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

Supporting Information

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Supporting information includes 4 tables and 3 figures.

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)		$C_4HF_7O_2$	375-22-4	3	4
Perfluoropentanoic acid (PFPeA)		$C_5HF_9O_2$	2706-90-3	4	5
Perfluorohexanoic acid (PFHxA)		$C_6HF_{11}O_2$	307-24-4	5	6
Perfluoroheptanoic acid (PFHpA)		$C_7HF_{13}O_2$	375-85-9	6	7
Perfluorooctanoic acid (PFOA)		$C_8HF_{15}O_2$	335-67-1	7	8
Perfluorononanoic acid (PFNA)		$C_9HF_{17}O_2$	375-95-1	8	9
Perfluorodecanoic acid (PFDA)		$C_{10}HF_{19}O_2$	335-76-2	9	10
Perfluorosulfonic acids (PFSAs)					
Perfluorobutane sulfonic acid (PFBS)		$C_4HF_9SO_3$	29420-49-3	4	5
Perfluorohexane sulfonic acid (PFHxS)		$C_6HF_{13}SO_3$	355-46-4	6	7
Perfluorooctane sulfonic acid (PFOS)		$C_8HF_{17}SO_3$	111873-33-7	8	9
Perfluoroalkyl ether carboxylic acids with one ether group (mono-ether PFECAs)					
Perfluoro-2-methoxyacetic acid (PFMOAA)		$C_3HF_5O_3$	674-13-5	2	4
Perfluoro-3-methoxypropanoic acid (PFMOPrA)		$C_4HF_7O_3$	377-73-1	3	5
Perfluoro-4-methoxybutanoic acid (PFMOBA)		$C_5HF_9O_3$	863090-89-5	4	6
Perfluoro-2-propoxypropanoic acid (PFPrOPrA)		$C_6HF_{11}O_3$	13252-13-6	5	7
Perfluoroalkyl ether carboxylic acids with multiple ether group (multi-ether PFECAs)					
Perfluoro(3,5-dioxahexanoic) acid (PFO2HxA)		$C_4HF_7O_4$	39492-88-1	3	6
Perfluoro(3,5,7-trioxaoctanoic) acid (PFO3OA)		$C_5HF_9O_5$	39492-89-2	4	8
Perfluoro(3,5,7,9-tetraoxadecanoic) acid (PFO4DA)		$C_6HF_{11}O_6$	39492-90-5	5	10

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Figure S1. Molecular structures of PEFCAs in this study

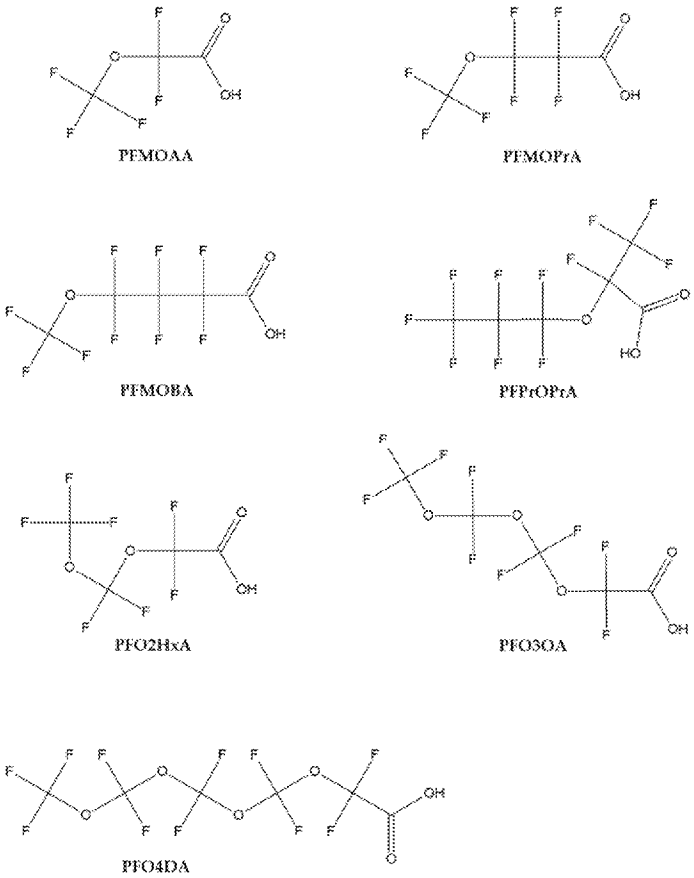

Table S2. LC gradient method for PFAS analysis

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 S3. LC Gradient Method for PFAS Analysis

	Compound	MS/MS Transition	Internal standard
Traditional 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 > 468.8	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	~~330.0 > 7~~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)	~~415.0 > 369.8~~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 S4. 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
∑ PFASs**	1502	18	212	355	189	0	47	62	4560	55	304	631

* 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

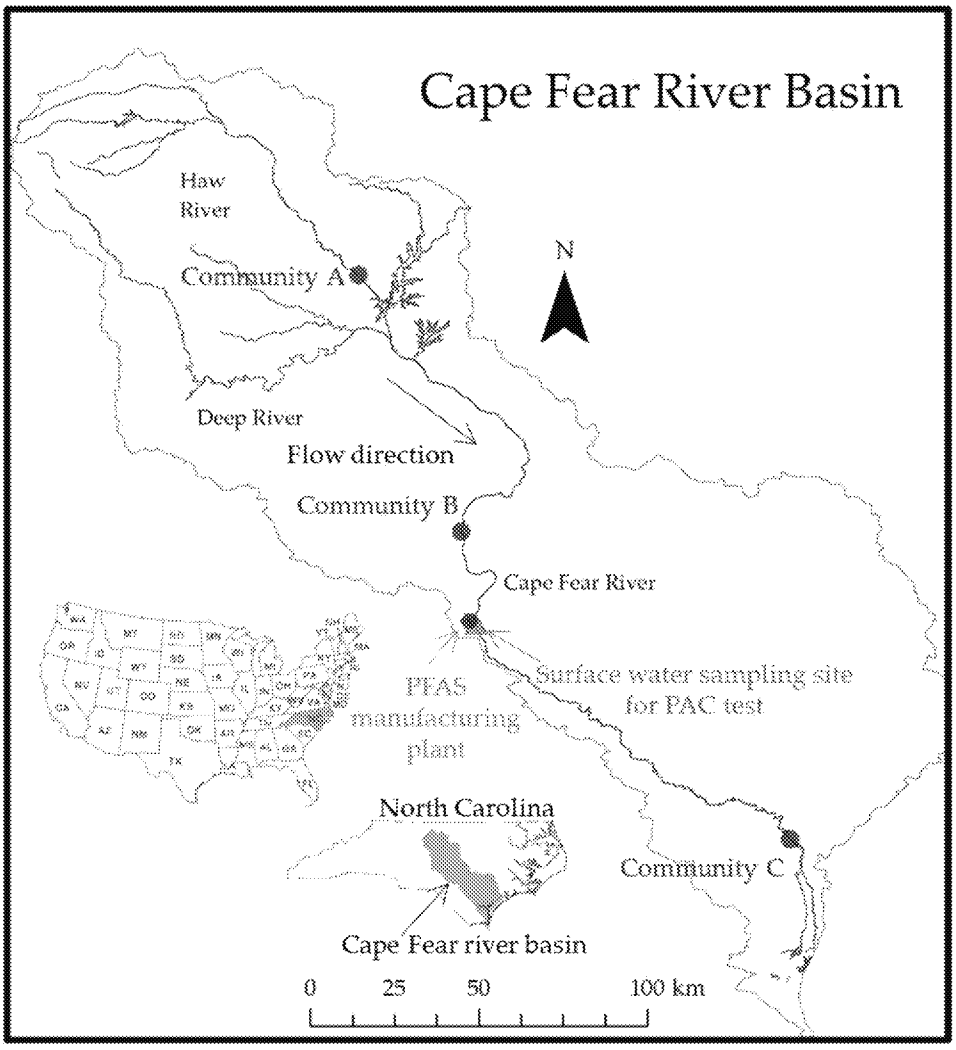

Figure S2. Sampling sites in Cape Fear River watershed, North Carolina

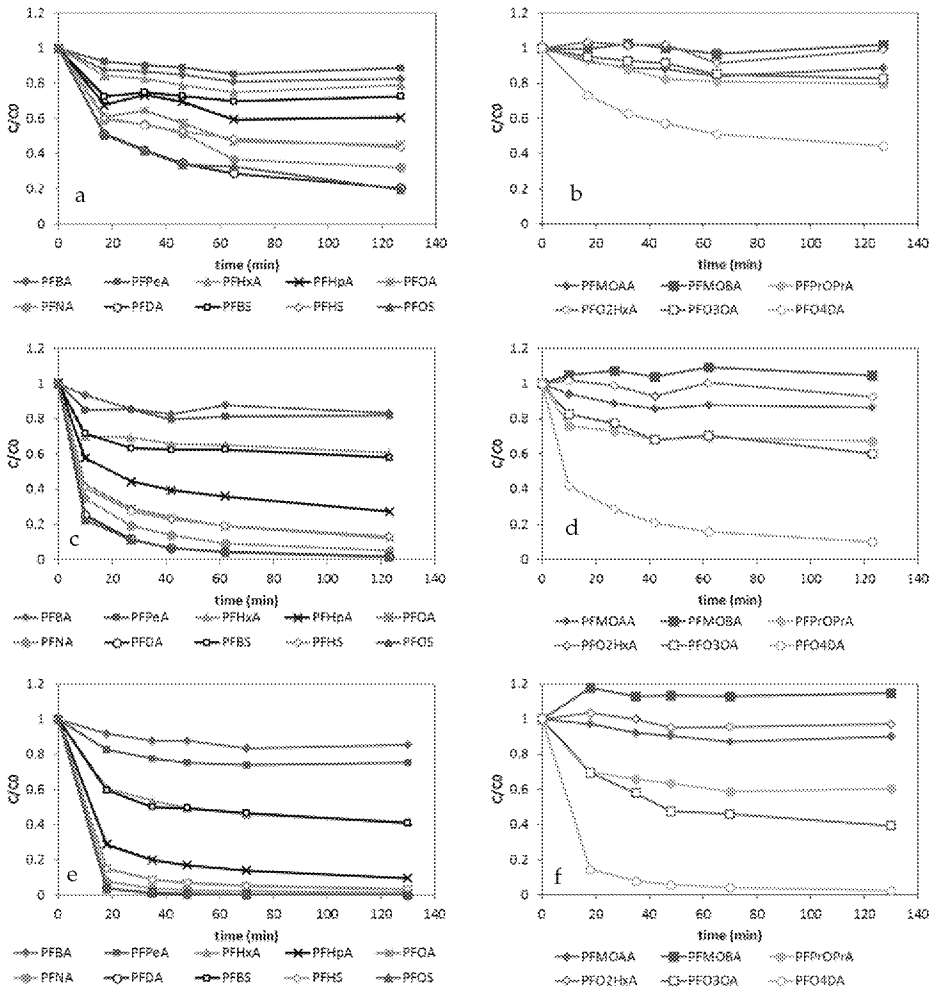

Figure S3. PFAS adsorption to PAC at carbon does of (a, b) 30 mg/L, (c, d) 60 mg/L and (e, f) 100 mg/L. The chart shows the average of remaining PFAS percentage of duplicate tests.