated drinking water from the 25 Phase II DWTPs.

2. Materials and methods

2.1. Sampling

A detailed description of the criteria used to select sampling sites, sample collection procedures, analysis methods, and quality assurance and control protocols has been previously published (Glassmeyer et al., 2017). In brief, in Phase II of this project, source and treated drinking water grab samples were collected from 25 drinking water treatment plants (DWTPs) and analyzed for PFAS. The sampling locations represented 24 states within the contiguous United States. Attempts were made to find locations with known or suspected sources of wastewater in the source water, but ultimately the selection process was driven by the willing participation of the DWTPs. Table 1 provides a description of each participating DWTP; the specific identity of each location will not be released to maintain anonymity. Personnel at the participating DWTPs conducted the sampling. The sampling bottles specific to each method were supplied to the DWTPs; for the PFAS method, a 1-L amber Nalgene™ bottle with no preservative or dechlorination agent was used. For all utilities except DWTP 10, the intake (source water) samples were collected from a tap within the plant that provided untreated water; a second tap situated after all treatment steps, but before the clearwell, provided treated drinking water. DWTP 10 was dip sampled from the source water body using the PFAS sample bottle (Glassmeyer et al., 2017). Samples were packed on ice and shipped overnight to the USEPA Office of Chemical Safety and Pollution Prevention laboratory at the John C. Stennis Space Center, MS, for analysis. Within 8 h of arrival, 5 g of Trizma pre-set crystals (Fisher Scientific), pH 7.0, was added to each sample, the caps replaced, and the bottles shaken to mix the sample. Citric acid monohydrate (Fisher Scientific) and sodium citrate dihydrate (Fisher Scientific), 1 g each, were added to each sample, caps replaced, and the bottles shaken. The samples were stored at room temperature and extracted within 5 days of sampling. Extracted samples were archived in freezers.

2.2. Analytical methodology

Extraction and analysis methods for 17 perfluoroalkyl acids (PFAA) including four perfluoroalkyl sulfonic acids and 13 perfluoroalkyl carboxylic acids were as previously described in Boone et al. (2014). At

Table 1
Background information on drinking water treatment plants sampled for this study.
Adapted from Glassmeyer et al., 2017.

Location	Water body type	Watershed size (1000s km^2)	Pop served[a] (1000s)	Production at sampling[a] (MGD)[b]	Residence time of treatment[c] (h)	Sampling interval[c] (h)	Primary disinfectant[d]	GAC depth (ft)	GAC recharge rate (years)	Treatment processes used[f]
DWTP 1	River	6.6	>500	>100	10	8	$O_3 + NH_2Cl$	na[e]	na	O_3, coag/floc, NH_2Cl, C, floc, C, F
DWTP 2	River	198	>500	>100	72	73	Cl_2	11.4	0.6	Coag/floc, S, SF, GAC, Cl_2
DWTP 3	River	50.5	50–500	10–100	6	7	Cl_2 + UV	2.5	3	Coag/floc, C/S, F, GAC, Cl_2, UV
DWTP 4	River	4.9	>500	10–100	46	48	$Cl_2 + NH_2Cl$	na	na	Pre-Cl_2, coag/floc, S, secondary Cl_2, SF, NH_3
DWTP 5	Ground	na	<50	<10	0.13	0	Cl_2	na	na	Cl_2
DWTP 10	River	3256	50–500	>100	7	9.25	NH_2Cl	na	na	Coag/floc, S, NH_2Cl, F
DWTP 11	River	21.5	<50	<10	7	2.25	$O_3 + Cl_2$	6	4	Coag/floc, S, C, O_3, GAC and SF, Cl_2
DWTP 12	Ground	na	<50	<10	30.72	23.75	Cl_2	1.25	As needed	Coag/floc, pre-Cl_2, C, GAC and SF, post-Cl_2
DWTP 13	Lake/Res[g]	0.03	>500	>100	1	0.75	Cl_2	na	na	Cl_2
DWTP 14	Lake/Res	1.1	50–500	10–100	10	3.25	$ClO_2 + Cl_2$	0.75	8	Coag/floc, pre-ClO_2, GAC and SF, Cl_2
DWTP 15	River	3.4	<50	<10	1	4	Cl_2	na	na	Coag/floc, S, F, Cl_2
DWTP 16	River	222	50–500	10–100	6	9	NH_2Cl	2.5	3	Coag/floc, S, GAC and SF, NH_2Cl
DWTP 17	River	2.4	<50	<10	2	4	Cl_2	na	na	C, coag/floc, pre-Cl_2, F, Cl_2
DWTP 18	River	1	<50	<10	7.3	7.25	$O_3 + NH_2Cl$	4	2	O_3, floc, S, pre-Cl_2, GAC and SF, NH_2Cl
DWTP 19	River	95.6	50–500	10–100	26	57.25	NH_2Cl	na	na	Coag/floc, PAC, S, ultrafiltration, NH_2Cl.
DWTP 20	River	44.5	>500	10–100	30	46.75	$O_3 + Cl_2$	5	> 4	Floc, S, O_3, GAC and SF, Cl_2
DWTP 21	River	198	50–500	10–100	90	14.5	Cl_2	na	na	PAC pre-Cl_2, coag, S, Cl_2 F
DWTP 22	River	13.6	50–500	10–100	10	1.5	$O_3 + Cl_2$ + UV	4	As needed	Pre-O_3, coag, S, O_3, GAC and SF, UV, Cl_2
DWTP 23	Lake/Res	0.02	50–500	10–100	7	6.5	ClO_2 + UV + Cl	na	na	Pre-ClO_2, coag/floc, S, dual media F, UV, Cl_2
DWTP 24	Ground	na	50–500	10–100	8	6.25	NH_2Cl	1.7	3	PAC, GAC and SF, NH_2Cl
DWTP 25	Lake/Res	0.02	50–500	10–100	13.6	12	$O_3 + NH_2Cl$	3	5–10	Pre-O_3, coag, GAC and SF, NH_2Cl
DWTP 26	River	0.8	50–500	10–100	24–36	3.25	Cl_2	na	na	Pre-Cl_2, PAC, coag, S, Cl_2, F, Cl_2
DWTP 27	River	3.1	50–500	<10	4	13.75	NH_2Cl + UV	na	na	PAC, coag/floc, S, F, UV, NH_2Cl
DWTP 28	Lake/Res	442	>500	>100	1	1.5	$O_3 + NH_2Cl$	na	na	NH_2Cl, O_3, F
DWTP 29	Lake/Res	0.02	<50	<10	8	8.75	Cl_2	na	na	PAC, pre-Cl_2, coag/floc, S, Cl_2, F

[a] Population sizes and production binned to give indication of DWTP size variation while maintaining plant anonymity.
[b] MGD = million gallons per day.
[c] DWTPs were asked to match the residence time of treatment to the sampling interval, with varying degrees of success.
[d] O_3 = ozone; NH_2Cl = chloramine; Cl_2 = chlorine; UV = ultraviolet radiation; ClO_2 = chlorine dioxide.
[e] na = not applicable.
[f] Major steps in treatment in each plant. Coag = coagulation; floc = flocculation; C = clarification; F = filtration; S = sedimentation; SF = sand filter; NH_3 = ammonia; PAC = powdered activated carbon; GAC = granular activated carbon.
[g] Lake/Res = Lake or reservoir.

the time of extraction, the buffered samples (see above) were spiked with ^{13}C labeled surrogates (Wellington Laboratories), loaded onto solid phase extraction (SPE) cartridges [6 cc Oasis® Weak Anion Exchange (WAX) cartridge (150 mg, 30 μm [#186002493]) for source water and the 6 cc Oasis® WAX Plus Extraction cartridge (225 mg, 60 μm [#186003519]) for treated water]. The SPE cartridges were washed with reagent water (Optima grade, Fisher Scientific) and methanol (Optima grade, Fisher Scientific), eluted with 1% ammonium hydroxide (Fisher Scientific) in 9:1 methyl *tert*-butyl ether (HPLC grade, Fisher Scientific): methanol, concentrated to 250 μL, spiked with ^{13}C labeled injection standard and analyzed by liquid chromatography, tandem mass spectrometry (LC/MS-MS). For the analysis, a PerkinElmer (PE) HPLC 200 Series, with dual micro pumps and solvent mixer, interfaced with a PE Sciex, API 3000 triple quadrupole mass spectrometer was used. A Betasil C18 LC column [2.1 mm × 100 mm × 5 μm (i.d. × L × particle size)]: [Thermo Scientific, P/N 70105-102130] interfaced with a security guard cartridge [3 mm × 4 mm (i.d. × L)]: [Phenomenex, C18, P/N AJ0-4287] provided the chromatographic separation. The mobile phases were 20 mM ammonium acetate (Sigma Aldrich) in Optima water and methanol. Supplementary information Table 1 lists experimental parameters, such as the mobile phase gradient, instrument conditions, the parent and fragment ions monitored during analysis, and calibration curve information. After using the 225-mg cartridge for treated water samples on the first 10 DWTPs, the two subsequent DWTPs had lower than expected recovery of some of the PFAS. Method development was revisited to see if the 150-mg column was able to extract treated drinking water samples within the QA/QC guidelines. It was decided to run both treated and source waters with the 150-mg column method for the remainder of the study. This experience demonstrated the importance of monitoring the ^{13}C labeled surrogate recovery to assess the performance of the method. Performance could be affected by extraction cartridges, buffers, solvents, filters and sample conditions described in Boone et al. (2014). Supplementary information Table 2 lists surrogate recoveries for this study.

2.3. Quality assurance/quality control

This project used a strict quality assurance/quality control (QA/QC) protocol to characterize data variability (Glassmeyer et al., 2017; Batt et al., 2017). Every sample in the study was collected in triplicate. The first was the primary sample, the analytical results from which are the basis of this paper. The second sample was analyzed as a duplicate, to monitor variability within co-collected samples as well as the method. The third was a laboratory fortified matrix (LFM) sample; this matrix spike sample served to monitor for any matrix-induced signal enhancement or suppression that could occur. The source water samples were spiked at 5 ng/L of each analyte, the treated drinking water with 1 ng/L of each analyte. Any sample with a laboratory fortified matrix recovery > 150% after accounting for any detections in the primary sample was deemed to be experiencing matrix enhancement, and the associated primary sample result was considered to be a qualitative detection (i.e. considered a detection, but no quantitative concentration was reported). The lowest concentration minimal reporting level (LCMRL; USEPA, 2010) process was used to set minimum reporting levels. Any detection above the instrument reporting level (lowest calibration concentration of the curve) but below the LCRML was also considered a qualitative detection. For the remainder of the text, when discussing "qualitative frequencies of detection" the data referred to combine both qualitative and quantitative detections, while "quantitative frequency of detection" includes only the measurements reported numerically. A field blank sample consisting of laboratory grade water poured into the sample bottle by the field personnel was collected alongside all source and treated drinking water samples. The concentration in the primary sample had to exceed any detections in the field blank or any associated laboratory blank by a factor of three to be considered a valid detection; those sample results with concentrations that were less than three times the field blank were treated as non-detects. Laboratory blank samples and laboratory fortified blank samples (LFBs; prepared by spiking a laboratory water with 1 ng/L (or 5 ng/L) of each PFAS analyte), also were analyzed with each batch of samples to monitor analytical performance. An extraction batch included the six samples described above (primary, duplicate, LFM, field blank, lab blank, and LFB); the analytical batch also included concentration check and spike check samples that are not extracted but are analyzed along with the extracted samples.

3. Results and discussion

3.1. PFAS detections and concentrations

Of the 17 PFAS monitored in this study, 14 were qualitatively detected and 12 quantitatively detected at least once in source water samples, while 13 were qualitatively detected and 12 were quantitatively detected in treated drinking water samples. Table 2 provides a synopsis of the detections and measured concentrations; data for all analytes at all locations are listed in Supplementary information Tables 3 and 4. Table 3 summarizes the results of the duplicate and laboratory fortified matrix analyses; Supplementary information Tables 5 and 6 provide additional data for these QA/QC samples. Supplementary information Table 7 details the detections in the blank samples. PFBS and PFOA were the only analytes qualitatively detected in the source water samples at all 25 DWTPs, however, another 8 analytes, perfluorobutanoic acid (PFBA), perfluorodecanoic acid (PFDA), PFHpA, PFHxS, perfluorohexanoic acid (PFHxA), PFNA, PFOS, and perfluoropentanoic acid (PFPeA), were qualitatively detected in at least 90% of the samples (Table 2). In the treated samples, PFBS, PFHxA, and PFOA were qualitatively detected in all samples, while PFHpA, PFNA, PFOS, and PFPeA were again qualitatively detected in over 90% of the samples. Perfluorohexadecanoic acid (PFHxDA) and perfluorooctadecanoic acid (PFOcDA) were not detected quantitatively or qualitatively in any source or treated water sample. When the concentrations of each of the 12 quantitatively detected analytes are plotted (Fig. 1), the range of concentrations measured across the study, as well as the similarity between the source water samples and the treated water samples for any given analyte becomes evident, even as the median concentration ranges of individual PFAS analytes span two orders of magnitude. Note that for some analytes, the LCMRL value was substituted for the minimum concentration (see figure footnote for more detailed explanation). For most analytes, the measured concentrations ranged from sub-ng/L to 10s or even 100 s of ng/L (Fig. 1); the median concentrations were <10 ng/L for all analytes. These measurements were within an order of magnitude compared to those of surface water samples collected in Europe (Möller et al., 2010; Wilhelm et al., 2010), and tropical locations in South America, the Caribbean, Indian Ocean (Munoz et al., 2017) and Singapore (Nguyen et al., 2011). Higher concentrations compared to this study were measured in areas in China (Lu et al., 2017), the Netherlands (Gebbink et al., 2017), and Japan (Shiwaku et al., 2016) near industrial locations, but most of samples collected in Vietnam were an order of magnitude lower (Lam et al., 2017). The frequency of drinking water detections was greater in this study than in Germany (range of non-detects 9–100% for different PFAS; Wilhelm et al., 2010), presumably due to the lower detection limits used in this study. The frequency was also greater than that measured in UCMR 3 sampling conducted in the United States; see Section 3.5 for detailed comparison between these studies. Jian et al. (2017) summarized sixteen drinking water studies from around the world, while Mak et al. (2009) analyzed tap water samples from five countries. While the average concentrations of total PFAS in this study was commensurate with the concentrations measured in the 16 studies captured in the Jian et al. (2017) summary, or measured in the Mak et al. (2009) study, the maximum measurements of PFDA, PFHpA, PFHxA, and PFNA for this study were greater. Using the one-tailed Wilcoxon Paired-Sample

Table 2
Frequency of detection, maximum and median concentration of PFAS chemicals. Each analyte was measured at 25 locations.

Analytes	CAS number	LCMRL[a] (ng/L)	Source water				Treated drinking water			
			Qual[b] freq (%)	Quant[c] freq (%)	Med.[d] conc. (ng/L)	Max.[e] conc. (ng/L)	Qual[b] freq (%)	Quant[c] freq (%)	Med.[d] conc. (ng/L)	Max.[e] conc. (ng/L)
Perfluorobutanesulfonic acid (PFBS)	375-73-5	0.032	100	96	1.12	11.1	100	96	1.17	11.9
Perfluorohexanesulfonic acid (PFHxS)	355-46-4	0.034	92	92	0.86	44.8	84	80	0.79	21.1
Perfluorooctanesulfonic acid (PFOS)	1763-23-1	0.13	96	88	2.28	48.3	92	80	1.62	36.9
Perfluorodecanesulfonic acid (PFDS)	335-77-3	0.049	12	0	QL	QL	0	0	ND	ND
Perfluorobutanoic acid (PFBA)	375-22-4	0.24	92	92	3.05	96.8	88	88	3.62	104
Perfluoropentanoic acid (PFPeA)	2706-90-3	0.051	92	92	1.95	501	96	96	1.78	514
Perfluorohexanoic acid (PFHxA)	307-24-4	0.044	96	96	2.02	55.1	100	100	1.43	60.8
Perfluoroheptanoic acid (PFHpA)	375-85-9	0.04	96	96	1.13	184	92	92	0.79	177
Perfluorooctanoic acid (PFOA)	335-67-1	0.56	100	76	6.32	112	100	76	4.15	104
Perfluorononanoic acid (PFNA)	375-95-1	0.094	96	96	0.86	41.4	92	88	0.74	38.6
Perfluorodecanoic acid (PFDA)	335-76-2	0.084	92	60	0.43	31.1	80	52	0.33	24.7
Perfluoroundecanoic acid (PFUnDA)	2058-94-8	0.067	36	32	0.14	2.90	32	16	0.54	1.85
Perfluorododecanoic acid (PFDoDA)	307-55-1	0.062	20	8	0.21	0.28	12	4	0.09	0.09
Perfluorotridecanoic acid (PFTrDA)	72629-94-8	0.072	12	0	QL	QL	0	0	ND	ND
Perfluorotetradecanoic acid (PFTeDA)	376-06-7	0.13	0	0	ND	ND	4	0	QL	QL
Perfluorohexadecanoic acid (PFHxDA)	67905-19-5	0.4	0	0	ND	ND	0	0	ND	ND
Perfluorooctadecanoic acid (PFOcDA)	16517-11-6	0.29	0	0	ND	ND	0	0	ND	ND

QL = all measurements qualitative (such as below LCMRL or with matrix enhancement) therefore no median or maximum can be determined. ND = non-detection.
[a] LCMRL = lowest concentration minimum reporting level.
[b] Qualitative frequency of detection - Includes the quantitative measurements as well as those below the LCMRL as well as analytes with matrix enhancement in the associated laboratory fortified matrix samples.
[c] Quantitative frequency of detection. Includes only measurements that exceed the RL or LCMRL and did not have matrix enhancement.
[d] Median concentration of quantified detections.
[e] Maximum concentration of quantified detections.

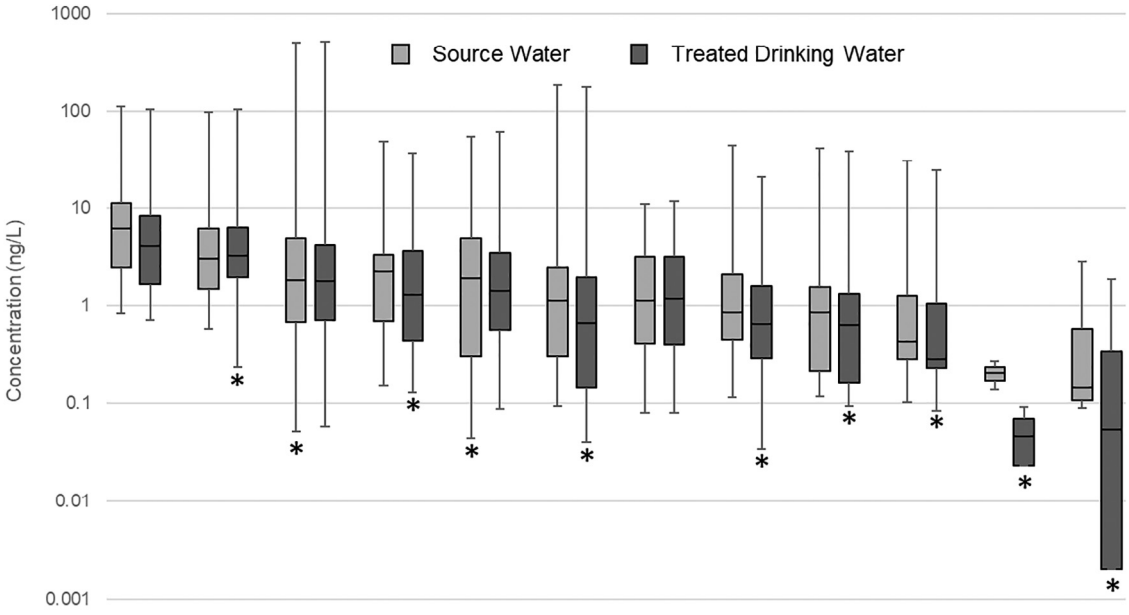
Test (statistiXL version 2.0 for Microsoft Excel), only PFOS, PFHpA, PFHxS, and perfluoroundecanoic acid (PFUnDA) show statistically significant differences ($P < 0.05$) between source water and treated drinking water concentrations. The lack of PFAS removal during treatment was also observed by Boiteux et al. (2017) and Post et al. (2013).

3.1.1. QA/QC results

The QA/QC data demonstrated that the method performed well for all analytes, with the median relative percent difference (RPD) between duplicates of 10% or less for both the source water and the treated drinking water (Table 3). The maximum source water RPD was 22.1% for PFNA at DWTP 29; the maximum treated drinking water RPD was 30.3%, for PFPeA at DWTP 29 (Supplementary information Table 5). The median laboratory fortified matrix recoveries were >90% for all analytes except PFHxDA and PFOcDA; these two analytes along with perfluorodecanesulfonic acid (PFDS), perfluorotetradecanoic acid (PFTeDA), and perfluorotridecanoic acid (PFTrDA) were never quantitatively detected in any sample (Table 2). Method precision for most analytes, calculated as the nonparametric estimate of variance, f-pseudosigma, was <10% in source or treated waters (Table 3). In source water, four analytes, PFHpA, PFHxDA, PFOcDA, and PFTeDA, had variances > 10%. In treated water, two additional analytes. PFOS and PFPeA, had variances equal or >10%. As described in Boone et al. (2014), the higher molecular weight compounds adhere more readily to surfaces. During method development these compounds had not been detected in drinking waters, thus the method was developed to enhance the recoveries of the detectible compounds. The method can be altered to increase the recovery of the higher molecular weight compounds but will decrease the recovery of the lower molecular weight compounds. The LFM recoveries for DWTP 22 were likely outliers

Table 3
Summary of quality assurance/quality control results.

Analytes	Median (range) relative percent difference between duplicate pairs		Median (range) laboratory fortified matrix percent recovery		Median laboratory fortified matrix percent recovery variance, as f-pseudosigma	
	Source water (%)	Treated drinking water (%)	Source water (%)	Treated drinking water (%)	Source water (%)	Treated drinking water (%)
Perfluorobutanesulfonic acid (PFBS)	1.9 (0–15)	2.5 (0–12)	91 (74–105)	92 (75–115)	7.0	5.6
Perfluorohexanesulfonic acid (PFHxS)	4.1 (0–19)	5.2 (0.7–22)	96 (78–106)	97 (25–295)	5.5	5.0
Perfluorooctanesulfonic acid (PFOS)	5.1 (1.0–14)	7.2 (1.6–20)	98 (69–106)	99 (−215–177)	6.5	11
Perfluorodecanesulfonic acid (PFDS)	–	–	92 (75–113)	98 (85–112)	7.5	7.7
Perfluorobutanoic acid (PFBA)	1.3 (0–5.9)	1.0 (0–4.5)	96 (71–104)	100 (−50–145)	3.9	5.9
Perfluoropentanoic acid (PFPeA)	2.7 (0–9.5)	2.6 (0–30)	94 (62–190)	93 (−450–112)	5.4	10
Perfluorohexanoic acid (PFHxA)	1.7 (0–16)	1.3 (0–25)	96 (76–102)	100 (80–130)	4.0	8.2
Perfluoroheptanoic acid (PFHpA)	3.5 (0–21)	3.8 (0–19)	98 (40–110)	95 (−50–115)	11	11
Perfluorooctanoic acid (PFOA)	3.6 (0–13)	2.7 (0–11)	94 (26–110)	91 (−810–119)	4.2	8.5
Perfluorononanoic acid (PFNA)	5.6 (0–22)	5.5 (0.3–17)	96 (67–106)	99 (−330–108)	5.3	6.1
Perfluorodecanoic acid (PFDA)	4.1 (0.5–15)	10 (0.3–22)	97 (83–106)	101 (−55–109)	7.2	6.6
Perfluoroundecanoic acid (PFUnDA)	4.8 (0.2–14)	8.9 (4.1–13)	97 (79–108)	97 (87–102)	3.7	2.3
Perfluorododecanoic acid (PFDoDA)	9.9 (3.7–16)	8.8 (8.8–8.8)	97 (82–120)	97 (87–103)	3.6	3.8
Perfluorotridecanoic acid (PFTrDA)	–	–	99 (51–124)	99 (81–110)	8.4	3.7
Perfluorotetradecanoic acid (PFTeDA)	–	–	94 (74–183)	106 (79–140)	15	19
Perfluorohexadecanoic acid (PFHxDA)	–	–	69 (38–204)	83 (29–130)	23	17
Perfluorooctadecanoic acid (PFOcDA)	–	–	74 (32–199)	87 (34–148)	17	18



	PFOA	PFBA	PFPeA	PFOS	PFHxA	PFHpA	PFBS	PFHxS	PFNA	PFDA	PFDoDA	PFUnDA
Number of pairs[b]	19	23	24	22	25	24	24	23	24	15	2	8
LCMRL (ng/L)	0.56	0.24	0.051	0.13	0.044	0.04	0.032	0.034	0.094	0.084	0.062	0.067
Wilcoxon *P*	0.063	0.932	0.400	**0.030**	0.923	**0.000**	0.734	**0.047**	0.088	0.096	0.250	**0.008**

Fig. 1. Boxplots of the 12 quantitatively detected PFAS. Shoulders of the boxplots are 25th and 75th percentile, the belt is the median, whiskers are minimum[a] and maximum measured concentrations. [a]Due to the nature of the log scale concentration axis, concentrations equal to 0 ng/L cannot be plotted; alternatively, the LCMRL was substituted for non-detects as the minimum concentration. Compounds using this substitution are denoted with an asterisk. Non-detects were considered as equal to 0 ng/L to calculate quartiles and median; only pairs with at least one quantitative concentration measurement were considered in these calculations. [b]Number of source and treated drinking water pairs where at least one of the pair has a quantitative concentration measurement. *P* values in bold are statistically significant (<0.05).

from the remaining samples (Supplementary information Table 6). The recovery calculation subtracted the detections in the primary sample from the spiked sample; the high concentrations in DWTP 22 relative to the matrix spike concentrations resulted in some negative recoveries. Lower spiking levels were used to ensure optimal method performance at the lower concentrations anticipated, and is especially necessary when reporting levels at or near the LCMRL. As expected (Foreman et al., 2012), when spiking at lower levels into a sample that contains the compound of interest at higher levels the spike did not meet expected recovery (e.g. spiking 1 ng/L on top of 100 ng/L in sample). The 1 ng/L and 5 ng/L values were chosen to help eliminate false positives at the lower levels of detection since the LCMRLs were between 0.032 and 0.56 ng/L. These levels were not used as a consideration for detection at higher levels of each specific compound since the signal of higher detectable compounds would overwhelm the signal from the lower spikes. Because we used isotopically labeled surrogates, we can use surrogate recovery to monitor whether the failure is due to the elevated compounds of interest or from other matrix effects (Boone et al., 2014). In this case, effects from interferences were minimal due to the extraction and clean-up procedures combined with the use of ^{13}C-labeled surrogates and analysis by LC/MS/MS. Only one data point, the PFHxS in DWTP 24 treated water, was censored due to matrix enhancement.

3.2. Long range conservation of PFAS patterns in large rivers

Six of the utilities monitored in this study draw their source water from two large river systems. DWTPs 2, 21, and 12 (a groundwater proximal to, and under the influence of, the surface water) draw from Large River A, while DWTPs 10, 16, and 19 have Large River B as their source (rivers are not identified to maintain anonymity). Comparing the fractional load of the different PFAS in the source water (relative percentages were used instead of concentrations to account for differences in concentrations between DWTP 22 and the other locations; Fig. 2), Large River A was dominated by PFOA, while Large River B was dominated by PFBA. The analyte profiles of three other utilities DWTP 4, 22, and 24 are also shown in Fig. 2 to illustrate some of the other PFAS compositions found at other locations in this study. Similar trends of regional conservation of patterns were detected in China (Lu et al., 2017) and along stretches of the Rhine River (Möller et al., 2010). These data further demonstrate the persistence and mobility of PFAS in the environment.

3.3. Location-based concentrations and treatment effects

Except for the groundwater location DWTP 5, the number of PFAS measured at each location, particularly in the source water, was fairly consistent across locations with at least 9 and as many as 14 of the 17 PFAS monitored in this study detected (Fig. 3 top panel, Supplemental information Tables 3 and 4). After treatment, DWTP 2 was the only DWTP to exhibit a substantial change in the number of measured analytes, with 12 PFAS measured in the source water sample and only 6 PFAS measured in the corresponding treated drinking water. When total PFAS concentration was considered instead of frequency of analyte detection, the differences between locations becomes more pronounced (Fig. 3, middle panel, Supplemental information Tables 3 and 4). This dataset was evaluated using the De Facto Reuse in our Nation's Consumable Supply (DRINCS) model (Nguyen et al., 2018). Unlike pharmaceuticals and anthropogenic waste indicator compounds, PFAS did not show a correlation to wastewater contribution in the source water. The PFAS concentrations between locations differed by four orders of magnitude. For most locations, the total concentration was <100 ng/L,

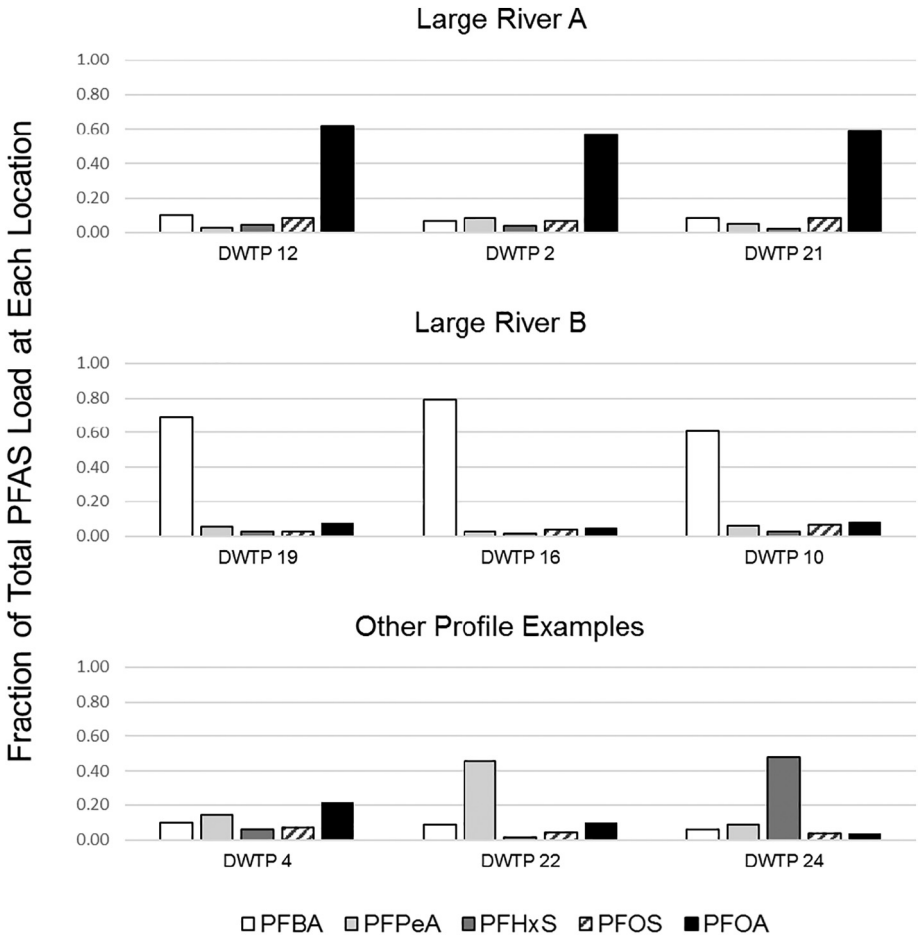
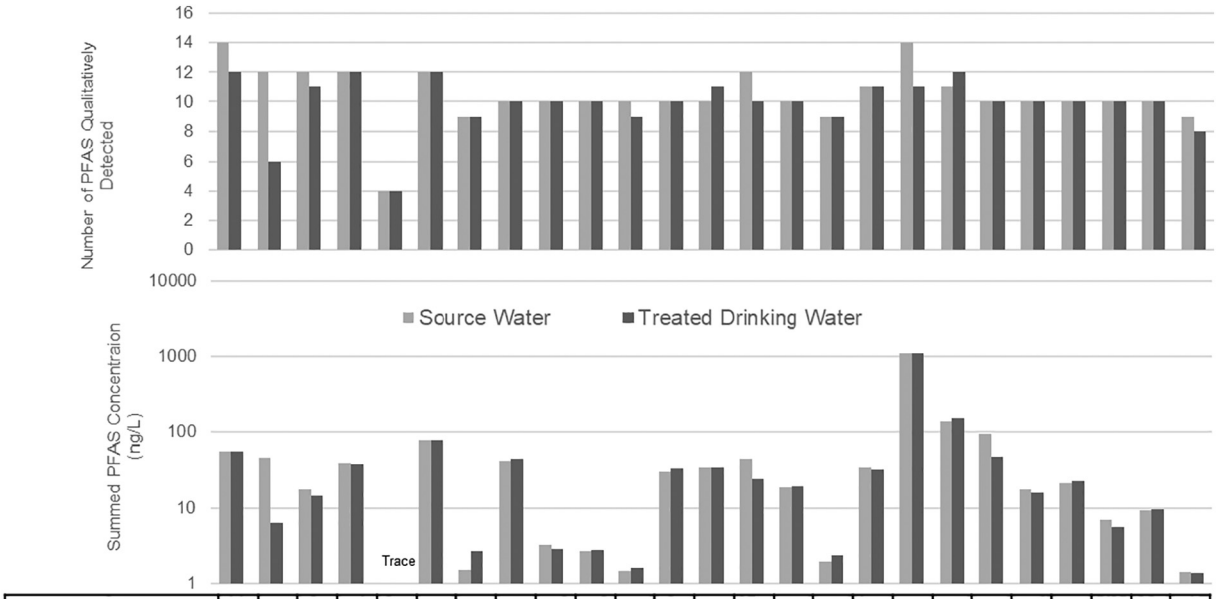


Fig. 2. PFAS analyte patterns along two rivers. Locations for Large Rivers A and B are ordered by river flow progressing left to right. Other Profile Examples are not related to each other.

but DWTP 22 and 23 were greater than that threshold, with DWTP 22 having a maximum total PFAS concentration of 1095 ng/L in the source water and 1102 ng/L in the treated drinking water. The median total PFAS concentration was 21.4 ng/L in the source water and 19.5 ng/L in the treated drinking water. The Wilcoxon one-tailed paired sample test was performed to determine if the concentrations of PFAS in the source water were significantly different than the treated drinking water. At five utilities, DWTP 2, 3, 18, 25, and 27, the concentrations were significantly different ($P < 0.05$) between the source and treated drinking water (Fig. 3, bottom panel). The reductions of the longer chain PFAS was generally greater than that of the shorter chained compounds (Supplemental information Tables 3 and 4). When looking across all of the DWTPs, the Wilcoxon one-tailed paired sample test for all C_4-C_6 PFAS measured in this study showed no significant difference between the source and treated ($P = 0.767$), while the longer chained (C_7 and longer) PFAS showed significance ($P = 0.000$). This was expected from the literature and adsorption theory. Experimental data has demonstrated faster breakthrough of the shorter chained PFAS compounds (Applebaum et al., 2013), as well as some of the components in aqueous film-forming foam (Xiao et al., 2017) relative to the longer chain. A summary of studies examining PFAS removal during drinking water treatment (Rahman et al., 2014) also showed limited effectiveness of treatment. Granular activated carbon (GAC) is one of the few treatment processes that has demonstrated significant PFAS removal from water. This removal comes at a high but reasonable cost (Hoslett et al., 2018). Among the plants where statistically significant reductions in PFAS were observed, the two DWTPs with the largest reductions from source to treated water, DWTP 2 and 18, were also those that recharged their (GAC) treatment beds most frequently (Fig. 3, bottom panel). GAC has also shown not to unduly influence water quality in a way that would lead to a utility to adjust other aspects of their operations such as corrosion control (Kucharzyk et al., 2017). Since GAC is a non-steady state treatment technology, reporting a percentage removal as an instantaneous measurement is not valid over a long period of time. If designed appropriately, the GAC will completely remove a contaminant until the contaminant breaks through the bed at a specific time that is a function of type of GAC, properties of the contaminant, flow rate, bed size and dimensions, temperature, pH, and competition for adsorption sites from other contaminants and background organic matter (Rahman et al., 2014). This breakthrough can be a steep or relatively flat profile over time, ultimately reaching the influent concentration. This removal is improved with increased contact time (Pramanik et al., 2015), but decreases with the number of bed volumes treated (McNamara et al., 2018). Some of the utilities that did not show significant removal may use GAC as a biological filter to control taste and odor episodes or to remove biologically degradable constituents such as a certain percentage of their disinfection byproduct precursors (Korotta-Gamage and Sathasivan, 2017; Zhang et al., 2017). This work is consistent with others that show to increase PFAS removal, an active approach to replacing or reactivating GAC on a frequent basis that is much shorter than that seen for utilities using GAC to control taste and odor episodes or biologically degradable constituents is required. Any design implemented for PFAS control should include breakthrough monitoring to maintain performance.

Several of the utilities (see DWTP 11, 12, 16, 23, 26, 28 as examples) showed slight increases in concentration in the treated drinking water relative to the source water. Recent studies (Xiao et al., 2018) have demonstrated the possibility of PFOS and PFOA generation from precursor



	DWTP 1	DWTP 2	DWTP 3	DWTP 4	DWTP 5	DWTP 10	DWTP 11	DWTP 12	DWTP 13	DWTP 14	DWTP 15	DWTP 16	DWTP 17	DWTP 18	DWTP 19	DWTP 20	DWTP 21	DWTP 22	DWTP 23	DWTP 24	DWTP 25	DWTP 26	DWTP 27	DWTP 28	DWTP 29
Wilcoxon *P*	0.29	**0.00**	**0.02**	0.23	-	0.06	0.53	0.94	0.91	0.73	0.47	0.99	0.47	**0.00**	0.50	0.85	0.65	0.37	0.76	0.32	**0.04**	1.00	**0.04**	0.88	0.29
Granular Activated Carbon Bed Depth (feet)	-	11.4	2.5	-	-	-	6	1.25	-	0.75	-	2.5	-	4	-	5	-	4	-	1.7	3	-	-	-	-
Estimated Bed Contact Time (EBCT; minutes)	-	15	9.4	-	-	-	10.3	-	-	-	-	12	-	-	-	7.5	-	-	-	-	-	-	-	-	-
Granular Activated Carbon Recharge Rate (years)	-	0.66	3	-	-	-	4	-	-	8	-	3	-	2	-	>4	-	-	-	3	5-10	-	-	-	-

Fig. 3. Frequency of detection and summed concentration of PFAS at participating DWTPs. Numbers in bold are statistically significant.

compounds during drinking water treatment. While the sampling design of this project (Phase II) is unable to determine if the relatively elevated treated water concentrations were due to generation or due to poor residence time match of the sampling, the possibility of generation should be incorporated into future project designs.

3.4. Health significance of PFAS occurrence

The USEPA has developed lifetime drinking water health advisories for PFOS (USEPA, 2016b) and PFOA (USEPA, 2016c) of 70 ng/L for each and 70 ng/L for the sum of the concentrations of PFOS and PFOA when both occur in the same drinking water supply. Both chemicals cause developmental toxicity in pups (mice for PFOA, rats for PFOS) following gestational and lactational exposure. As described in Section 6.2 of both health advisories (USEPA, 2016b, 2016c), this leads to the use of the exposure factor for lactating women when calculating the final health advisory values. Thorough supporting documents detailing the data behind the advisories are also available (USEPA, 2016d; USEPA, 2016e).

Because the reference doses (RfDs) for both PFOA and PFOS are based on similar developmental effects and are numerically identical, where these two chemicals co-occur at the same time and location in drinking water, a conservative and health protective approach that EPA recommends would be to compare the sum of the concentrations ([PFOA] + [PFOS]) to the USEPA health advisory (70 ng/L). The data for each DWTP in this study are presented in Table 4. The PFOA concentration for DWTP 22, 104 ng/L, exceeded the PFOA health advisory. As a result, the summed concentrations of PFOA + PFOS also exceeded the health advisory. In no other case did the concentration of either PFOA, PFOS, or their sum exceed the health advisory. Fig. 4 depicts the summed PFOS and PFOA concentrations in both source and treated drinking water relative to the 70 ng/L drinking water health advisory. This figure also suggests that fresh GAC is able to remove PFOS and PFOA in DWTPs 2, 3, 18, and 25.

Table 4
Health significance of PFOS and PFOA. Values in bold exceed the health advisory of 70 ng/L.

Location	PFOS (ng/L)	PFOA (ng/L)	∑PFOS + PFOA (ng/L)
DWTP 1	5.82	8.33	14.2
DWTP 2	ND[a]	1.06	1.06
DWTP 3	1.21	2.74	3.95
DWTP 4	3.14	8.41	11.6
DWTP 5	ND	<LCMRL[b]	QL[c]
DWTP 10	4.59	5.67	10.3
DWTP 11	0.184	<LCMRL	0.184
DWTP 12	3.87	28.3	32.2
DWTP 13	0.451	0.910	1.36
DWTP 14	0.351	<LCMRL	0.351
DWTP 15	<LCMRL	<LCMRL	QL
DWTP 16	1.14	1.55	2.69
DWTP 17	1.88	6.11	7.99
DWTP 18	2.25	4.15	6.40
DWTP 19	0.433	1.55	1.98
DWTP 20	<LCMRL	<LCMRL	QL
DWTP 21	2.71	19.0	21.7
DWTP 22	36.9	**104**	**141**
DWTP 23	12.6	23.7	36.3
DWTP 24	4.45	3.10	7.55
DWTP 25	0.783	3.08	3.86
DWTP 26	1.35	5.22	6.57
DWTP 27	0.350	0.713	1.06
DWTP 28	0.811	1.80	2.61
DWTP 29	<LCMRL	<LCMRL	QL

[a] ND = not detected.
[b] <LCMRL - the concentration was less than the reporting limit, and is considered a qualitative detection.
[c] QL - all detections at a given location were qualitative.

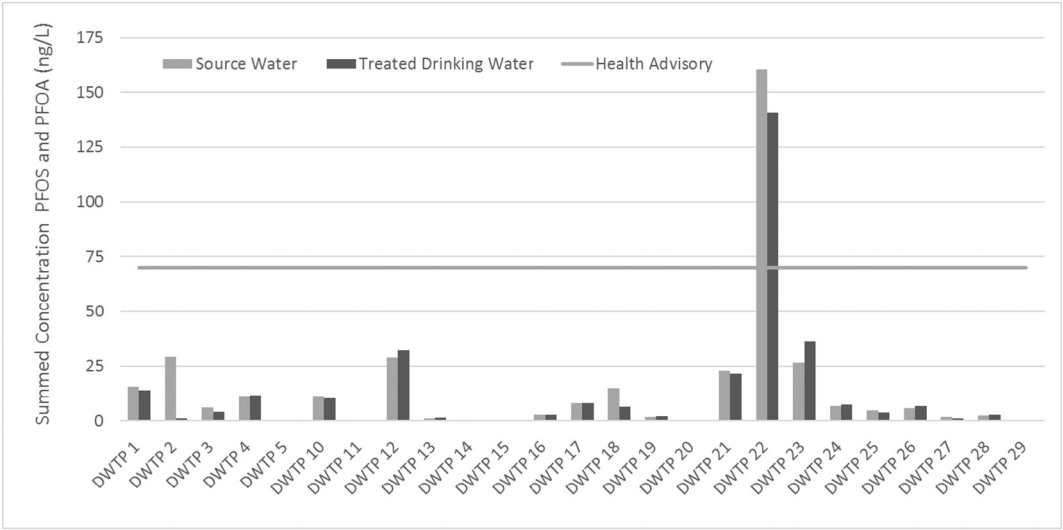


Fig. 4. Summed PFOS and PFOA concentrations.

USEPA drinking water guideline values are not currently available for the other PFAS evaluated in this study. Although states and other countries have developed guidance values for other PFAS, and some have adopted values lower than the USEPA's values for PFOA and PFOS (ITRC, 2017), we have chosen to only use the USEPA health advisory values in our work.

3.5. Comparison with the unregulated contaminant monitoring rule sampling

Six of the PFAS analytes (PFBS, PFHxS. PFHpA, PFOA, PFOS, and PFNA) were analytes in UCMR 3. For UCMR 3, USEPA Method 537 (Shoemaker et al., 2009) was used to analyze all collected samples. As part of the method validation process, this method and all USEPA drinking water methods use interlaboratory comparison testing to establish the minimum reporting level (MRL; USEPA, 2012). This is done so that the UCMR produces a quantitative dataset that is comparable across laboratories. For these six PFAS, the MRLs used in UCMR 3 range from 10 to 90 ng/L (Table 5; USEPA, 2012), whereas the single laboratory LCMRL used in Phase II range from 0.032 to 0.56 ng/L Because of the lower LCMRLs, the frequencies of detection for the six PFAS were higher in this study (Phase II) than in UCMR 3. The quantitative frequency of detection ranged from 76 to 96% in this study (Supplementary information Table 4), compared to 0.16 to 2.38% of sampled public water systems in UCMR 3 (USEPA, 2017). Interestingly, the most commonly detected PFAS in UCMR 3, PFOA, was the least quantitatively detected of the six in Phase II, while the least frequently detected UCMR 3 PFAS, PFBS, was the most frequently detected in Phase II.

Since DWTP 22 had results above the drinking water health advisory level, the UCMR data for that utility and for 23 of the other participating DWTPs in this drinking water study (Phase II) were extracted from the UCMR 3 database (USEPA, 2017; Supplementary information Table 8) to determine if these relatively high concentrations persisted over time. As presented in Table 5, 127 of the 144 Phase II detections reported here were below the UCMR 3 MRLs. In ten instances, the data for both Phase II and UCMR 3 were below the reporting limits. For two measurement pairs (PFOA in DWTP 12 and PFHpA in DWTP 22), both Phase II and the UCMR 3 registered quantifiable detections; the relative percent difference between measurements were 59% and 164%, respectively. For five of the measurement pairs (PFNA and PFOA in DWTP 22, PFHpA, and PFOA in DWTP 23, and PFHxS in DWTP 24), Phase II measurements were above the UCMR 3 MRL, but the UCMR 3 measurements were below the MRL. The Phase II samples were collected between 2010 and 2012, while the UCMR sampling was conducted between 2013 and 2015. It is unknown if variations in concentrations and flow conditions over time or changes in sources or changes in treatment could be the reason that locations with measured PFAS in Phase II did not have reportable concentrations in UCMR 3. As seen in other studies (Boone et al., 2014), river flow conditions may play a role in the concentrations of detected PFAS; a 5- to 7-fold difference was seen for PFBA and PFBS when river stage differed between 2.95 ft and 8.23 ft. It is important to monitor the concentrations of compounds at differing river flow conditions as effects such as dilution by precipitation and inundation of local sources can affect source contributions and will likely play a role in the observed concentrations of PFAS in surface water. Recording information about river flow at time of sampling also is necessary when comparing data from the same site across time.

Table 5
Comparison between different sampling events.

Analyte	Phase II LCMRL (this study) (ng/L)	UCMR 3 MRL (ng/L)	Number above LCMRL or MRL in both Phase II and UCMR 3	Number of Phase II measurements above UCMR 3 MRL but reported as non-detects in UCMR 3	Number of Phase II measurements below UCMR 3 MRL	Not detected in both Phase II and UCMR 3
PFBS	0.032	90	0	0	24	0
PFHpA	0.04	10	1	1	20	2
PFHxS	0.034	30	0	1	19	4
PFNA	0.094	20	0	1	21	2
PFOA	0.56	20	1	2	21	0
PFOS	0.13	40	0	0	22	2
Totals			2	5	127	10

4. Conclusions

PFAS compounds have become ubiquitous in the environment. While source determination was beyond the scope, in this study, PFAS compounds were qualitatively detected in the source and treated drinking water of every sampled location, and overall compositions and concentrations were similar between source and treated water at a given location. While detection frequencies were high, greater than that found in UCMR 3, individual PFAS concentration were low, with one DWTP exceeding the current USEPA drinking water health advisory. The relative composition of the PFAS compounds was consistent between samples co-collected from the same river system, further highlighting PFAS persistence. GAC may have helped remove some long-chain PFAS, but the removal efficiency was correlated to the operational run time of the GAC, with the highest removal at locations that frequently replaced their GAC with virgin or reactivated GAC. Using methods capable of reporting PFAS concentrations with LCMRLs at or below 1 ng/L provides insight into the low ambient PFAS concentrations that appear to be ubiquitously present in source waters that are known or suspected to be affected by wastewater and that persist through treatment to finished drinking water. Further research is required to better assess the importance of exposure to the wider array of PFAS homologues typically present in water supplies than has been previously identified by routine monitoring studies with higher detection limits such as UCMR 3. This data should be re-evaluated as health reference guidelines for additional PFAS analytes (both individual compounds and mixtures) are determined.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2018.10.245.

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