Legacy and emerging perfluoroalkyl substances in the Cape Fear River Watershed of North Carolina: Occurrence and fate during conventional and advanced water treatment processes

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Supporting information includes analytical method description, 6 tables, and 5 figures.

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Analytical standards: PFASs studied in this research are listed in Table S1. For legacy PFASs, native and isotopically labeled standards were purchased from Wellington Laboratories (Guelph, Ontario, Canada). Native PFPrOPrA was purchased from Thermo Fisher Scientific (Waltham, MA). No analytical standards were available for other PFECAs.

PFAS quantification: PFAS concentrations in samples from DWTPs and adsorption tests were determined by liquid chromatography tandem mass spectrometry (LC-MS/MS) using a large-volume (0.9 mL) direct injection method. An Agilent 1100 Series LC pump and PE Sciex API 3000 LC-MS/MS system equipped with a 4.6 mm x 50 mm HPLC column (Kinetex C18 5μm 100Å, Phenomenex Inc.) was used for PFAS analysis. The eluent gradient is shown in Table S4 in SI. All samples, calibration standards, and quality control samples were spiked with isotopically labeled internal standards, filtered through 0.45-μm glass microfiber syringe filters, and analyzed in duplicate. The MS transitions for PFAS analytes and internal standards are shown in Table S5 in SI. The quantitation limit (QL) was 25 ng/L for PFOS and perfluorodecanoic acid, and 10 ng/L for other legacy PFASs and PFPrOPrA. For PFECAs without analytical standards, chromatographic peak areas are reported.

PFAS concentrations along the treatment train of DWTP C were analyzed using a Waters Acquity ultra performance liquid chromatograph interfaced with a Waters Quattro Premier XE triple quadrupole mass spectrometer (Waters, Milford, MA, USA) after solid phase extraction. Method details are described elsewhere.[1] The QL for all PFASs with analytical standards was 0.2 ng/L, and peak areas were recorded for PFECAs without standards.

Table S1. Perfluoroalkyl substances (PFASs) detected in the Cape Fear River (CFR) watershed

Compound	Molecular weight	Formula	CAS #	# of perfluorinated carbons	Chain length (including all C, O and S)
Perfluorocarboxylic acids (PFCAs)					
Perfluorobutanoic acid (PFBA)	214.0	$C_4HF_7O_2$	375-22-4	3	4
Perfluoropentanoic acid (PFPeA)	264.0	$C_5HF_9O_2$	2706-90-3	4	5
Perfluorohexanoic acid (PFHxA)	314.1	$C_6HF_{11}O_2$	307-24-4	5	6
Perfluoroheptanoic acid (PFHpA)	364.1	$C_7HF_{13}O_2$	375-85-9	6	7
Perfluorooctanoic acid (PFOA)	414.1	$C_8HF_{15}O_2$	335-67-1	7	8
Perfluorononanoic acid (PFNA)	464.1	$C_9HF_{17}O_2$	375-95-1	8	9
Perfluorodecanoic acid (PFDA)	514.1	$C_{10}HF_{19}O_2$	335-76-2	9	10
Perfluorosulfonic acids (PFSAs)					
Perfluorobutane sulfonic acid (PFBS)	300.1	$C_4HF_9SO_3$	29420-49-3	4	5
Perfluorohexane sulfonic acid (PFHxS)	438.2	$C_6HF_{13}SO_3$	355-46-4	6	7
Perfluorooctane sulfonic acid (PFOS)	500.1	$C_8HF_{17}SO_3$	111873-33-7	8	9
Perfluoroalkyl ether carboxylic acids with one ether group (mono-ether PFECAs)					
Perfluoro-2-methoxyacetic acid (PFMOAA)	180.0	$C_3HF_5O_3$	674-13-5	2	4
Perfluoro-3-methoxypropanoic acid (PFMOPrA)	230.0	$C_4HF_7O_3$	377-73-1	3	5
Perfluoro-4-methoxybutanoic acid (PFMOBA)	280.0	$C_5HF_9O_3$	863090-89-5	4	6
Perfluoro-2-propoxypropanoic acid (PFPrOPrA)	330.1	$C_6HF_{11}O_3$	13252-13-6	5	7
Perfluoroalkyl ether carboxylic acids with multiple ether group (multi-ether PFECAs)					
Perfluoro(3,5-dioxahexanoic) acid (PFO2HxA)	246.0	$C_4HF_7O_4$	39492-88-1	3	6
Perfluoro(3,5,7-trioxaoctanoic) acid (PFO3OA)	312.0	$C_5HF_9O_5$	39492-89-2	4	8
Perfluoro(3,5,7,9-tetraoxadecanoic) acid (PFO4DA)	378.1	$C_6HF_{11}O_6$	39492-90-5	5	10

Table S2. Operational conditions of DWTP C on sampling day (August 18, 2014)

Parameter	Value
Raw water ozone dose	3.1 mg/L
Raw water total organic carbon concentration	6.0 mg/L
Aluminum sulfate coagulant dose	43 mg/L
Coagulation pH	5.70
Settled water ozone dose	1.3 mg/L
Settled water total organic carbon concentration	1.90 mg/L
Empty bed contact time in biological activated carbon filters	9.4 minutes for granular activated carbon layer 2.3 minutes for sand layer
Medium pressure UV dose	25 mJ/cm^2
Free chlorine dose	1.26 mg/L as Cl_2
Free chlorine contact time	17.2 hours

Table S3. Water quality characteristics of surface water used in adsorption tests

Non-purgeable organic carbon (mg/L)	Ultraviolet absorbance at a wavelength of 254 nm	pH	Alkalinity (mg/L as $CaCO_3$)	Conductivity (µS/cm)
9.036	0.399	7.53	19	133.5

Table S4. LC gradient method for PFAS analysis

Time (min)	Mobile Phase A% (v/v)	Mobile Phase B%	Flow Rate (mL/min)
0 – 2	95	5	0.9
2 – 5	95	5	0.9
5 – 10	95 → 10	5 → 90	0.9
10 – 10.1	10	90	0.9
10.1 – 14	10 → 95	90 → 5	0.9

Mobile phase A: 2 mM ammonium acetate in ultrapure water with 5% methanol

Mobile phase B: 2 mM ammonium acetate in acetonitrile with 5% ultrapure water

Table S5. MS transitions for PFAS Analysis

	Compound	MS/MS Transition	Internal standard
Legacy PFASs	PFBA	212.8 → 168.8	13C4-PFBA
	PFPeA	262.9 → 218.8	13C2- PFHxA
	PFHxA	313.6 → 268.8	13C2- PFHxA
	PFHpA	362.9 → 318.8	13C4- PFOA
	PFOA	413.0 → 368.8	13C4- PFOA
	PFNA	463.0 → 418.8	13C4- PFOA
	PFDA	513.1 → 68.8	13C2-PFDA
	PFBS	299.1 → 98.8	18O2-PFHxS
	PFHxS	399.1 → 98.8	18O2-PFHxS
	PFOS	498.9 → 98.8	13C4-PFOS
PFECAs	PFMOAA	180.0 → 85.0	N/A
	PFMOPrA	229.1 → 184.9	N/A
	PFMOBA	279.0 → 234.8	N/A
	PFPrOPrA	329.0 → 284.7	13C2- PFHxA
	PFO2HxA	245.1 → 85.0	N/A
	PFO3OA	311. → 84.9	N/A
	PFO4DA	377.1 → 85.0	N/A
Internal standards	Perfluoro-n-[1,2,3,4-$^{13}C_4$]butanoic acid (13C4-PFBA)	217.0 → 172	Not applicable
	Perfluoro-n-[1,2-$^{13}C_2$]hexanoic acid (13C2-PFHxA)	315.1 → 269.8	
	Perfluoro-n-[1,2,3,4-$^{13}C_2$]octanoic acid (13C4-PFOA)	417.0 → 372.0	
	Perfluoro-n-[1,2-$^{13}C_2$]decanoic acid (13C2-PFDA)	515.1 → 469.8	
	Sodium perfluoro-1-hexane[$^{18}O_2$]sulfonate (18O2-PFHxS)	403.1 → 83.8	
	Sodium perfluoro-1-[1,2,3,4-$^{13}C_4$]octane sulfonate (13C4-PFOS)	502.9 → 79.9	

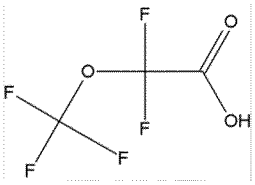
Table S6. Maximum, minimum, mean and median concentrations (ng/L) of PFASs in CFR watershed surface water as drinking water sources. *

	Community A				Community B				Community C			
	max	**min**	**median**	**mean**	**max**	**min**	**median**	**mean**	**max**	**min**	**median**	**mean**
PFBA	99	<10	26	33	38	<10	12	12	104	<10	12	22
PFPeA	191	14	44	62	38	<10	19	19	116	<10	30	36
PFHxA	318	<10	48	78	42	<10	<10	11	24	<10	<10	<10
PFHpA	324	<10	39	67	85	<10	<10	11	24	<10	<10	<10
PFOA	137	<10	34	46	32	<10	<10	<10	17	<10	<10	<10
PFNA	38	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
PFDA	35	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25
PFBS	80	<10	<10	<10	11	<10	<10	<10	<10	<10	<10	<10
PFHxS	193	<10	10	14	14	<10	<10	<10	14	<10	<10	<10
PFOS	346	<25	29	44	43	<25	<25	<25	40	<25	<25	<25
PFPrOPrA	<10	<10	<10	<10	10	<10	<10	<10	4560	55	304	631
PFOA+PFOS	447	0	64	90	59	0	0	9	55	<10	<10	<10
∑ PFASs**	1502	18	212	355	189	0	47	62	4696	55	345	710

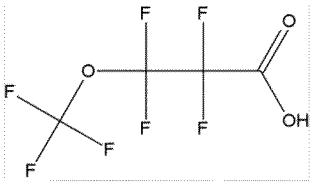
* Concentrations < quantification limits were considered as zero to calculate means and ∑ PFASs.

** Other PFECAs were present in water samples from community C but could not be quantified and were therefore not included in ∑ PFASs

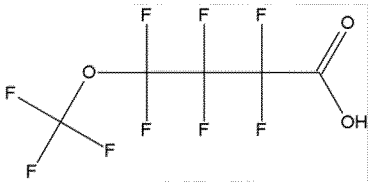
Figure S1. Molecular structures of PEFCAs in this study



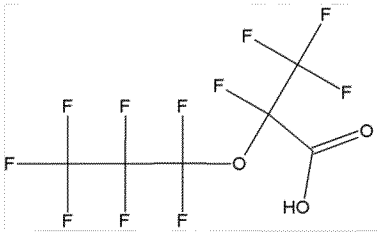
PFMOAA



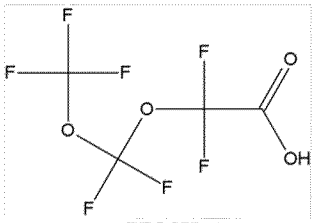
PFMOPrA



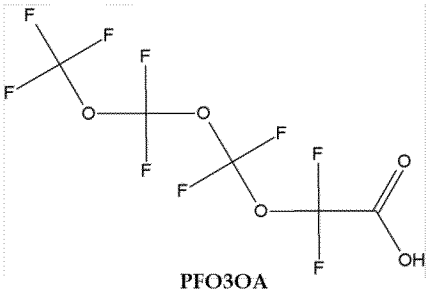
PFMOBA



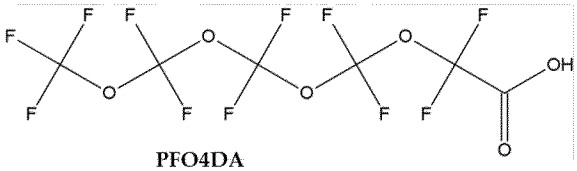
PFPrOPrA



PFO2HxA



PFO3OA



PFO4DA

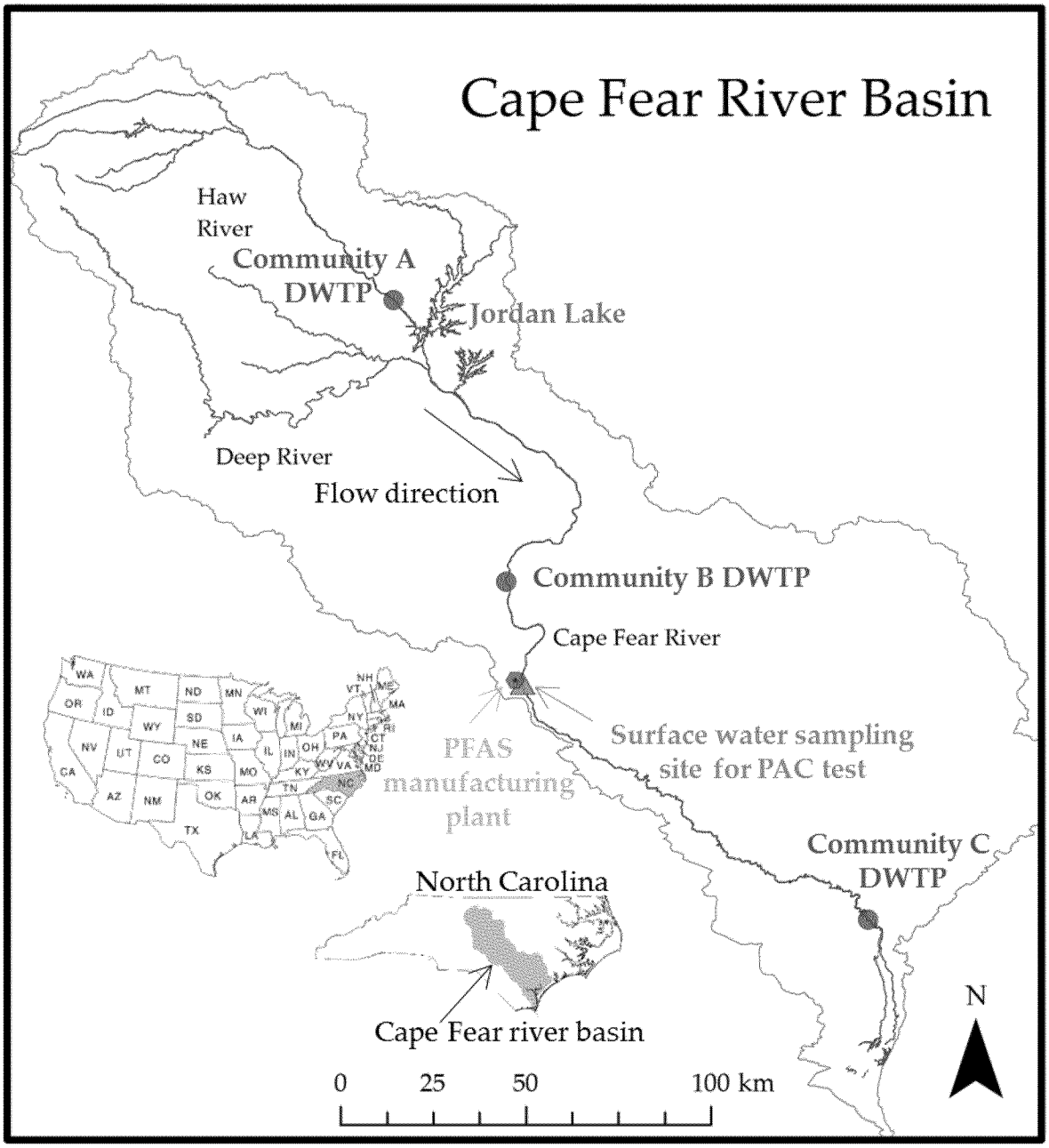
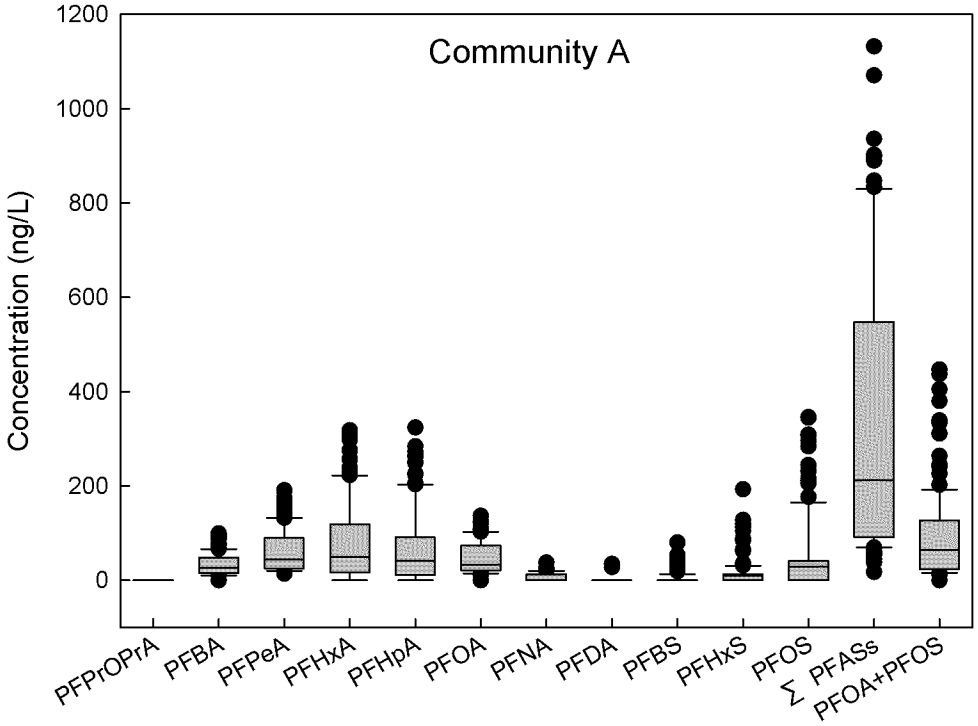
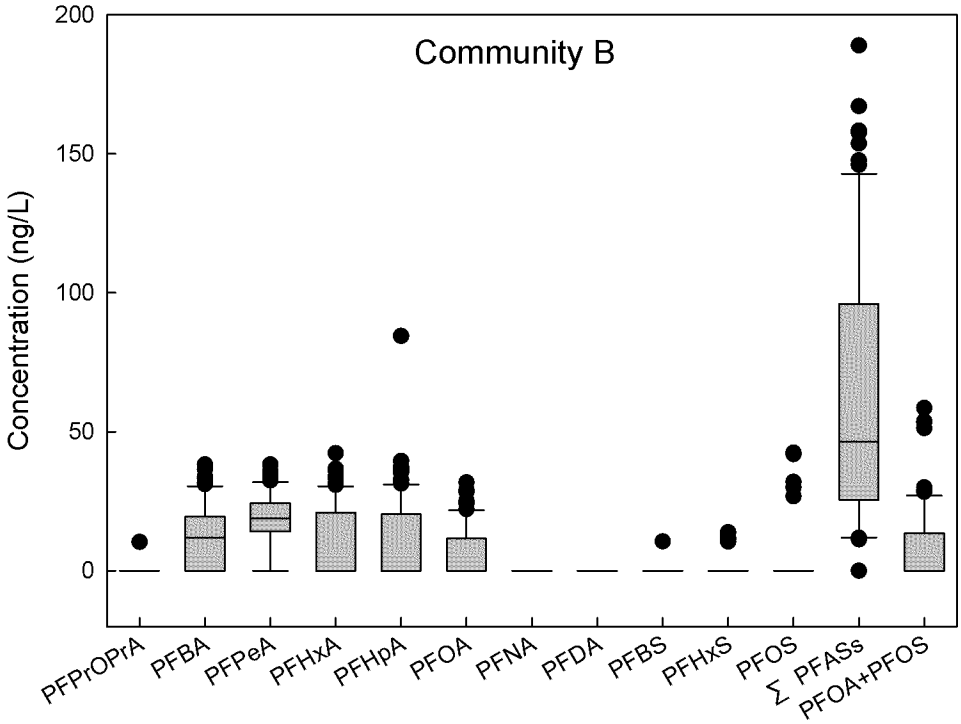


Figure S2. Sampling sites in the Cape Fear River watershed, North Carolina


Community A
Concentration (ng/L)
1200
1000
800
600
400
200
0
PFPrOPrA
PFBA
PFPeA
PFHxA
PFHpA
PFOA
PFNA
PFDA
PFBS
PFHxS
PFOS
∑ PFASs
PFOA+PFOS


Community B
Concentration (ng/L)
200
150
100
50
0
PFPrOPrA
PFBA
PFPeA
PFHxA
PFHpA
PFOA
PFNA
PFDA
PFBS
PFHxS
PFOS
∑ PFASs
PFOA+PFOS

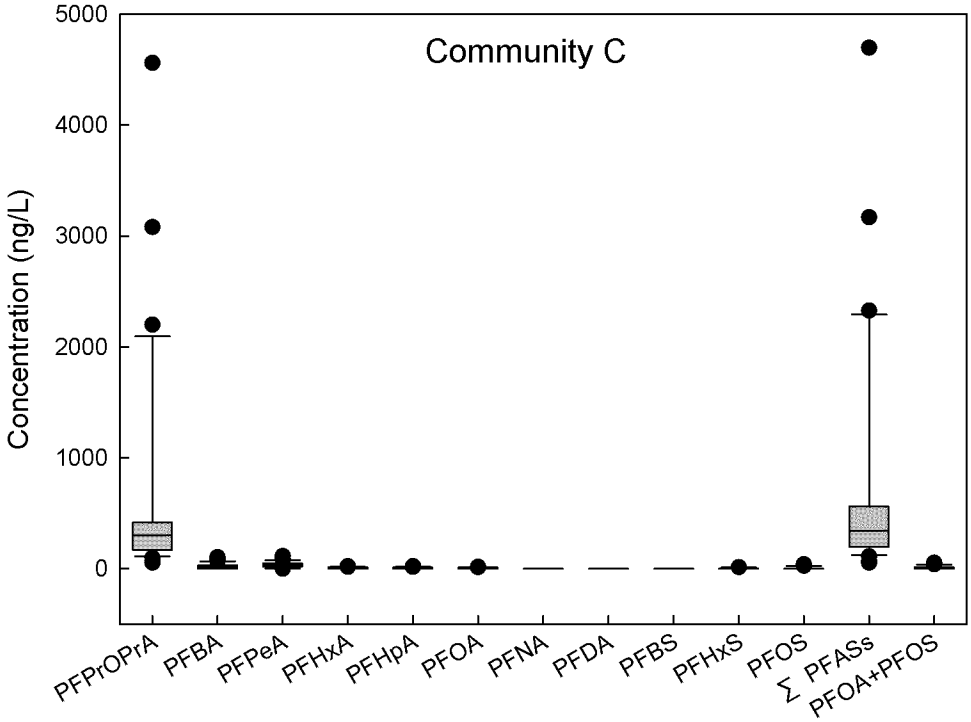


Figure S3. PFAS concentration distributions in the CFR watershed at three drinking water intakes. Concentrations < quantification limits were considered as zero. The upper and lower edges of a box represent the 75th and 25th percentile, respectively; the middle line represents the median; the upper and lower bars represent the 90th and 10th percentile, respectively; the dots represent outliners (>90th or <10th percentile).

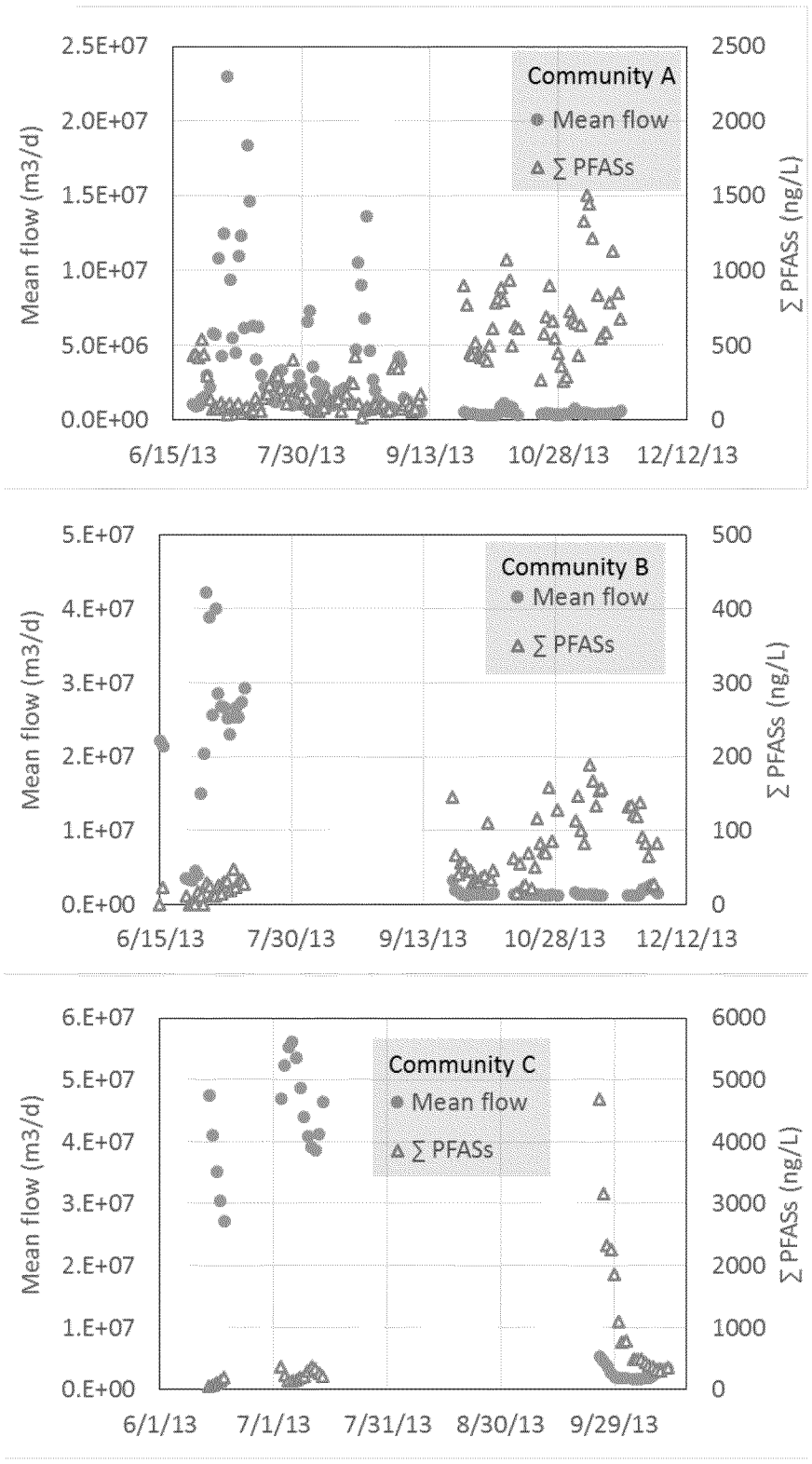


Figure S4. Total PFAS concentrations in the source water and stream flow at the three studied DWTPs. Stream flow data were acquired from US Geological Survey stream gage records

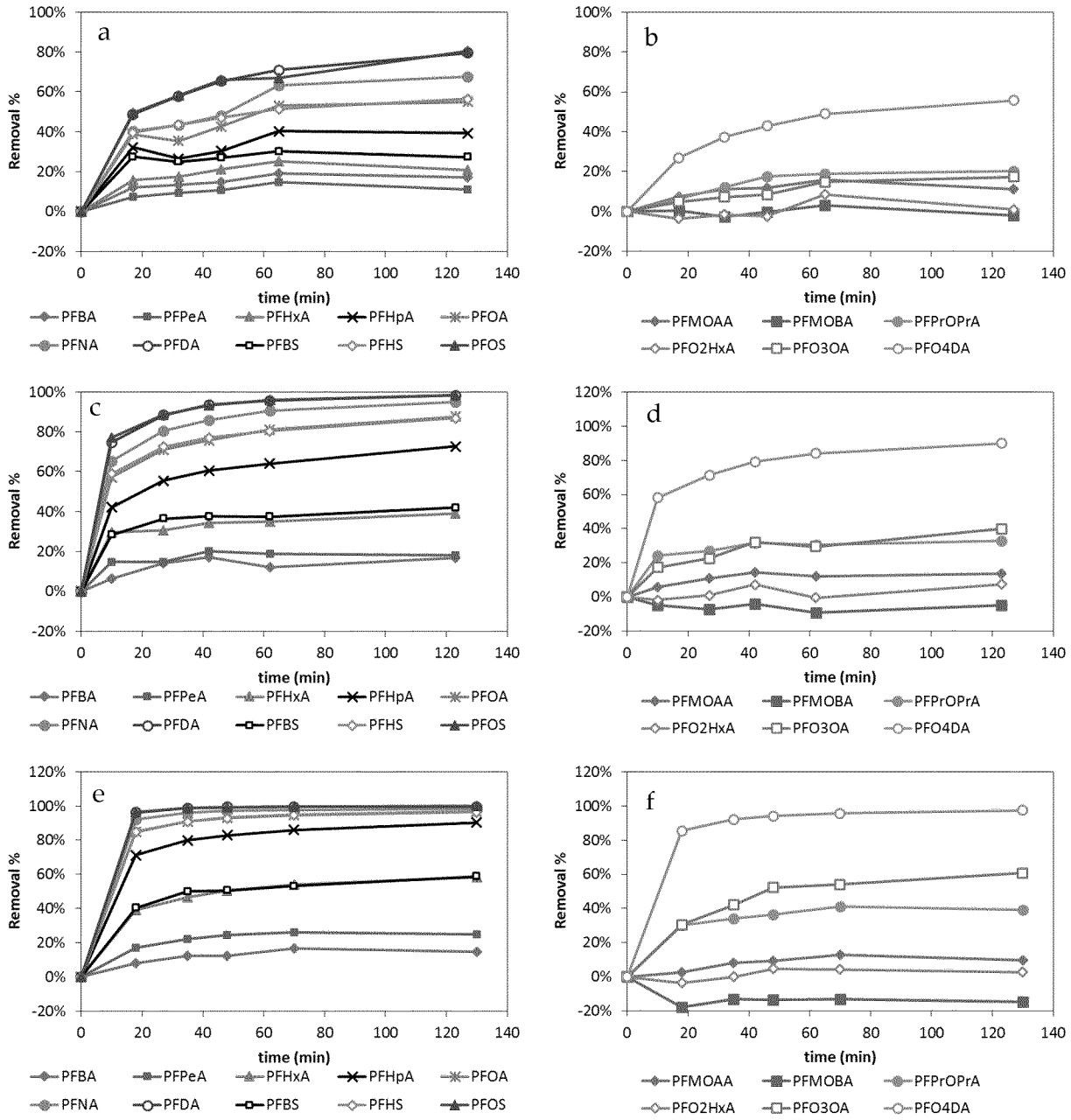


Figure S5. PFAS adsorption on PAC at carbon does of (a, b) 30 mg/L, (c, d) 60 mg/L and (e, f) 100 mg/L. Figures show average PFAS removal percentages of duplicate tests.

Reference

1. Nakayama, S.; Strynar, M. J.; Helfant, L.; Egeghy, P.; Ye, X.; Lindstrom, A. B., Perfluorinated compounds in the Cape Fear drainage basin in North Carolina. *Environmental Science & Technology* **2007,** *41*, (15), 5271-5276.