# Supporting information

# Legacy and Emerging Perfluoroalkyl Substances Are Important Drinking Water Contaminants in the Cape Fear River Watershed of North Carolina

**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. The QL was defined as the first point of the standard curve, for which the regression equation yielded a calculated value within ±30% error. 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.[ ADDIN EN.CITE <EndNote><Cite><Author>Nakayama</Author><Year>2007</Year><RecNum>24</RecNum><DisplayText><style face="superscript">1</style></DisplayText><record><rec-number>24</rec-number><foreign-keys><key app="EN" db-id="rx5ets9t3v5ta9e2vz0xv2a2erzffpfvrtea" timestamp="1469820266">24</key></foreign-keys><ref-type name="Journal Article">17</ref-type><contributors><authors><author>Nakayama, Shoji</author><author>Strynar, Mark J.</author><author>Helfant, Laurence</author><author>Egeghy, Peter</author><author>Ye, Xibiao</author><author>Lindstrom, Andrew



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B.</author></authors></contributors><titles><title>Perfluorinated compounds in the Cape Fear drainage basin in North Carolina</title><secondary-title>Environmental Science and Technology</secondary-title></titles><periodical><full-title>Environmental Science and Technology</full-title><abbr-1>Environ. Sci. Technol.</abbr-1><abbr-2>Environ Sci Technol</abbr-2></periodical><pages>5271-5276</pages><volume>41</volume><number>15</number><dates><year>2007</year><pub-dates><date>2007/08/01</date></pub-dates></dates><publisher>American Chemical Society</publisher><isbn>0013-936X</isbn><urls><related-urls><url>http://dx.doi.org/10.1021/es070792y</url></related-urls></urls><electronic-resource-num>10.1021/es070792y</electronic-resource-num></record></Cite></EndNote>] The QL for all PFASs with analytical standards was 0.2 ng/L, and peak areas were recorded for PFECAs without standards.



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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 | $C_4HF_9SO_3$ | 375-73-5 | 4 | 5 |
| Perfluorohexane sulfonic acid (PFHxS) | 400.1 | $C_6HF_{13}SO_3$ | 355-46-4 | 6 | 7 |
| Perfluorooctane sulfonic acid (PFOS) | 500.1 | $C_8HF_{17}SO_3$ | 1763-23-1 | 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 |



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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<br>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



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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 | |



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Table S6. Maximum, minimum, mean and median concentrations (ng/L) of PFASs at three drinking water intakes. *

| | 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 less than quantitation 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



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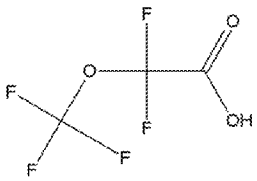
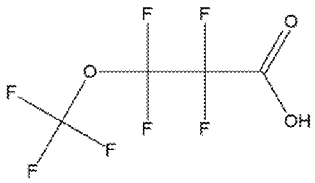


PFMOAA



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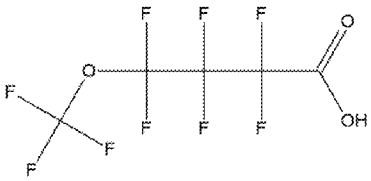
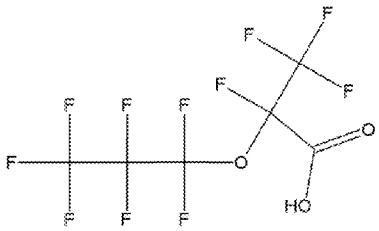
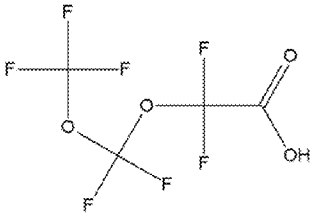


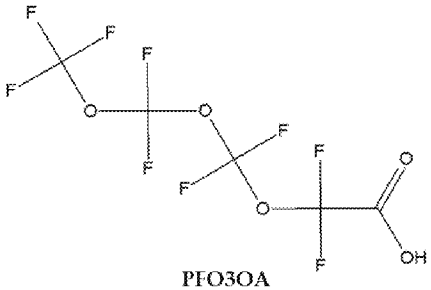
PFMOBA



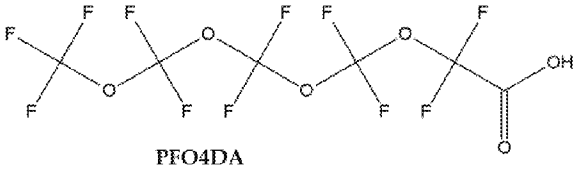
PFPrOPrA



PFO2HxA



PFO3OA



PFO4DA

Figure S1. Molecular structures of PFECAs evaluated in this study



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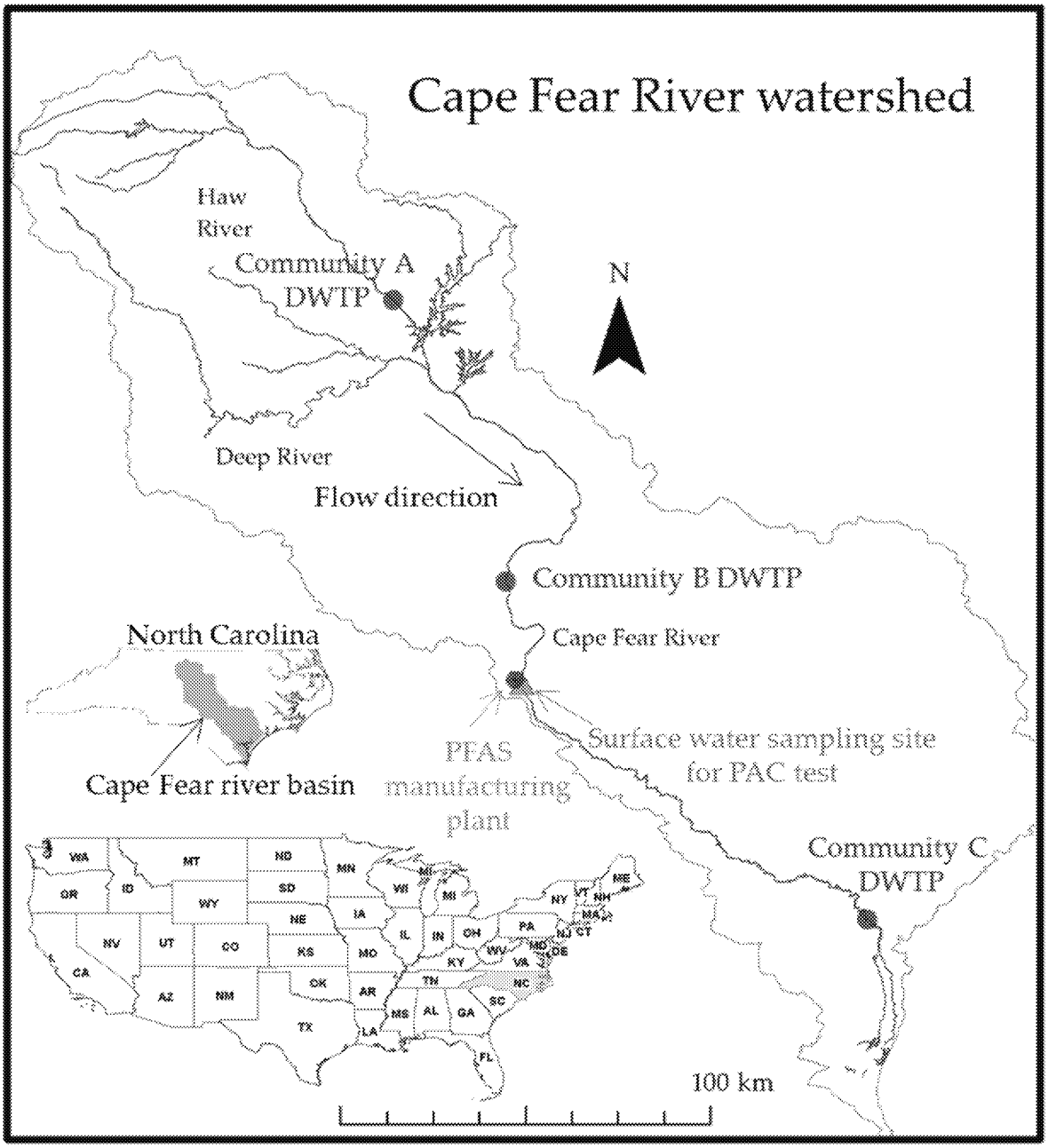
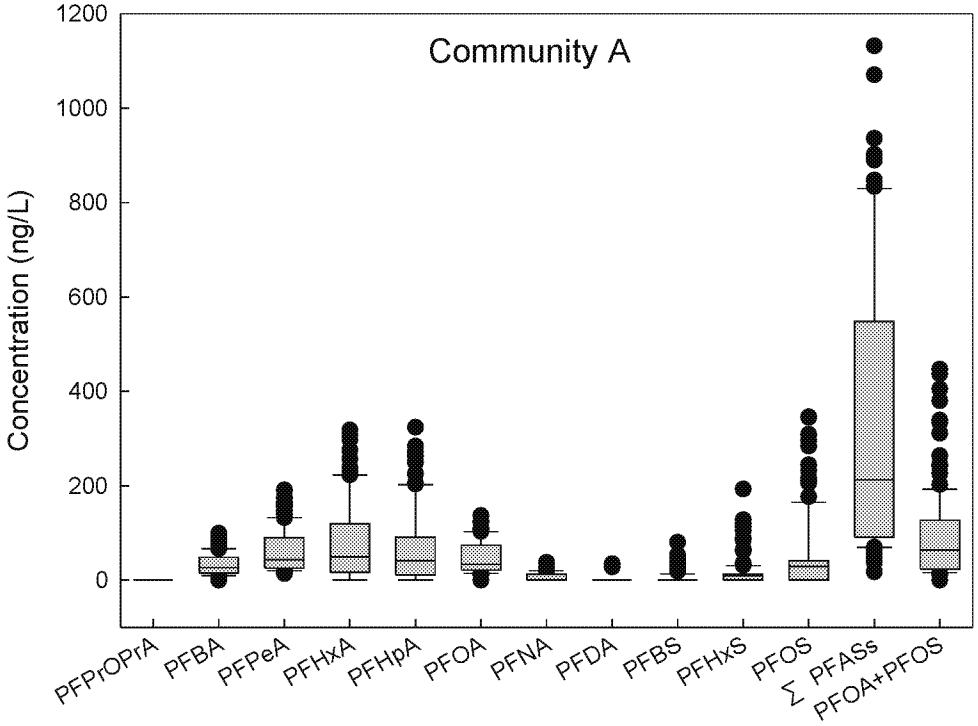
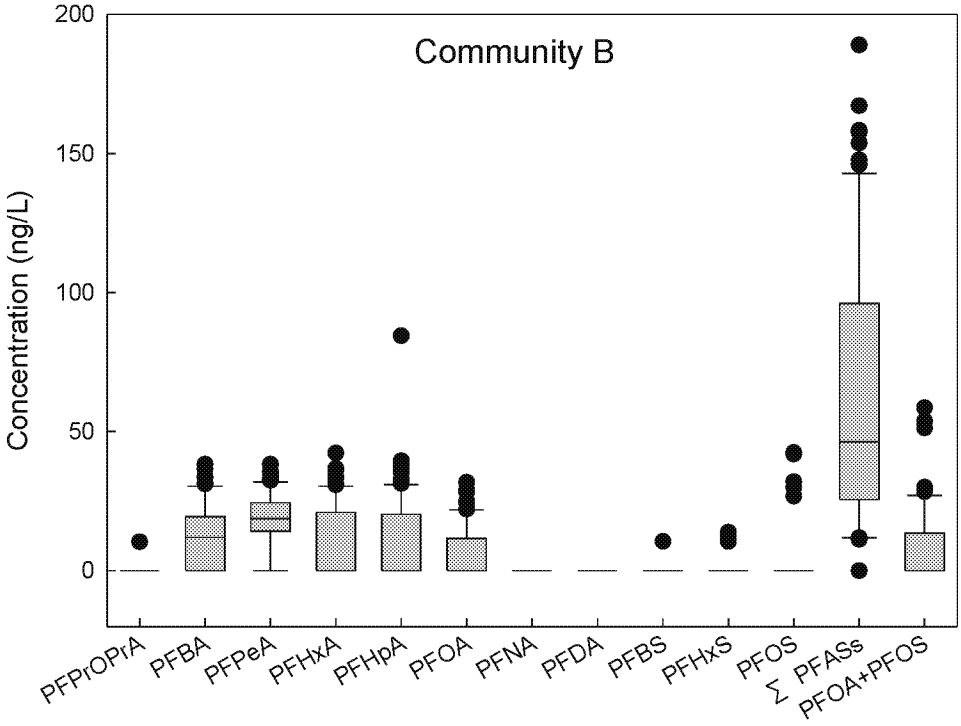



Figure S2. Sampling sites in the Cape Fear River watershed, North Carolina. The scale is for the Cape Fear River watershed map.


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

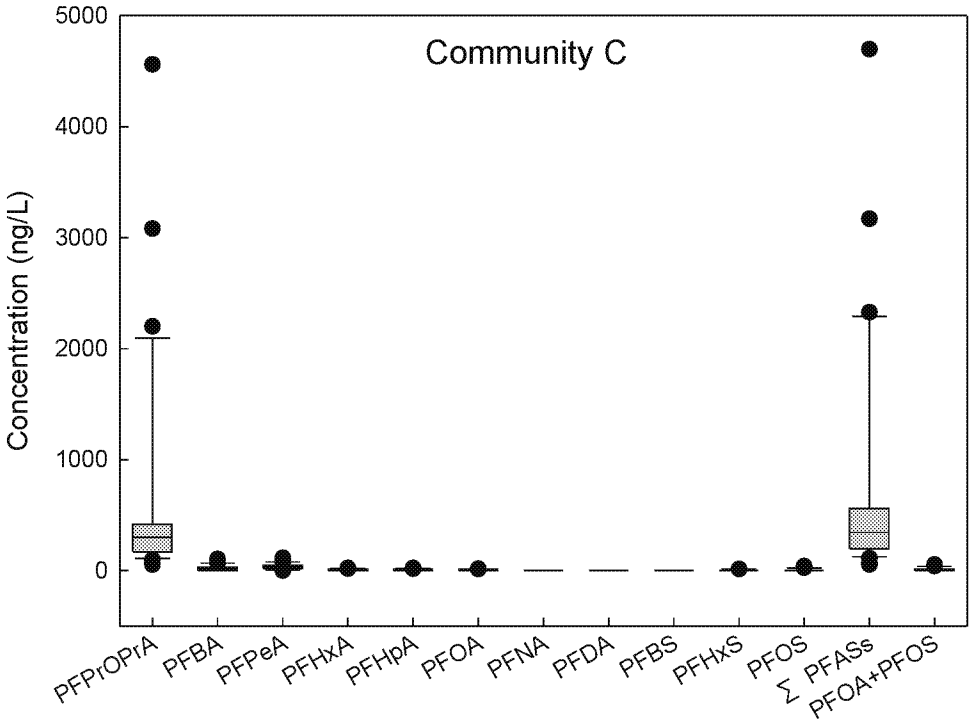



Figure S3. PFAS concentration distributions in the CFR watershed at three drinking water intakes. Concentrations less than quantitation limits were considered as zero. Upper and lower edges of a box represent the 75th and 25th percentile, respectively; the middle line represents the median; upper and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

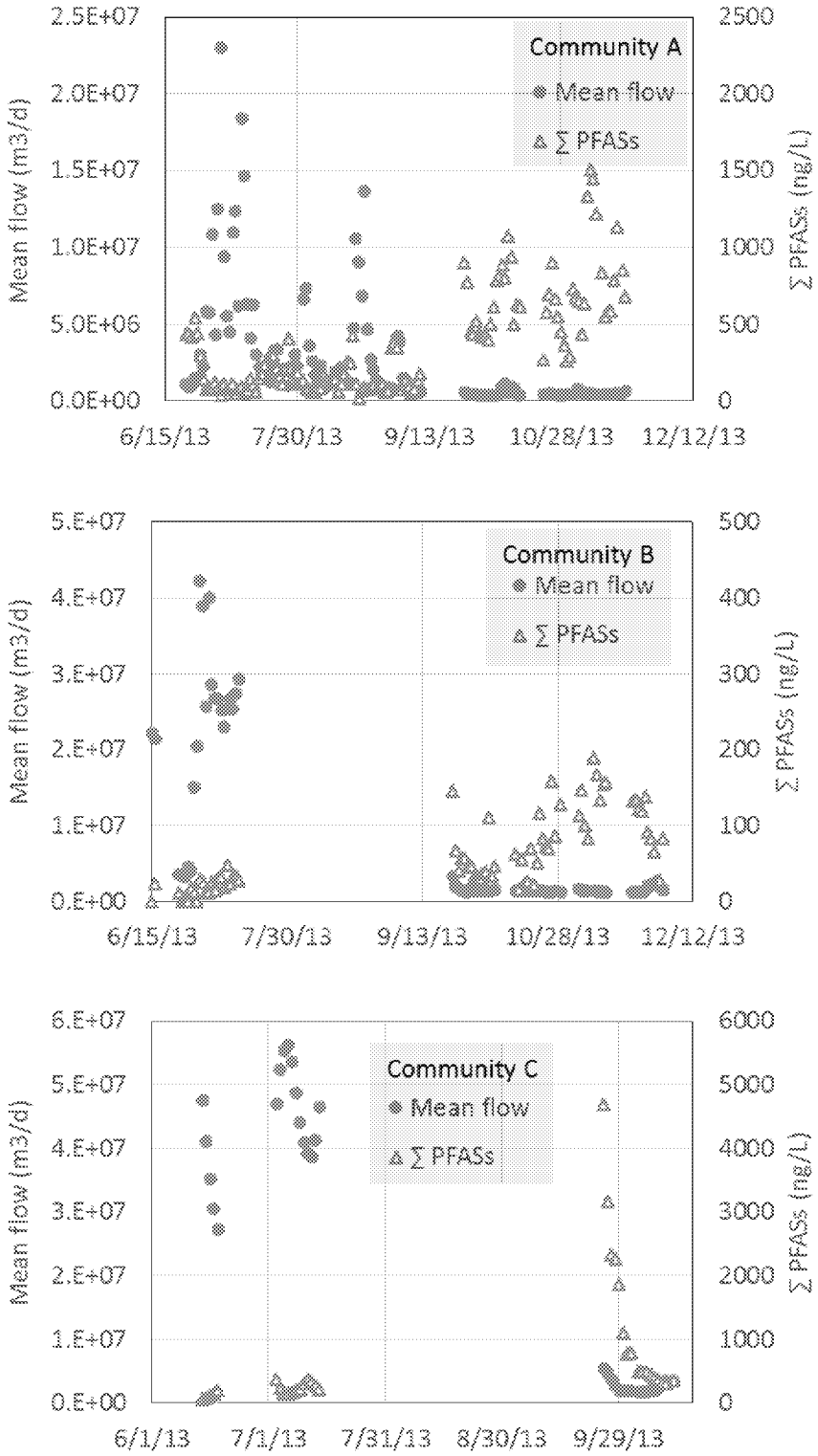



Figure S4. Total PFAS concentrations in the source water and stream flow at the three studied DWTPs. Stream flow data were acquired from US Geological Survey stream gage records

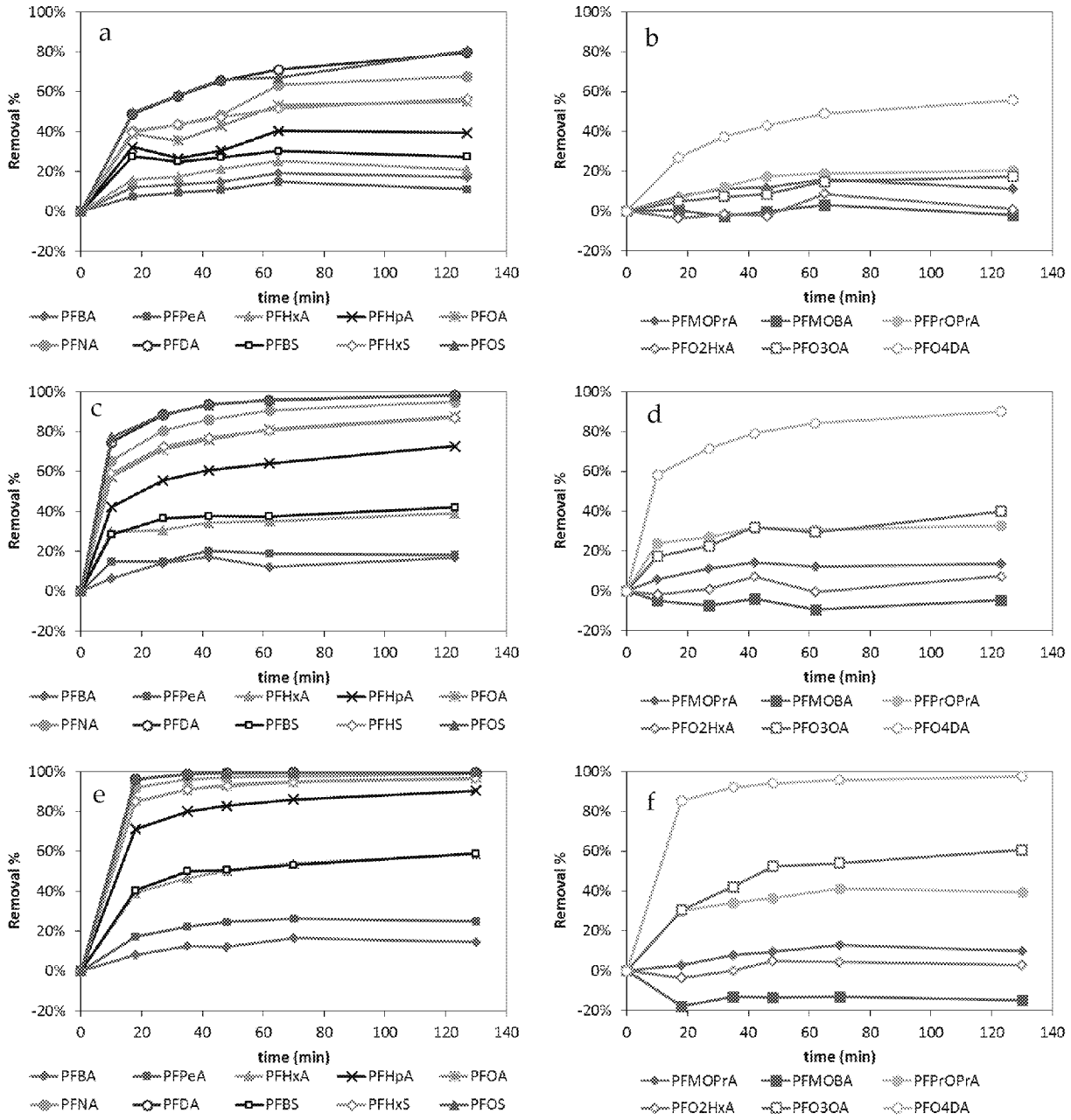



Figure S5. PFAS adsorption at powdered activated carbon doses of (a, b) 30 mg/L, (c, d) 60 mg/L and (e, f) 100 mg/L. Figures show average PFAS removal percentages of duplicate tests.

**Reference**

[ ADDIN EN.REFLIST ]