Relating total PFAS concentration to average daily streamflow (Figure S4) illustrated a general trend of low PFAS concentrations at high flow, and high concentrations at low flow, consistent with the hypothesis of one or more upstream point sources.

In community B, perfluorobutanoic acid (PFBA) and perfluoropentanoic acid (PFPeA) were most frequently detected with mean concentrations of 12 and 19 ng/L, respectively. Mean PFOA and PFOS concentrations were below the QLs, and the maximum sum concentration of PFOA and PFOS was 59 ng/L. Lower PFAS concentrations in community B relative to community A can be explained by the absence of substantive PFAS sources between the two communities, dilution by tributaries, and the buffering effect of Jordan Lake, a large reservoir located between communities A and B.

In community C (downstream of a PFAS manufacturing site), only mean concentrations of PFBA and PFPeA were above the QLs. The relatively low concentrations of legacy PFASs in the finished drinking water of community C are consistent with results from the USEPA's third unregulated contaminant monitoring rule for this DWTP.[32] However, high concentrations of PFPrOPrA were detected (up to ∼4500 ng/L). The average PFPrOPrA concentration (631 ng/L) was approximately 8 times the average summed PFCA and PFSA concentrations (79 ng/L). Other PFECAs had not yet been identified at the time of analysis. Similar to communities A and B, the highest PFAS concentrations for community C were also observed at low flow (Figure S4). Stream flow data were used in conjunction with PFPrOPrA concentration data to determine PFPrOPrA mass fluxes at the intake of DWTP C. Daily PFPrOPrA mass fluxes ranged from 0.6 to 24 kg/day with a mean of 5.9 kg/day.

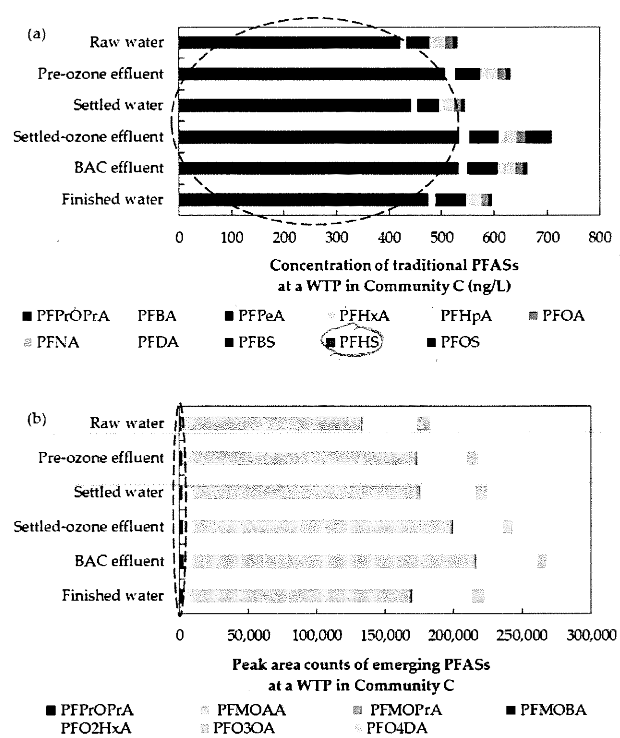


**Figure 2.** Fate of (a) legacy PFASs and PFPrOPrA and (b) PFECAs through a full-scale water treatment plant. Because authentic standards were not available for PFECAs other than PFPrOPrA, chromatographic peak area counts are shown in panel b. PFPrOPrA data are shown in both panels and highlighted with dashed ovals for reference. Compounds with concentrations below the QLs were not plotted.

**Fate of PFASs in Conventional and Advanced Water Treatment Processes.** To investigate whether PFASs can be removed from impacted source water, samples from DWTP C were collected at the intake and after each treatment step. Results in Figure 2 suggest conventional and advanced treatment processes (coagulation/flocculation/sedimentation, raw and settled water ozonation, BAC filtration, and disinfection by medium-pressure UV lamps and free chlorine) did not remove legacy PFASs, consistent with previous studies.[22−26] The data further illustrate that no measurable PFECA removal occurred in this DWTP. Concentrations of some PFCAs, PFSAs, PFMOPrA, PFPrOPrA, and PFMOAA may have increased after ozonation, possibly because of the oxidation of precursor compounds.[25] Disinfection with medium-pressure UV lamps and free chlorine (located between the BAC effluent and the finished water) may have decreased concentrations of PFMOAA, PFMOPrA, PFMOBA, and PFPrOPrA, but only to a limited extent. Small concentration changes between treatment processes may also be related to temporal changes in source water PFAS concentrations that occurred in the time frame corresponding to the hydraulic residence time of the DWTP.

Results in Figure 2 further illustrate that the PFAS signature of the August 2014 samples was similar to the mean PFAS signature observed during the 2013 sampling campaigns shown in Figure 1; i.e., PFPrOPrA concentrations (400−500 ng/L) greatly exceeded legacy PFAS concentrations. Moreover, three PFECAs (PFMOAA, PFO2HxA, and PFO3OA) exhibited peak areas 2−113 times greater than that of PFPrOPrA (Figure 2b). The existence of high levels of emerging PFASs suggests a need for their incorporation into routine monitoring.

**Adsorption of PFASs by PAC.** PAC can effectively remove long-chain PFCAs and PFSAs, but its effectiveness decreases with decreasing PFAS chain length.[24,25,29] It is unclear, however, how the presence of ether group(s) in PFECAs impacts adsorbability. After a contact time of 1 h, a PAC dose of 100 mg/L achieved >80% removal of legacy PFCAs with total carbon chain lengths of ≥7. At the same PAC dose, removals were 95% for PFO4DA and 54% for PFO3OA, but <40% for other PFECAs. Detailed removal percentage data as a function of PAC contact time are shown in Figure S5. There was no meaningful removal of PFMOBA or PFMOPrA, and the variability shown in Figure S5 is most likely associated with analytical variability. PFMOAA could not be quantified by the analytical method used for these experiments; however, on the basis of the observations that PFAS adsorption decreases with decreasing carbon chain length and that PFECAs with one or two more carbon atoms than PFMOAA (i.e., PFMOPrA and PFMOBA) exhibited negligible removal (Figure 3), it is expected that PFMOAA adsorption is also negligible under the tested conditions.

To compare the affinity of different PFASs for PAC, PFAS removal percentages were plotted as a function of PFAS chain length [the sum of carbon (including branched), ether oxygen, and sulfur atoms] (Figure 3b). The adsorbability of both legacy and emerging PFASs increased with increasing chain length. PFSAs were more readily removed than PFCAs of matching chain length, a result that agrees with those of previous


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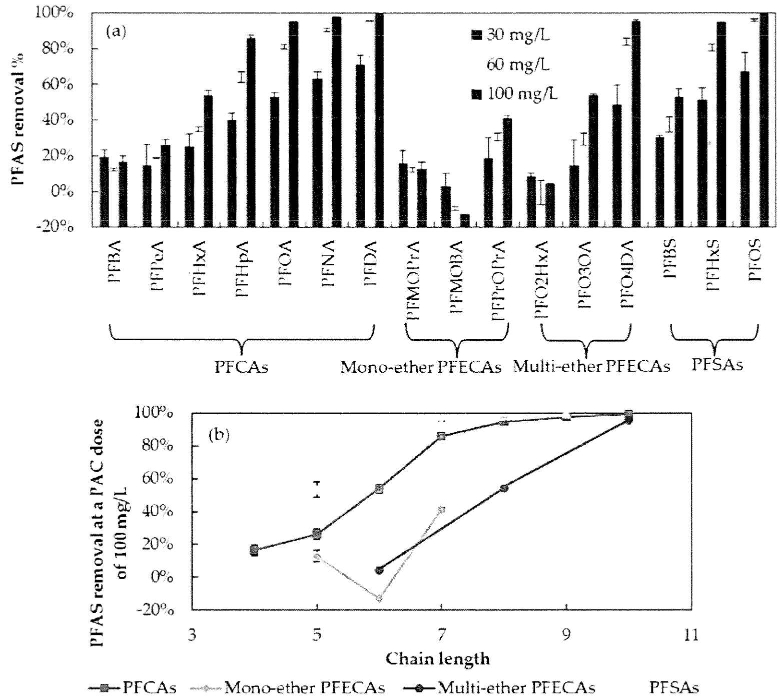


**Figure 3.** PFAS adsorption on PAC (a) at carbon doses of 30, 60, and 100 mg/L and (b) as a function of PFAS chain length. The PAC contact time in CFR water was 1 h. Legacy PFASs were spiked at ~1000 ng/L, and the emerging PFASs were at ambient concentrations. Figures show average PFAS removal percentages, and error bars show one standard deviation of replicate experiments.

studies.[24,25,29] PFECAs exhibited adsorbabilities lower than those of PFCAs of the same chain length (e.g., PFMOBA < PFHxA), suggesting that the replacement of a $CF_2$ group with an ether oxygen atom decreases the affinity of PFASs for PAC. However, the replacement of additional $CF_2$ groups with ether groups resulted in small or negligible affinity changes among the studied PFECAs (e.g., PFMOBA ~ PFO2HxA, PFPrOPrA ~ PFO3OA). Alternatively, if only the number of perfluorinated carbons were considered as a basis of comparing adsorbability, the interpretation would be different. In that case, with the same number of perfluorinated carbons, PFCAs have an affinity for PAC higher than that of monoether PFECAs (e.g., PFPeA > PFMOBA) but an affinity lower than that of multi-ether PFECAs (e.g., PFPeA < PFO3OA).

To the best of our knowledge, this is the first paper reporting the behavior of recently identified PFECAs in water treatment processes. We show that PFECAs dominated the PFAS signature in a drinking water source downstream of a fluorochemical manufacturer and that PFECA removal by many conventional and advanced treatment processes was negligible. Our adsorption data further show that PFPrOPrA ("GenX") is less adsorbable than PFOA, which it is replacing. Thus, PFPrOPrA presents a greater drinking water treatment challenge than PFOA does. The detection of potentially high levels of PFECAs, the continued presence of high levels of legacy PFASs, and the difficulty of effectively removing legacy PFASs and PFECAs with many water treatment processes suggest the need for broader discharge control and contaminant monitoring.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.6b00398.

Six tables, five figures, information about PFASs, analytical methods, and detailed results (PDF)

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**Notes**

The views expressed in this article are those of the authors and do not necessarily represent the views or policies of the USEPA.

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# 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.[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 | $C_4HF_9SO_3$ | 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 |

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

Table S5. MS transitions for PFAS Analysis

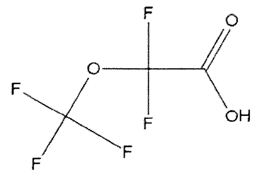
| | Compound | MS/MS Transition | Internal standard |
|---|---|---|---|
| Legacy PFASs | PFBA | 212.8 → 168.8 | 13C4-PFBA |
| | PFPeA | 262.9 → 218.8 | 13C2- PFHxA |
| | PFHxA | 313.6 → 268.8 | 13C2- PFHxA |
| | PFHpA | 362.9 → 318.8 | 13C4- PFOA |
| | PFOA | 413.0 → 368.8 | 13C4- PFOA |
| | PFNA | 463.0 → 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 at three drinking water intakes. *

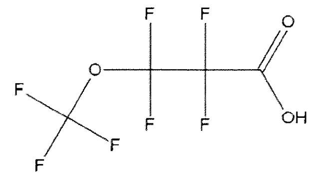
| | Community A | | | | Community B | | | | Community C | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | max | min | median | mean | max | min | median | mean | max | min | median | mean |
| **PFBA** | 99 | <10 | 26 | 33 | 38 | <10 | 12 | 12 | 104 | <10 | 12 | 22 |
| **PFPeA** | 191 | 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.

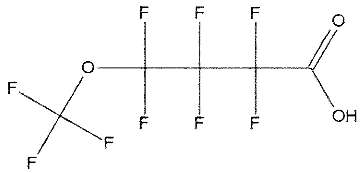
** Other PFECAs were present in water samples from community C but could not be quantified and were therefore not included in ∑ PFASs



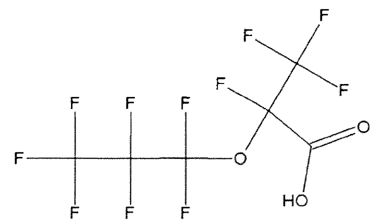
PFMOAA



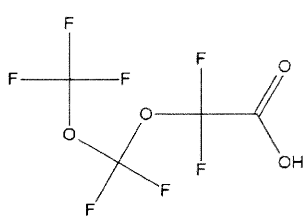
PFMOPrA



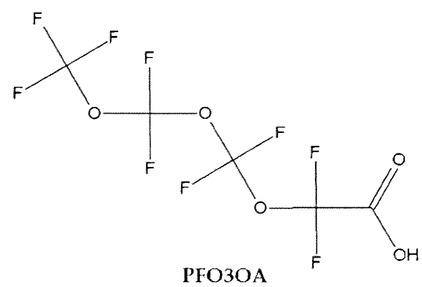
PFMOBA



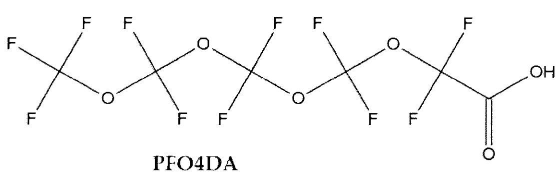
PFPrOPrA



PFO2HxA



PFO3OA



PFO4DA

Figure S1. Molecular structures of PFECAs evaluated in this study

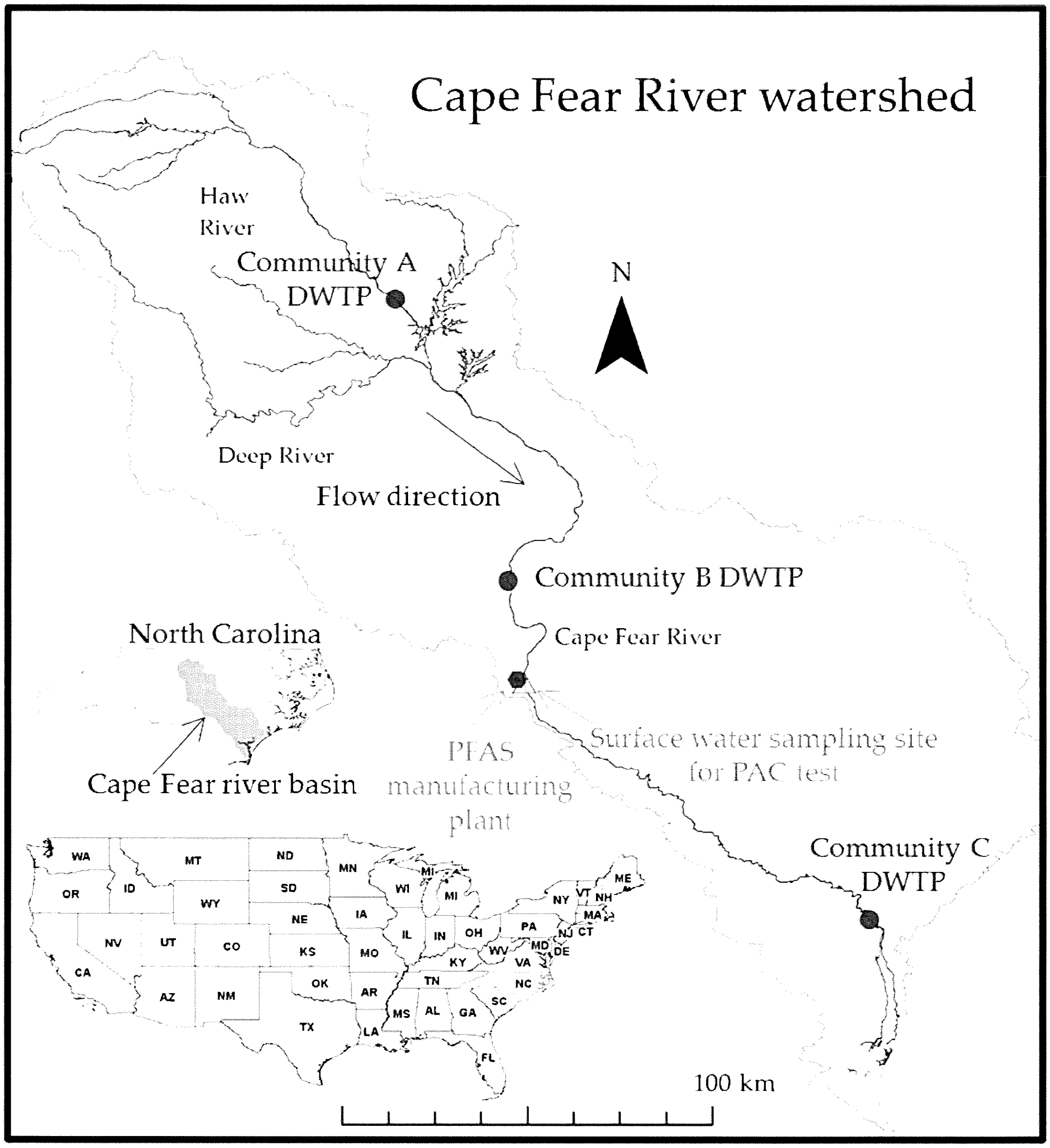
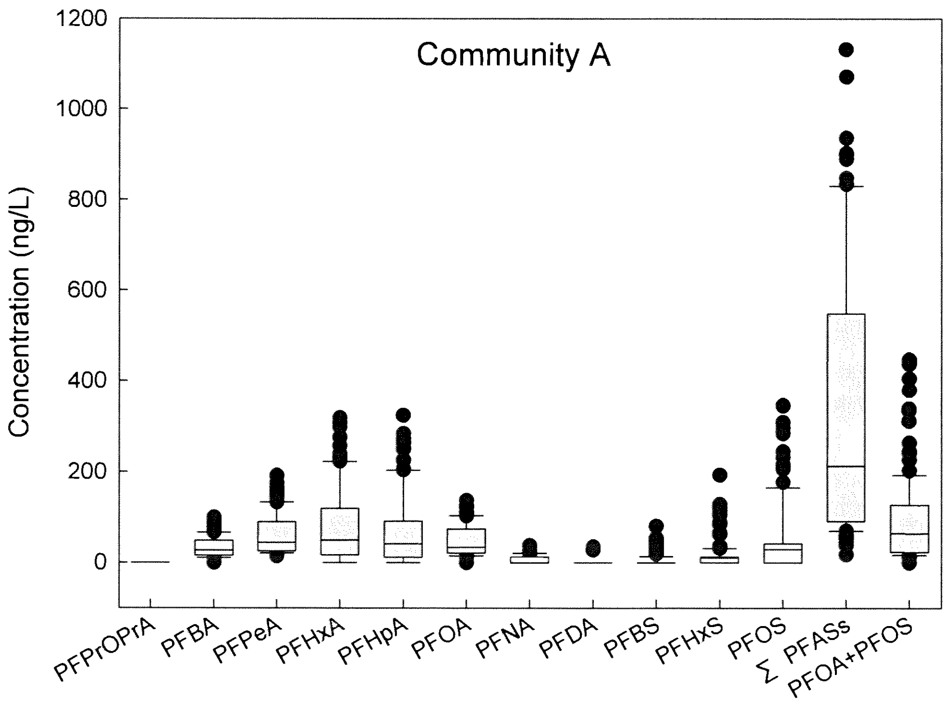
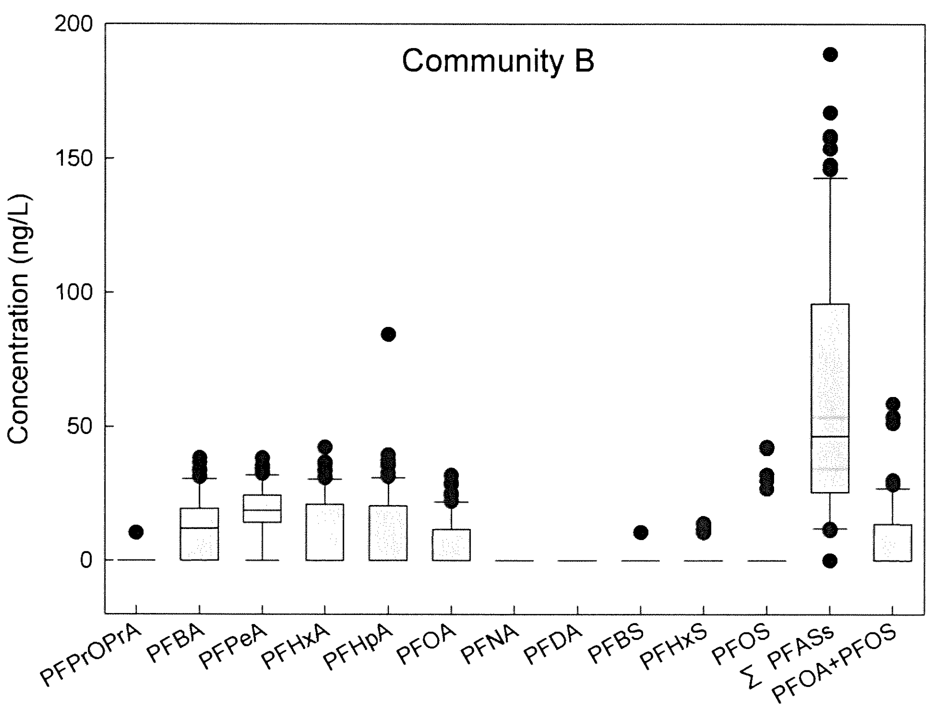



Figure S2. Sampling sites in the Cape Fear River watershed, North Carolina. The scale is for the Cape Fear River watershed map.


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

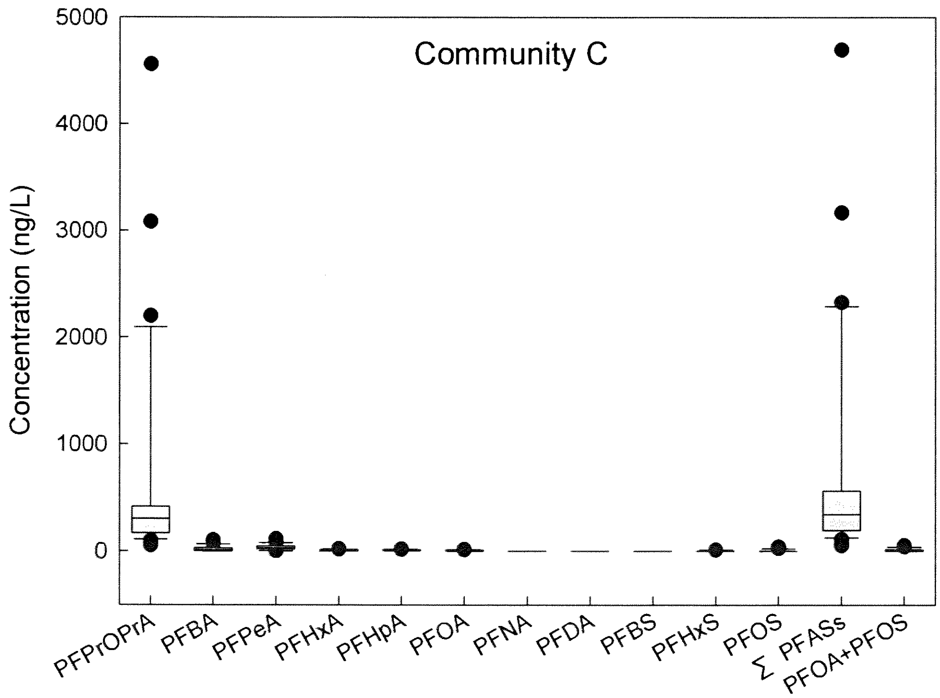
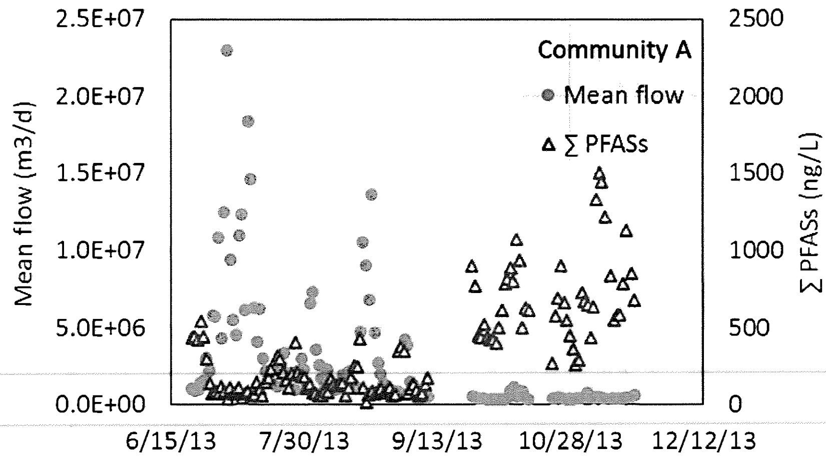
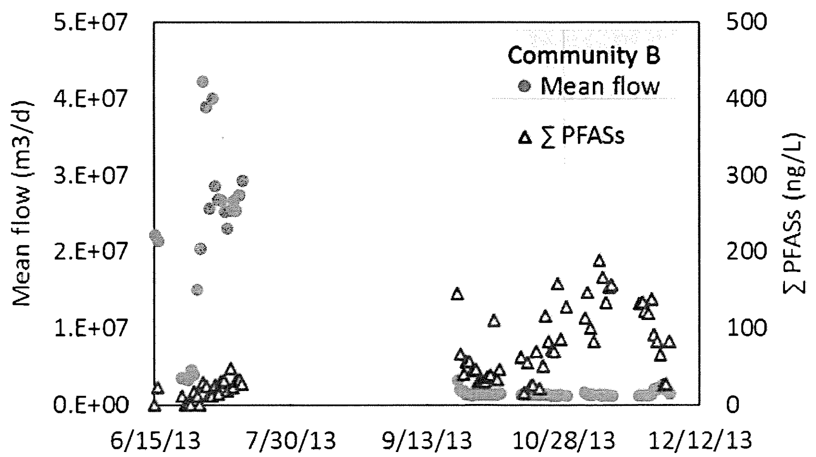



Figure S3. PFAS concentration distributions in the CFR watershed at three drinking water intakes. Concentrations less than quantitation limits were considered as zero. Upper and lower edges of a box represent the 75th and 25th percentile, respectively; the middle line represents the median; upper and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



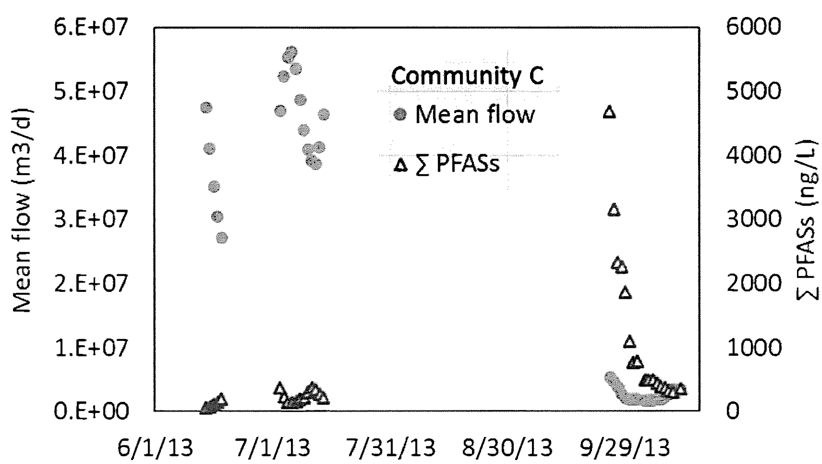




Figure S4. Total PFAS concentrations in the source water and stream flow at the three studied DWTPs. Stream flow data were acquired from US Geological Survey stream gage records

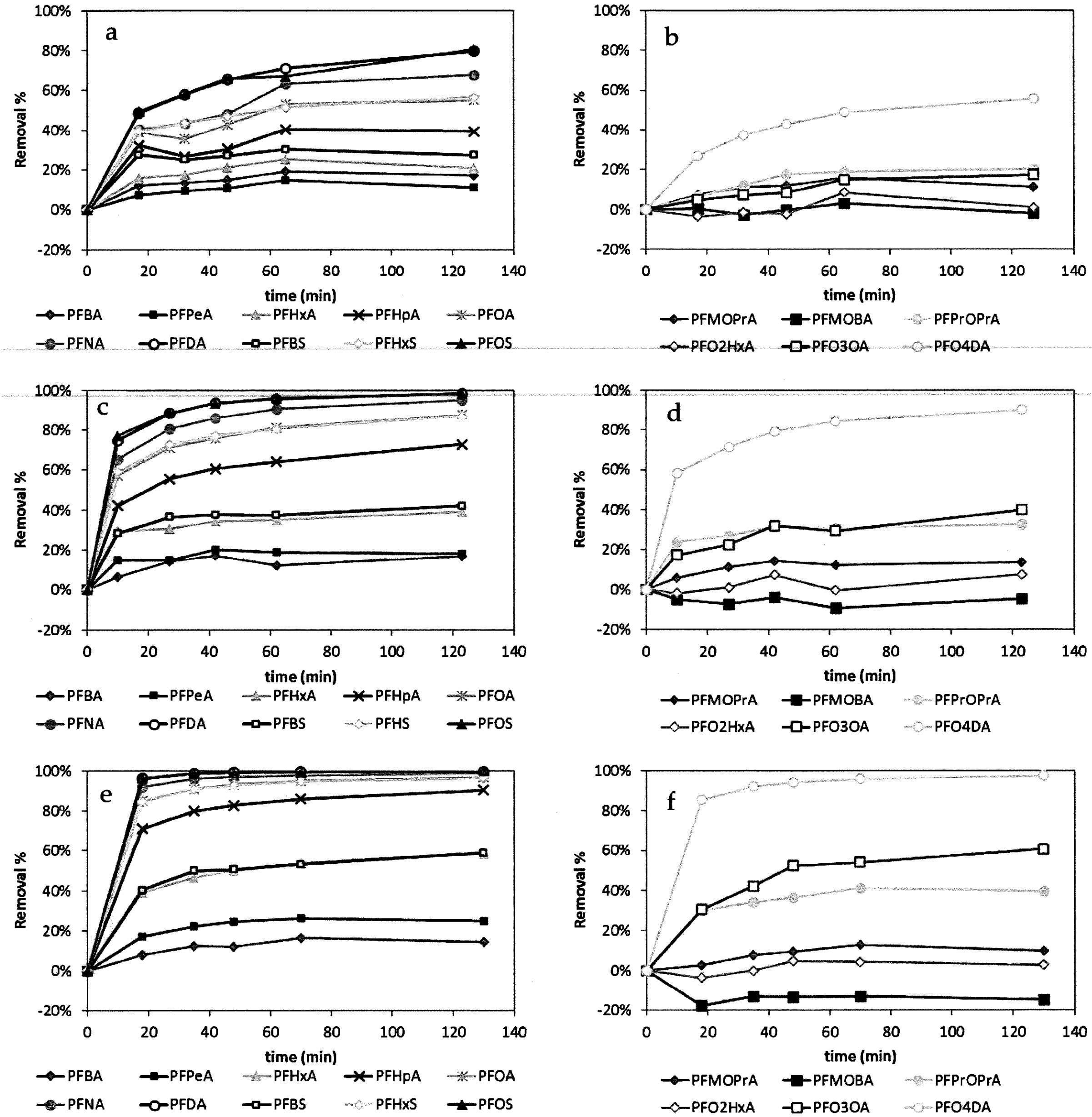



Figure S5. PFAS adsorption at powdered activated carbon doses of (a, b) 30 mg/L, (c, d) 60 mg/L and (e, f) 100 mg/L. Figures show average PFAS removal percentages of duplicate tests.

## Reference

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. *Environ. Sci. Technol.* **2007,** *41,* (15), 5271-5276.

| | |
|---|---|
| **From:** | Dittman, Elizabeth |
| **To:** | Risen, Amy J; Shehee, Mina; Holt, Kennedy |
| **Subject:** | FW: Emailing - Evaluation+of+substances+used+in+the+GenX+technology+by+Chemours,+Dordrecht.pdf |
| **Date:** | Tuesday, June 13, 2017 11:51:13 AM |
| **Attachments:** | Evaluation+of+substances+used+in+the+GenX+technology+by+Chemours,+Dordrecht.pdf<br>image002.png |

I think we've all seen this, but just passing along for your records.


Beth Dittman

Toxicologist and Public Health Assessor

Division of Public Health, Occupational and Environmental Epidemiology Branch

North Carolina Department of Health and Human Services

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Raleigh, NC 27699

From: Brower, Connie
Sent: Tuesday, June 13, 2017 11:32 AM
To: Dittman, Elizabeth <Beth.Dittman@dhhs.nc.gov>
Subject: Emailing - Evaluation+of+substances+used+in+the+GenX+technology+by+Chemours,+Dordrecht.pdf

Per request - Nice “orange” report… dated ~ September 2016 .

Regard,

Connie

______

| | |
|---|---|
| **From:** | Culpepper, Linda |
| **To:** | Shehee, Mina; ptarte@nhcgov.com; Cris Harrelson; "cmoser@pendercountync.gov"; dhoward@bladenco.org; Staley, Danny; Wooten, Maribeth T; Moore, Zack; Langley, Rick; Risen, Amy J; Holt, Kennedy; Gregson, Jim; Allen, Trent |
| **Cc:** | Munger, Bridget; Brower, Connie; Manning, Jeff; Godreau, Jessica; Grzyb, Julie; Sink, Marla; Holman, Sheila |
| **Subject:** | FW: Gen X Sampling |
| **Date:** | Wednesday, June 14, 2017 6:59:45 PM |

Jim – I promised to forward the sampling locations to all those on the public health call this morning, so I am using your email below.

Trent – in discussion with local governments later this morning, an attorney George House, indicated they thought the Chemour sampling

location should be at outfall 001 rather than outfall 002. After Sheila and I discussed it further, I now understand that wastewater from

outfall 001 and other wastewaters flow into the collection line for outfall 002 within the plant site. Outfall 002 is the point the combined

wastewater actually enters the river. Therefore the sampling should be done at outfall 002. If not, we will be losing potential contributions

from other parts of the wastewater that also flow into outfall 002. We want to make sure you agree before discussing this further.

Appreciate everyone’s time in all the discussions today.

Linda Culpepper

Deputy Director

Division of Water Resources

North Carolina Department of Environmental Quality

1611 Mail Service Center

Phone: 919-707-9014

From: Gregson, Jim
Sent: Wednesday, June 14, 2017 12:34 PM
To: Kritzer, Jamie <jamie.kritzer@ncdenr.gov <mailto:jamie.kritzer@ncdenr.gov> >
Subject: Gen X Sampling

Jamie,

My proposal was to sample once per week to coincide with Chenours' samples at the four intakes, the five water treatment plants (CFPUA, Pender County, Brunswick County, International Paper, and Smithfield Packing) finished water, the CFPUA ASR well and one Wrightsville Beach Well. There would be three sets of samples over a three week period.

Jim Gregson

Regional Supervisor

Water Quality Regional Operations Section

Division of Water Resources

Department of Environmental Quality

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Wilmington Regional Office

<x-apple-data-detectors://3/1> 127 Cardinal Drive Ext

<x-apple-data-detectors://3/1> Wilmington, NC 28405

| | |
|---|---|
| **From:** | Holt, Kennedy |
| **To:** | Langley, Rick |
| **Cc:** | Risen, Amy J; Dittman, Elizabeth |
| **Subject:** | FW: GenX detected in Cape Fear River |
| **Date:** | Friday, June 9, 2017 1:05:09 PM |
| **Attachments:** | image001.png<br>image002.png<br>image001.png |

Hello,

Dr. Moore just sent me this and wanted your input before responding.


**Kennedy Holt, MSPH**
Chemical Risk Assessor
Public Health, Occupational and Environmental Epidemiology
North Carolina Department of Health and Human Services

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kennedy.holt@dhhs.nc.gov

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Raleigh, NC 27609


Nothing Compares



**From:** Moore, Zack
**Sent:** Friday, June 09, 2017 12:58 PM
**To:** Holt, Kennedy <Kennedy.Holt@dhhs.nc.gov>
**Cc:** Shehee, Mina <mina.shehee@dhhs.nc.gov>; Staley, Danny <Danny.Staley@dhhs.nc.gov>; Lauffer, Pierre K <Pierre.Lauffer@dhhs.nc.gov>
**Subject:** Re: GenX detected in Cape Fear River

Hi Kennedy,

I know Mina is out today and Monday, but I wanted to ask if you or Dr. Risen (whose email I don't have yet) have shared this information with any other potentially affected counties. It seems likely that there will be similar concerns raised to other health departments.

It might be good to create a billeted summary of the information below that could be shared if needed and also could be shared with the Division and Department FYI. Please let me know if you or others there could work on that. I'm copying Pierre since I'm not sure who's in charge today. Thanks.

Zack Moore, MD, MPH
State Epidemiologist and Epidemiology Section Chief
Division of Public Health
North Carolina Department of Health and Human Services

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919 733 0490 fax (secure)
zack.moore@dhhs.nc.gov

225 N. McDowell St.
Raleigh, NC 27603
1902 Mail Service Center
Raleigh, NC 27699-1902

NC Nothing Compares

On Jun 8, 2017, at 4:19 PM, Cris Harrelson <cris.harrelson@brunswickcountync.gov> wrote:

> Mina,
> Thank you for your prompt response to this issue. It was a pleasure speaking with you earlier today and the information provided is both valuable and pertinent in helping us put the health risk in perspective.
> Cris
>
> Cris Harrelson, Director
> Brunswick County Health Services
> P.O. Box 9
> 25 Courthouse Dr. NE
> Bolivia, NC 28422
> (910) 253-2298
>
> <image001.png>
>
> ---
>
> **From:** Shehee, Mina [mailto:mina.shehee@dhhs.nc.gov]
> **Sent:** Thursday, June 8, 2017 3:54 PM

**To:** Cris Harrelson <cris.harrelson@brunswickcountync.gov>
**Cc:** Moore, Zack <zack.moore@dhhs.nc.gov>; Staley, Danny <Danny.Staley@dhhs.nc.gov>
**Subject:** GenX detected in Cape Fear River

Dear Cris,

Currently, there is little health effect literature on the chemical making up "GenX" (2,3,3,3 -tetrafluoro-2-(heptafluoropropoxy)propionic acid, ammonium salt CAS # 62037-80-3). In the U.S. there are no regulatory levels for GenX in drinking water and no health guidelines. However, Dr. Risen found an assessment by the European Chemical Agency (https://echa.europa.eu/registration-dossier/-/registered-dossier/2679/7/1) which calculated a derived no effect level for oral exposure of 0.01 mg/kg/day.

I used the mean value cited in Sun et al 2016, 631 parts per trillion, as the concentration in drinking water and calculated reasonable maximum exposure doses for people drinking the water. The maximum dose was 0.00009 mg/kg/day, more than 100 times lower than the derived no effect level. Please note the samples taken for the Sun et al 2016 paper were collected in 2013-2014, so the concentrations of GenX in the waterway may be different now.  This is an emerging contaminant so the OEEB toxicologists will continue to monitor the latest scientific literature.

We asked the cancer registry to look at likely cancers of the kidney, liver, testicular, and pancreas that could be expected in a similar compound (e.g. C8) in Brunswick and New Hanover Counties compared to the state rate.  The rate and confidence interval comparisons do not show elevated rates of the selected cancers in these counties. Caution - this is only 6 years of data.  Development of cancer can take decades.

Please let me know if you need any further from us.
Mina

Mina Shehee, PhD
Branch Head
Division Public Health, Occupational and Environmental Epidemiology
North Carolina Department of Health and Human Services

919 707 5920 office
919 870 4807 fax
mina.shehee@dhhs.nc.gov

5505 Six Forks Road
1912 Mail Service Center
Raleigh, NC 27699-1912

<image002.png>

| | |
|---|---|
| **From:** | Holt, Kennedy |
| **To:** | Shehee, Mina |
| **Cc:** | Risen, Amy J; Dittman, Elizabeth; Langley, Rick |
| **Subject:** | FW: GenX in Cape Fear River |
| **Date:** | Tuesday, June 13, 2017 1:12:44 PM |
| **Attachments:** | image001.png |


**Kennedy Holt, MSPH**
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kennedy.holt@dhhs.nc.gov

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Raleigh, NC 27609




**From:** David Howard [mailto:dhoward@bladenco.org]
**Sent:** Tuesday, June 13, 2017 1:10 PM
**To:** Holt, Kennedy <Kennedy.Holt@dhhs.nc.gov>
**Subject:** RE: GenX in Cape Fear River

Hi Kennedy, thank you for reaching out!

Yes, please add me to your “update” list of contacts!
We have the situation where we are not only subject to the effects via water systems, but also the home county to the facility.

I have actually been in contact with my counterpart in New Hanover, Phillip Tarte, and have spoken briefly to our county manager here and our CC chair.
Sounds like a lot more questions than information to this point.
A few I have:

1. Was the NC State professor testing for GenX for a particular purpose in 13/14? Was he working for Chemours/Dupont at the time? From what I’ve read this is not a substance that pops up on a general water testing protocol, it has to be looked for specifically.

2. What are the added mitigation measures (I've read about) by Chemours since the 13/14 test results? Resulting in improved capture? Testing since 13/14?
3. Will there be levels in a re-written discharge permit with the Company on the tab for running a monitoring program?
4. Will all stakeholders be getting invitations to meetings, conference calls, regarding this

David

David G. Howard, MPH, BS
Director – Health and Human Services
Bladen County, North Carolina
dhoward@bladenco.org

---

**From:** Holt, Kennedy [mailto:Kennedy.Holt@dhhs.nc.gov]
**Sent:** Tuesday, June 13, 2017 11:41 AM
**To:** dhoward@bladenco.org
**Subject:** GenX in Cape Fear River

Hello David,

Due to media reports last week citing levels of the chemical GenX in the Cape Fear River we have been working with Pender, New Hanover, and Brunswick County to provide them information after they reached out to us. They were concerned about their public water utilities being affected by this contamination. I'm reaching out to you because we have not heard from Bladen County and wanted to make sure you were aware of the situation since the Cape Fear River goes through your county. We want to make sure that if any public utilities in Bladen County draw water from the Cape Fear River that we provide you the same information that the other counties are receiving. Please let me know if you have any questions or if you would like to receive information as we continue to work on this issue.

**Kennedy Holt, MSPH**
Chemical Risk Assessor
Public Health, Occupational and Environmental Epidemiology
North Carolina Department of Health and Human Services

919 707 5910 office
kennedy.holt@dhhs.nc.gov

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| | |
|---|---|
| **From:** | Holt, Kennedy |
| **To:** | Shehee, Mina |
| **Cc:** | Risen, Amy J; Dittman, Elizabeth; Langley, Rick; Lauffer, Pierre K |
| **Subject:** | FW: GenX in Cape Fear River |
| **Date:** | Tuesday, June 13, 2017 1:55:44 PM |
| **Attachments:** | image001.png |

---

**Kennedy Holt, MSPH**
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Public Health, Occupational and Environmental Epidemiology
North Carolina Department of Health and Human Services

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kennedy.holt@dhhs.nc.gov

5505 Six Forks Rd
Raleigh, NC 27609



---

**From:** David Howard [mailto:dhoward@bladenco.org]
**Sent:** Tuesday, June 13, 2017 1:44 PM
**To:** Holt, Kennedy <Kennedy.Holt@dhhs.nc.gov>
**Subject:** RE: GenX in Cape Fear River

Hi again Kennedy,
I just spoke to our General Services Manager for the county.
The county water system pulls all of our water supply from wells, so the county system does not pull surface water from the river.
Also, per his latest information, the town water supply systems also pull from wells only, I am confirming that with the towns.

Smithfield Foods in Tar Heel operates their own treatment system, and of course pulls water for their processing operations, but I am not able to confirm yet whether they use county well supply for potable water or if they are pulling from their own sources and treating for consumption themselves?

So, unless I learn differently, it appears that most if not all water supply in Bladen County is via wells, not surface water from the Cape Fear River.  I will continue to verify all of this.

The subsequent question for us of course is whether the GenX compound is detectable in our well supplies.  We of course don't know at this point because, like other supply entities, GenX like so many other substances is not tested for as part of the treatment process.  My General Services Manager indicates that, based on prior geological studies, most if not all of our well supply is coming from the Pee Dee and Black River aquifers, and only some is coming from the Cape Fear aquifer.

David

David G. Howard, MPH, BS
Director – Health and Human Services
Bladen County, North Carolina
dhoward@bladenco.org

---

**From:** Holt, Kennedy [mailto:Kennedy.Holt@dhhs.nc.gov]
**Sent:** Tuesday, June 13, 2017 11:41 AM
**To:** dhoward@bladenco.org
**Subject:** GenX in Cape Fear River

Hello David,

Due to media reports last week citing levels of the chemical GenX in the Cape Fear River we have been working with Pender, New Hanover, and Brunswick County to provide them information after they reached out to us. They were concerned about their public water utilities being affected by this contamination. I'm reaching out to you because we have not heard from Bladen County and wanted to make sure you were aware of the situation since the Cape Fear River goes through your county. We want to make sure that if any public utilities in Bladen County draw water from the Cape Fear River that we provide you the same information that the other counties are receiving. Please let me know if you have any questions or if you would like to receive information as we continue to work on this issue.

**Kennedy Holt, MSPH**
Chemical Risk Assessor
Public Health, Occupational and Environmental Epidemiology
North Carolina Department of Health and Human Services

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| | |
|---|---|
| **From:** | Langley, Rick |
| **To:** | Risen, Amy J; Holt, Kennedy; Dittman, Elizabeth |
| **Cc:** | Shehee, Mina |
| **Subject:** | FW: GenX |
| **Date:** | Friday, June 9, 2017 3:35:25 PM |
| **Attachments:** | Evaluation+of+substances+used+in+the+GenX+technology+by+Chemours,+Dordre....pdf<br>170607 letter to Ms. Holman from CFPUA NCDEQ-river water quality.pdf<br>PFAS_Wilmington_041917.pdf |

From: Gregson, Jim
Sent: Friday, June 09, 2017 3:05 PM
To: Langley, Rick <rick.langley@dhhs.nc.gov>
Subject: GenX


Jim Gregson

Regional Supervisor

Water Quality Regional Operations Section

Division of Water Resources

Department of Environmental Quality

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<x-apple-data-detectors://3/1> Wilmington, NC 28405

| | |
|---|---|
| **From:** | Dittman, Elizabeth |
| **To:** | Holt, Kennedy; Risen, Amy J |
| **Subject:** | FW: More resources - Your GenX question |
| **Date:** | Tuesday, June 13, 2017 8:51:23 AM |
| **Attachments:** | Sun et al. GenX in the Cape Fear River 2016.pdf<br>Newton Final.pdf<br>image002.png |

---

Beth Dittman

Toxicologist and Public Health Assessor

Division of Public Health, Occupational and Environmental Epidemiology Branch

North Carolina Department of Health and Human Services

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919 870 4807 fax

Beth.Dittman@dhhs.nc.gov

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Raleigh, NC 27699

From: Henry, Audra E. (ATSDR/DCHI/OD) [mailto:ate1@cdc.gov]
Sent: Tuesday, June 13, 2017 8:24 AM
To: Dittman, Elizabeth <Beth.Dittman@dhhs.nc.gov>
Cc: Henry, Audra E. (ATSDR/DCHI/OD) <ate1@cdc.gov>
Subject: More resources - Your GenX question

Beth,

I enclosed two papers that might be useful. Both reports are out of EPA's National Exposure Research Lab. One looks at these species in the Cape Fear River Basin and the other in the Tennessee River near Decatur, AL. I hope this helps.

Audra Henry, MS

Technical Project Officer

ATSDR Division of Community Health Investigations

770-488-3758

ate1@cdc.gov <mailto:ate1@cdc.gov>

| | |
|---|---|
| **From:** | Dittman, Elizabeth |
| **To:** | Risen, Amy J |
| **Subject:** | FW: Your question about GenX |
| **Date:** | Monday, June 12, 2017 9:46:41 AM |
| **Attachments:** | image002.png |

See below. I don't think it includes any articles we haven't already seen, but a potential EPA contact for you if you want to reach out directly. Additionally, I looked on the Sharepoint site and the most useful thing would be this: https://www.atsdr.cdc.gov/substances/toxsubstance.asp?toxid=237

**Beth Dittman**
Toxicologist and Public Health Assessor
Division of Public Health, Occupational and Environmental Epidemiology Branch
North Carolina Department of Health and Human Services

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Beth.Dittman@dhhs.nc.gov

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**From:** Henry, Audra E. (ATSDR/DCHI/OD) [mailto:ate1@cdc.gov]
**Sent:** Monday, June 12, 2017 9:32 AM
**To:** Dittman, Elizabeth <Beth.Dittman@dhhs.nc.gov>
**Cc:** Henry, Audra E. (ATSDR/DCHI/OD) <ate1@cdc.gov>
**Subject:** Your question about GenX

Hi Beth,

We do not have a specific person to consult with about general GenX questions as this is an emerging chemical. However, we have related PFAS resources on our SharePoint site (https://partner.cdc.gov/Sites/NCEH/ATSDR/DCHI/science/PFAS/default.aspx) that may be useful to you. Please see the information from EPA below as an additional resource. Let me know if you have a specific site request regarding GenX/PFAS. If our SharePoint site does not help, we can then better identify other subject matter experts or resources for you.

Audra Henry, MS
Technical Project Officer
ATSDR Division of Community Health Investigations
770-488-3758
ate1@cdc.gov

---

**From:** Wheeler, John (CDC epa.gov)
**Sent:** Friday, June 09, 2017 3:07 PM
**To:** Henry, Audra E. (ATSDR/DCHI/OD) <ate1@cdc.gov>
**Cc:** Forrester, Tina (ATSDR/DCHI/OD) <txf5@cdc.gov>; Moore, Susan (ATSDR/DCHI/SSB) <sym8@cdc.gov>; Webster, James <Webster.James@epa.gov>
**Subject:** FW: NC contaminant

Audra,
Here is some information on this chemical, GenX, provided by Brian Englert. You may share this email with the state (I am missing Beth's email address).

Let me know if I can help further.
John
470-426-9231

---

**From:** Englert, Brian
**Sent:** Friday, June 09, 2017 2:29 PM
**To:** Webster, James <Webster.James@epa.gov>; Wheeler, John <Wheeler.John@epa.gov>
**Cc:** Moore, Tony <moore.tony@epa.gov>
**Subject:** Re: NC contaminant

Here is some more information on this.

Per the source below, the Gen X chemical is made at Chemours Co. which is about 50 miles upstream of the raw water intakes for the Cape Fear Public Utility Authority. GenX was detected there by independent researchers in 2013.

Couple that with the claim it causes cancer in lab animals and the company and Cape Fear Public Utility have made statements to the press. Both can be found in these links.

http://www.starnewsonline.com/news/20170607/toxin-taints-cfpua-drinking-water/1

Toxin taints CFPUA drinking water

[www.starnewsonline.com](www.starnewsonline.com)

Utility can't filter out chemical produced upriver at Fayetteville plant

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http://www.wect.com/story/35622396/companies-react-to-study-indicating-presence-of-unregulated-toxin-in-water-supply

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## Companies react to study indicating presence of unregulated toxin in water supply

www.wect.com

Water companies and local officials are reacting to a study published in the Wilmington StarNews this week indicating the presence of an unregulated chemical known in the trade market as GenX in th...

---

Brian Englert, PhD
Federal On-Scene Coordinator
U.S. EPA, Region 4
ERRPB, 11th Floor, 11037
61 Forsyth Street. S.W.
Atlanta, Georgia 30303
Mail Code: 9T25
Office: (404) 562-8854
Cell: (404) 263-8775
Fax: (404) 562-8699
englert.brian@epa.gov

To report an oil or chemical spill please call the National Response Center at 1-800-424-8802

---

**From:** Englert, Brian
**Sent:** Friday, June 9, 2017 2:10 PM
**To:** Webster, James; Wheeler, John
**Cc:** Moore, Tony
**Subject:** Re: NC contaminant

Jim/John,

Its a Dupont patented technology that offers an alternative to use of PFOA. It is apparently more envionmentally friendly, less water soluble and excretes from the body faster (so Dupont says). See attached.

I believe GenX is actually the name Dupont uses to describe the technology the chemical is actually used in.

"GenX chemical" likely refers to one of the chemicals involved. Its appears to be a amide (carboxylic acid with a nitrogen) instead of an acid (PFOA) or sulfonate (PFOS). It also contains oxygen in the chain as opposed to just carbon and flourine.

Just checked and there are new stories circulating on this issue. The one I linked to below claims its been detected in the Cape Fear River. Several mention that a new study claims it may cause cancer in lab animals. That may have prompted new interest in this issue.

http://whqr.org/post/genx-compound-mystery-most#stream/0

Thats all the info I have right now. I'll see if I can learn more.

GenX Compound: A Mystery To Most

whqr.org

GenX. No, we don’t mean Generation X. GenX is a chemical compound we first reported on yesterday. That’s when the StarNews reported on this toxic

Brian Englert, PhD
Federal On-Scene Coordinator
U.S. EPA, Region 4
ERRPB, 11th Floor, 11037
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Office: (404) 562-8854
Cell: (404) 263-8775
Fax: (404) 562-8699
englert.brian@epa.gov

To report an oil or chemical spill please call the National Response Center at 1-800-424-8802



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| | |
|---|---|
| **From:** | Culpepper, Linda |
| **To:** | ptarte@nhcgov.com; Cris Harrelson; "cmoser@pendercountync.gov"; dhoward@bladenco.org; Staley, Danny; Wooten, Maribeth T; jim.flechtner@cfpua.org |
| **Cc:** | Moore, Zack; Holman, Sheila; Langley, Rick; Risen, Amy J; Holt, Kennedy; Shehee, Mina; Munger, Bridget; Brower, Connie; Manning, Jeff; Grzyb, Julie; Gregson, Jim; Allen, Trent |
| **Subject:** | Follow up on Lab info. - Chemour |
| **Date:** | Wednesday, June 14, 2017 7:52:15 PM |

Following up from a conversation this morning to share the lab contact information being used for analyzing the samples.

Just spoke with our Wilmington Regional Office and they have not received the sampling equipment yet so I do not have

the specific contact information right now. Searching the web I have basic information:

http://www.testamericainc.com/locations/

Test America

4955 Yarrow Street

Arvada, CO 80002-4517

Phone: 303.736.0100

The Water Protection Division in EPA Region 4 is checking to see if the EPA Office of Research and Development

(ORD) lab can help us with additional analysis. Inserting an email below from Dr. Knappe regarding his study's analysis at ORD.

From: Detlef Knappe <knappe@ncsu.edu <mailto:knappe@ncsu.edu> >
Date: June 14, 2017 at 6:28:05 PM EDT
To: "Grzyb, Julie" <julie.grzyb@ncdenr.gov <mailto:julie.grzyb@ncdenr.gov> >
Subject: RE: Presentation at DWR

My students did the analyses using LC tandem mass spectrometers at the EPA lab in RTP.

Detlef

We appreciate the discussion this morning and continued dialog tomorrow.

Linda Culpepper

Deputy Director

Division of Water Resources

North Carolina Department of Environmental Quality

1611 Mail Service Center

Phone: 919-707-9014



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| | |
|---|---|
| **From:** | Amy Risen |
| **To:** | Risen, Amy J |
| **Subject:** | Fwd: "DR" Removed Copy of Summary GenX |
| **Date:** | Tuesday, June 13, 2017 6:12:18 AM |
| **Attachments:** | image003.png<br>GenX Health Effects Summary DHHS 6_12_17 PDF.pdf |

---------- Forwarded message ----------
From: Shehee, Mina <mina.shehee@dhhs.nc.gov <mailto:mina.shehee@dhhs.nc.gov> >
Date: Mon, Jun 12, 2017 at 1:20 PM
Subject: "DR" Removed Copy of Summary GenX
To: "Holman, Sheila" <sheila.holman@ncdenr.gov <mailto:sheila.holman@ncdenr.gov> >
Cc: "Moore, Zack" <zack.moore@dhhs.nc.gov <mailto:zack.moore@dhhs.nc.gov> >, Amy Risen <amyjoyrisen@gmail.com <mailto:amyjoyrisen@gmail.com> >, "Holt, Kennedy" <Kennedy.Holt@dhhs.nc.gov <mailto:Kennedy.Holt@dhhs.nc.gov> >, "Dittman, Elizabeth" <Beth.Dittman@dhhs.nc.gov <mailto:Beth.Dittman@dhhs.nc.gov> >, "Staley, Danny" <Danny.Staley@dhhs.nc.gov <mailto:Danny.Staley@dhhs.nc.gov> >, "Wooten, Maribeth T" <Maribeth.Wooten@dhhs.nc.gov <mailto:Maribeth.Wooten@dhhs.nc.gov> >, "Mackey, Chris" <Chris.Mackey@dhhs.nc.gov <mailto:Chris.Mackey@dhhs.nc.gov> >, "Coleman, Scott" <Scott.Coleman@dhhs.nc.gov <mailto:Scott.Coleman@dhhs.nc.gov> >

See attached clean copy of PDF – GenX Health Effects summary.

Mina Shehee, PhD

Branch Head

Division Public Health, Occupational and Environmental Epidemiology

North Carolina Department of Health and Human Services

919 707 5920 <tel:(919)%20707-5920> office

919 870 4807 <tel:(919)%20870-4807> fax

mina.shehee@dhhs.nc.gov <mailto:mina.shehee@dhhs.nc.gov>

5505 Six Forks Road

1912 Mail Service Center

Raleigh, NC 27699-1912

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<https://twitter.com/ncdhhs> Twitter <https://www.youtube.com/user/ncdhhs> YouTube

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**From:** Holt, Kennedy
**To:** Dittman, Elizabeth; Risen, Amy J; Langley, Rick
**Cc:** Shehee, Mina
**Subject:** GenX Study
**Date:** Friday, June 9, 2017 1:28:26 PM
**Attachments:** image001.png
research 1..pdf

---

I managed to get a copy of the article that triggered the GenX media reports.


Kennedy Holt, MSPH

Chemical Risk Assessor

Public Health, Occupational and Environmental Epidemiology

North Carolina Department of Health and Human Services

919 707 5910 office

<mailto:kennedy.holt@dhhs.nc.gov> kennedy.holt@dhhs.nc.gov

5505 Six Forks Rd

Raleigh, NC 27609

| | |
|---|---|
| **From:** | Risen, Amy J |
| **To:** | Langley, Rick; Holt, Kennedy; Dittman, Elizabeth; Lee-Pow, Crystal SD; Shehee, Mina |
| **Subject:** | RE: C8 Heads up |
| **Date:** | Thursday, June 8, 2017 12:54:00 PM |

This pop news article has a link to health studies submitted to the EPA during chemical registration.

https://theintercept.com/2016/03/03/new-teflon-toxin-causes-cancer-in-lab-animals/

**The health studies are here

https://assets.documentcloud.org/documents/2746960/GenX8eFilings.pdf

From: Langley, Rick
Sent: Thursday, June 08, 2017 11:03 AM
To: Holt, Kennedy <Kennedy.Holt@dhhs.nc.gov>; Risen, Amy J <Amy.Risen@dhhs.nc.gov>; Dittman, Elizabeth <Beth.Dittman@dhhs.nc.gov>; Lee-Pow, Crystal SD <Crystal.Lee-Pow@dhhs.nc.gov>
Subject: C8 Heads up

Toxin taints CFPUA drinking water

Vaughn Hagerty

Wilmington StarNews; multiple outlets

June 7, 2017

<http://www.starnewsonline.com/news/20170607/toxin-taints-cfpua-drinking-water/1>
http://www.starnewsonline.com/news/20170607/toxin-taints-cfpua-drinking-water/1

WATER FAQs: What we know and what we don’t know

Wilmington StarNews

June 8, 2017

<http://www.starnewsonline.com/news/20170608/water-faqs-what-we-know-and-what-we-dont-know>
http://www.starnewsonline.com/news/20170608/water-faqs-what-we-know-and-what-we-dont-know

| | |
|---|---|
| **From:** | Lauffer, Pierre K |
| **To:** | Holt, Kennedy; Shehee, Mina |
| **Cc:** | Risen, Amy J; Dittman, Elizabeth; Langley, Rick |
| **Subject:** | RE: GenX in Cape Fear River |
| **Date:** | Tuesday, June 13, 2017 2:39:23 PM |
| **Attachments:** | image001.png |

The only issue would be the Lower Cape Fear River Water and Sewer Authority which pulls 6 MGD from the Cape Fear in Tarheel.

Pierre

---

**From:** Holt, Kennedy
**Sent:** Tuesday, June 13, 2017 1:56 PM
**To:** Shehee, Mina <mina.shehee@dhhs.nc.gov>
**Cc:** Risen, Amy J <Amy.Risen@dhhs.nc.gov>; Dittman, Elizabeth <Beth.Dittman@dhhs.nc.gov>; Langley, Rick <rick.langley@dhhs.nc.gov>; Lauffer, Pierre K <Pierre.Lauffer@dhhs.nc.gov>
**Subject:** FW: GenX in Cape Fear River

**Kennedy Holt, MSPH**
Chemical Risk Assessor
Public Health, Occupational and Environmental Epidemiology
North Carolina Department of Health and Human Services

919 707 5910 office
kennedy.holt@dhhs.nc.gov

5505 Six Forks Rd
Raleigh, NC 27609



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**From:** David Howard [mailto:dhoward@bladenco.org]
**Sent:** Tuesday, June 13, 2017 1:44 PM
**To:** Holt, Kennedy <Kennedy.Holt@dhhs.nc.gov>
**Subject:** RE: GenX in Cape Fear River

Hi again Kennedy,
I just spoke to our General Services Manager for the county.
The county water system pulls all of our water supply from wells, so the county system does not pull surface water from the river.
Also, per his latest information, the town water supply systems also pull from wells only, I am confirming that with the towns.

Smithfield Foods in Tar Heel operates their own treatment system, and of course pulls water for their processing operations, but I am not able to confirm yet whether they use county well supply for potable water or if they are pulling from their own sources and treating for consumption themselves?

So, unless I learn differently, it appears that most if not all water supply in Bladen County is via wells, not surface water from the Cape Fear River.  I will continue to verify all of this.

The subsequent question for us of course is whether the GenX compound is detectable in our well supplies.  We of course don't know at this point because, like other supply entities, GenX like so many other substances is not tested for as part of the treatment process.  My General Services Manager indicates that, based on prior geological studies, most if not all of our well supply is coming from the Pee Dee and Black River aquifers, and only some is coming from the Cape Fear aquifer.

David

David G. Howard, MPH, BS
Director –  Health and Human Services
Bladen County, North Carolina
dhoward@bladenco.org

---

**From:** Holt, Kennedy [mailto:Kennedy.Holt@dhhs.nc.gov]
**Sent:** Tuesday, June 13, 2017 11:41 AM
**To:** dhoward@bladenco.org
**Subject:** GenX in Cape Fear River

Hello David,

Due to media reports last week citing levels of the chemical GenX in the Cape Fear River we have been working with Pender, New Hanover, and Brunswick County to provide them information after they reached out to us. They were concerned about their public water utilities being affected by this contamination. I'm reaching out to you because we have not heard from Bladen County and wanted to make sure you were aware of the situation since the Cape Fear River goes through your county. We want to make sure that if any public utilities in Bladen County draw water from the Cape Fear River that we provide you the same information that the other counties are receiving. Please let me know if you have any questions or if you would like to receive information as we continue to work on this issue.

**Kennedy Holt, MSPH**
Chemical Risk Assessor

Public Health, Occupational and Environmental Epidemiology
North Carolina Department of Health and Human Services

919 707 5910 office
kennedy.holt@dhhs.nc.gov

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Raleigh, NC 27609

Nothing Compares



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Twitter YouTube



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Pursuant to North Carolina General Statutes Chapter 132, Public Records, this electronic mail message and any attachments hereto, as well as any electronic mail message(s) that may be sent in response to it may be considered public record and as such are subject to request and review by third parties.

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| | |
|---|---|
| **From:** | Risen, Amy J |
| **To:** | Dittman, Elizabeth; Shehee, Mina |
| **Cc:** | Holt, Kennedy; Langley, Rick |
| **Subject:** | RE: emerging contaminant |
| **Date:** | Thursday, June 8, 2017 2:27:00 PM |
| **Attachments:** | image001.png<br>image002.png<br>image003.png |

EU's REACH requirements bring forth this set of info
https://echa.europa.eu/brief-profile/-/briefprofile/100.124.803?_dissbriefprofile_WAR_dissbriefprofileportlet_printedVersion=true&_dissbriefprofile_WAR_dissbriefprofileportlet_closePrintWindow=true&_dissbriefprofile_WAR_dissbriefprofileportlet_PrintSectionB4=TOXICOLOGICAL_INFO

**With oral exposure predicted NOEL part way through this document (0.1 mg/kg bw/day)
https://echa.europa.eu/registration-dossier/-/registered-dossier/2679/7/1

**From:** Dittman, Elizabeth
**Sent:** Thursday, June 08, 2017 2:14 PM
**To:** Risen, Amy J <Amy.Risen@dhhs.nc.gov>; Shehee, Mina <mina.shehee@dhhs.nc.gov>
**Subject:** FW: emerging contaminant

**Beth Dittman**
Toxicologist and Public Health Assessor
Division of Public Health, Occupational and Environmental Epidemiology Branch
North Carolina Department of Health and Human Services

919 707 5906 office
919 870 4807 fax
Beth.Dittman@dhhs.nc.gov

5505 Six Forks Road
1912 Mail Service Center
Raleigh, NC 27699



**From:** Mort, Sandra L
**Sent:** Thursday, June 08, 2017 2:08 PM
**To:** Dittman, Elizabeth <Beth.Dittman@dhhs.nc.gov>
**Subject:** RE: emerging contaminant

Beth-
There are no draft ITRC PFAS workgroup documents that I can send, but attached are several (7) technical presentations from the March ITRC annual meeting relevant to PFAS compounds, that may have useful information. I will send the presentations in several emails.
Sandy

**Sandy Mort, PhD, MS**
Environmental Toxicologist / Risk Assessor
Division of Waste Management – Hazardous Waste & Brownfields
NC Department of Environmental Quality

(919) 707-8217 - Direct Line & Fax
sandy.mort@ncdenr.gov

1646 Mail Service Center
Raleigh, NC 27699-1646



**From:** Dittman, Elizabeth
**Sent:** Thursday, June 08, 2017 1:45 PM
**To:** Mort, Sandra L <sandy.mort@ncdenr.gov>
**Subject:** emerging contaminant

GenX
I believe the sci name is: 2,3,3,3 -tetrafluoro-2-(heptafluoropropoxy)propionic acid, ammonium salt CAS # 62037-80-3
chemical structure: CF3 CF2 CF2 OCF(CF3 )COOH.NH3
Generic Name: Perfluorinated aliphatic carboxylic acid

**Beth Dittman**
Toxicologist and Public Health Assessor
Division of Public Health, Occupational and Environmental Epidemiology Branch
North Carolina Department of Health and Human Services

919 707 5906 office
919 870 4807 fax
Beth.Dittman@dhhs.nc.gov

5505 Six Forks Road
1912 Mail Service Center
Raleigh, NC 27699

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| | |
|---|---|
| **From:** | Moore, Zack |
| **To:** | Holman, Sheila |
| **Cc:** | Culpepper, Linda; Kritzer, Jamie; Staley, Danny; Wooten, Maribeth T; Shehee, Mina; Holt, Kennedy; Dittman, Elizabeth; Risen, Amy J |
| **Subject:** | Re: Letter from New Hanover County regarding Drinking Water |
| **Date:** | Saturday, June 10, 2017 8:18:28 PM |
| **Attachments:** | image001.png |

Thanks for sending this. Please let us know when a date and time have been set and we can try to make someone available to join.

Zack Moore, MD, MPH
State Epidemiologist and Epidemiology Section Chief
Division of Public Health
North Carolina Department of Health and Human Services

919 546 1725 office
919 733 0490 fax (secure)
zack.moore@dhhs.nc.gov

225 N. McDowell St.
Raleigh, NC 27603
1902 Mail Service Center
Raleigh, NC 27699-1902

On Jun 10, 2017, at 7:48 PM, Holman, Sheila <sheila.holman@ncdenr.gov> wrote:

Zack,

I wanted you to be aware of this latest communication and the plan for a community meeting next week. Would you and your team be available to participate?

Sheila

Sent from my Verizon, Samsung Galaxy smartphone

-------- Original message --------
From: "Regan, Michael S" <Michael.Regan@ncdenr.gov>
Date: 6/10/17 5:45 PM (GMT-05:00)

To: "Smith, Ruth Ravitz" <rsmith@nhcgov.com>
Cc: County Commissioners <D_CCOM_CountyCommissioners@nhcgov.com>, Executive Leadership Team <D_CMGR_ExecutiveLeadershipTeam@nhcgov.com>, "Iannucci, Jim" <JIannucci@nhcgov.com>, Jim Flechtner <jim.flechtner@cfpua.org>, "O'Keefe, Chris" <COKeefe@nhcgov.com>, "Sterling.Cheatham (Sterling.Cheatham@wilmingtonnc.gov)" <Sterling.Cheatham@wilmingtonnc.gov>, "Tarte, Phillip" <ptarte@nhcgov.com>, Michael.Lee@ncleg.net, Senator Bill Rabon <Bill.Rabon@ncleg.net>, "Rep. . Holly Grange (holly.grange@ncleg.net)" <holly.grange@ncleg.net>, "Rep. Deb Butler (deb.butler@ncleg.net)" <deb.butler@ncleg.net>, "Rep. Ted Davis" <Ted.Davis@ncleg.net>, "Nicholson, John A." <John.Nicholson@ncdenr.gov>, "Talley, Noelle S" <Noelle.Talley@nc.gov>, "Kritzer, Jamie" <jamie.kritzer@ncdenr.gov>, "Holman, Sheila" <sheila.holman@ncdenr.gov>, "Miller, Anderson" <anderson.miller@ncdenr.gov>, "Lance, Kathleen C" <kathleen.lance@ncdenr.gov>, "Webster, Timothy J" <timothy.webster@ncdenr.gov>, "Lane, Bill F" <Bill.Lane@ncdenr.gov>
Subject: RE: Letter from New Hanover County regarding Drinking Water

Dear Ms. Ravitz,

Thank you for your letter concerning water service from the Cape Fear Public Utilities Authority (CFPUA). Representatives from my Department have been in contact with Chemours, the Cape Fear Public Utilities Authority, the U.S. EPA and elected officials representing the district. Although North Carolina is awaiting guidance from the U.S. EPA, I join you in your concern. The Department of Environmental Quality is working diligently with all partners to ensure we evaluate the nature, extent and potential impacts of GenX. We will also continue working with Chemours to assess waste streams containing GenX and the potential for reducing the amount of the chemical compound being discharged to the river while we evaluate this matter.

I, and members of my senior team stand ready to join New Hanover County, CFPUA, the City of Wilmington, Chemours and local community leaders in a meeting next week in Wilmington. We are committed to working with all interested stakeholders to address this potential public safety matter swiftly and thoroughly. If I can be of further assistance, please don't hesitate to contact me at Michael.Regan@ncdenr.gov or 919-707-8622.

Thank you,


**Michael S. Regan**
Secretary
NC Department of Environmental Quality

919.707.8622 office
michael.regan@ncdenr.gov

1601 Mail Service Center
Raleigh, NC 27699-1601

217 W. Jones St.
Raleigh, NC 27603

<image001.png>
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**From:** Smith, Ruth Ravitz [mailto:rsmith@nhcgov.com]
**Sent:** Friday, June 09, 2017 5:57 PM
**To:** Regan, Michael S <Michael.Regan@ncdenr.gov>
**Cc:** County Commissioners <D_CCOM_CountyCommissioners@nhcgov.com>; Executive Leadership Team <D_CMGR_ExecutiveLeadershipTeam@nhcgov.com>; Iannucci, Jim <JIannucci@nhcgov.com>; Jim Flechtner <jim.flechtner@cfpua.org>; O'Keefe, Chris <COKeefe@nhcgov.com>; Sterling.Cheatham (Sterling.Cheatham@wilmingtonnc.gov) <Sterling.Cheatham@wilmingtonnc.gov>; Tarte, Phillip <ptarte@nhcgov.com>; Michael.Lee@ncleg.net; Senator Bill Rabon <Bill.Rabon@ncleg.net>; Rep. . Holly Grange (holly.grange@ncleg.net) <holly.grange@ncleg.net>; Rep. Deb Butler (deb.butler@ncleg.net) <deb.butler@ncleg.net>; Rep. Ted Davis <Ted.Davis@ncleg.net>
**Subject:** Letter from New Hanover County regarding Drinking Water

Dear Secretary Regan,

I am sending this letter on behalf of County Manager Chris Coudriet.

Please have your staff contact me should you need additional information. I can be reached on my mobile phone: 910-899-2590 or in the office on Monday.

We expect to hear early next week from the Chemours Company on when they can be available to meet in Wilmington.

Thank you,

Ruth

**Ruth Smith | Chief Communications Officer**
County Manager - Office of Communications and Outreach
New Hanover County
230 Government Center Drive, Suite 195
Wilmington, NC 28403
(910) 798-7177 p | (910) 798-7277 f

www.nhcgov.com

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| | |
|---|---|
| **From:** | Risen, Amy J |
| **To:** | Holt, Kennedy |
| **Cc:** | Dittman, Elizabeth |
| **Subject:** | for GenX |
| **Date:** | Friday, June 9, 2017 4:57:00 PM |
| **Attachments:** | image001.png |

Given the limited health information available for GenX, we can look at similar fluorinated compounds PFOS and PFOA to understand possible effects. PFOA and PFOS were recently reviewed by the EPA and the most common effects observed in laboratory tests were kidney and testicular cancer, impaired fetal development, and effects on the liver, thyroid, and immune system. The EPA issued a Health Advisory with recommendations for drinking water not to exceed 70 parts per trillion (70 ng/L). This Health Advisory focused on the most sensitive population and a safe drinking water concentration was calculated based on the possibility of developmental effects when fetuses and infants are exposed at key stages. Additional information can be found in the EPA fact sheet.
https://www.epa.gov/sites/production/files/2016-06/documents/drinkingwaterhealthadvisories_pfoa_pfos_updated_5.31.16.pdf

In response to recently published research by Sun and colleagues, OEEB looked at the risk of exposure to GenX. There are no U.S. regulatory guideline levels for this compound. However, as part of the European chemical registration, a 2-year chronic toxicity and cancer study with rats was performed. They reported a Derived No Effect Level (DNEL) of 0.01 mg/kg bw/day. We applied the DNEL to our U.S. risk assessment calculations to find a safe concentration for drinking water of 70,909 ng/L of GenX. The value of 70,909 ng/L is more than 100 times greater than the mean value of 631 ng/L detected in the Cape Fear River, suggesting safety until further information can be gathered.

The European chemical registration gives us the total safe **daily dose**

- No Observed Adverse Effect Level of 1 mg/kg bw/day for liver and blood endpoints
- Assigned an assessment factor of 100.
- Derived No Effect Level of 0.01 mg/kg bw/day was calculated: *The DNEL is a hazard assessment value that means no adverse effects should occur at or below exposures to 0.01 milligrams of GenX per kg of body weight per day*.

Our calculations at OOEB give us an estimate for a safe **drinking water concentration**

- OEEB used Agency for Toxic Substances and Disease Registry (ATSDR) exposure factors for infants (7.8kg, 1.1 L water/day) to calculate the corresponding **concentration** in water that would result in an exposure to the DNEL of 0.01 mg/kg/day.
  - DOSE (mg/kg/day) = [Concentration (mg/L) x Intake rate (L/day)] / Body weight (kg)
  - 0.01 mg/kg/day = [Concentration (mg/L) x 1.1 L/day)] / 7.8 kg
  - Concentration = 0.07097 mg/L = 70,909 ng/L or parts per trillion

**Amy Risen, PhD**
Environmental Toxicologist
Division Public Health, Occupational and Environmental Epidemiology
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Raleigh, NC 27699-1912

| | |
|---|---|
| **From:** | Dittman, Elizabeth |
| **To:** | Holt, Kennedy; Risen, Amy J |
| **Subject:** | FW: More resources - Your GenX question |
| **Date:** | Tuesday, June 13, 2017 8:51:23 AM |
| **Attachments:** | Sun et al. GenX in the Cape Fear River 2016.pdf<br>Newton Final.pdf<br>image002.png |


**Beth Dittman**
Toxicologist and Public Health Assessor
Division of Public Health, Occupational and Environmental Epidemiology Branch
North Carolina Department of Health and Human Services

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Beth.Dittman@dhhs.nc.gov

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Raleigh, NC 27699




**From:** Henry, Audra E. (ATSDR/DCHI/OD) [mailto:ate1@cdc.gov]
**Sent:** Tuesday, June 13, 2017 8:24 AM
**To:** Dittman, Elizabeth <Beth.Dittman@dhhs.nc.gov>
**Cc:** Henry, Audra E. (ATSDR/DCHI/OD) <ate1@cdc.gov>
**Subject:** More resources - Your GenX question

Beth,

I enclosed two papers that might be useful. Both reports are out of EPA's National Exposure Research Lab. One looks at these species in the Cape Fear River Basin and the other in the Tennessee River near Decatur, AL. I hope this helps.


Audra Henry, MS
Technical Project Officer
ATSDR Division of Community Health Investigations
770-488-3758

ate1@cdc.gov

---

| | |
|---|---|
| **From:** | Dittman, Elizabeth |
| **To:** | Risen, Amy J |
| **Subject:** | FW: Your question about GenX |
| **Date:** | Monday, June 12, 2017 9:46:41 AM |
| **Attachments:** | image002.png |

See below. I don't think it includes any articles we haven't already seen, but a potential EPA contact for you if you want to reach out directly. Additionally, I looked on the Sharepoint site and the most useful thing would be this: https://www.atsdr.cdc.gov/substances/toxsubstance.asp?toxid=237


**Beth Dittman**
Toxicologist and Public Health Assessor
Division of Public Health, Occupational and Environmental Epidemiology Branch
North Carolina Department of Health and Human Services

919 707 5906 office
919 870 4807 fax
Beth.Dittman@dhhs.nc.gov

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1912 Mail Service Center
Raleigh, NC 27699


Nothing Compares



**From:** Henry, Audra E. (ATSDR/DCHI/OD) [mailto:ate1@cdc.gov]
**Sent:** Monday, June 12, 2017 9:32 AM
**To:** Dittman, Elizabeth <Beth.Dittman@dhhs.nc.gov>
**Cc:** Henry, Audra E. (ATSDR/DCHI/OD) <ate1@cdc.gov>
**Subject:** Your question about GenX

Hi Beth,

We do not have a specific person to consult with about general GenX questions as this is an emerging chemical. However, we have related PFAS resources on our SharePoint site (https://partner.cdc.gov/Sites/NCEH/ATSDR/DCHI/science/PFAS/default.aspx) that may be useful to you. Please see the information from EPA below as an additional resource. Let me know if you have a specific site request regarding GenX/PFAS. If our SharePoint site does not help, we can then better identify other subject matter experts or resources for you.

Audra Henry, MS
Technical Project Officer
ATSDR Division of Community Health Investigations
770-488-3758
ate1@cdc.gov

---

**From:** Wheeler, John (CDC epa.gov)
**Sent:** Friday, June 09, 2017 3:07 PM
**To:** Henry, Audra E. (ATSDR/DCHI/OD) <ate1@cdc.gov>
**Cc:** Forrester, Tina (ATSDR/DCHI/OD) <txf5@cdc.gov>; Moore, Susan (ATSDR/DCHI/SSB) <sym8@cdc.gov>; Webster, James <Webster.James@epa.gov>
**Subject:** FW: NC contaminant

Audra,
Here is some information  on this chemical, GenX, provided by Brian Englert.  You may share this email with the state (I am missing Beth's email address).

Let me know if I can help further.
John
470-426-9231

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**From:** Englert, Brian
**Sent:** Friday, June 09, 2017 2:29 PM
**To:** Webster, James <Webster.James@epa.gov>; Wheeler, John <Wheeler.John@epa.gov>
**Cc:** Moore, Tony <moore.tony@epa.gov>
**Subject:** Re: NC contaminant

Here is some more information on this.

Per the source below, the Gen X chemical is made at Chemours Co. which is about 50 miles upstream of the raw water intakes for the Cape Fear Public Utility Authority. GenX was detected there by independent researchers in 2013.

Couple that with the claim it causes cancer in lab animals and the company and Cape Fear Public Utility have made statements to the press. Both can be found in these links.

http://www.starnewsonline.com/news/20170607/toxin-taints-cfpua-drinking-water/1

Toxin taints CFPUA drinking water

www.starnewsonline.com

Utility can't filter out chemical produced upriver at Fayetteville plant

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http://www.wect.com/story/35622396/companies-react-to-study-indicating-presence-of-unregulated-toxin-in-water-supply

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## Companies react to study indicating presence of unregulated toxin in water supply

www.wect.com

Water companies and local officials are reacting to a study published in the Wilmington StarNews this week indicating the presence of an unregulated chemical known in the trade market as GenX in th...

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Brian Englert, PhD
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61 Forsyth Street. S.W.
Atlanta, Georgia 30303
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Fax: (404) 562-8699
englert.brian@epa.gov

To report an oil or chemical spill please call the National Response Center at 1-800-424-8802

---

**From:** Englert, Brian
**Sent:** Friday, June 9, 2017 2:10 PM
**To:** Webster, James; Wheeler, John
**Cc:** Moore, Tony
**Subject:** Re: NC contaminant

Jim/John,

Its a Dupont patented technology that offers an alternative to use of PFOA. It is apparently more envionmentally friendly, less water soluble and excretes from the body faster (so Dupont says). See attached.

I believe GenX is actually the name Dupont uses to describe the technology the chemical is actually used in.

"GenX chemical" likely refers to one of the chemicals involved. Its appears to be a amide (carboxylic acid with a nitrogen) instead of an acid (PFOA) or sulfonate (PFOS). It also contains oxygen in the chain as opposed to just carbon and flourine.

Just checked and there are new stories circulating on this issue. The one I linked to below claims its been detected in the Cape Fear River. Several mention that a new study claims it may cause cancer in lab animals. That may have prompted new interest in this issue.

http://whqr.org/post/genx-compound-mystery-most#stream/0

Thats all the info I have right now. I'll see if I can learn more.

GenX Compound: A Mystery To Most

whqr.org

GenX. No, we don't mean Generation X. GenX is a chemical compound we first reported on yesterday. That's when the StarNews reported on this toxic

Brian Englert, PhD
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Fax: (404) 562-8699
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To report an oil or chemical spill please call the National Response Center at 1-800-424-8802



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Cape Fear Public Utility Authority

Stewardship. Sustainability. Service.

James R. Flechtner, PE
Executive Director
235 Government Center Drive
Wilmington, NC 28403
910-332-6542
jim.flechtner@cfpua.org

June 7, 2017

Ms. Sheila Holman
State of North Carolina
Department of Environmental Quality
Assistant Secretary for Environment
1601 Mail Service Center
Raleigh, North Carolina 27699-1601

Dear Ms. Holman:

Cape Fear Public Utility Authority provides water and sewer service to nearly 200,000 customers in New Hanover County and the City of Wilmington. In addition to obtaining raw water from groundwater sources, the Authority uses surface water from the Cape Fear River, just upstream of Lock & Dam # 1 in Bladen County for treatment at the Sweeney Water Treatment Plant and distribution to customers. The Sweeney Water Treatment Plant uses advanced treatment processes such as advanced coagulation/flocculation/sedimentation, ozone and UV, and BAC filtration.

Recent research through N. C. State University shows that, since the year 2000 per and poly-fluoroalkyl substances have been introduced onto the market to replace long chain perfluoroalkyl acids (e.g. perfluoroctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) and their respective precursors). This research indicates these poly-fluoroalkyl substances are present in the Lower Cape Fear River source water. These compounds are currently not regulated at the state or federal levels for discharge into the river. Due to the persistence of these compounds and the ineffectiveness of existing water treatment technologies in removing these compounds, these substances should be regulated at the point of discharge into the river to ensure they do not compromise public water supplies.

Enclosed is a publication titled "Legacy and Emerging Perfluoroalkyl Substances Are Important Drinking Water Contaminates in the Cape Fear River Watershed of North Carolina" for your reference. As this is newly available information, we would welcome your assistance in evaluating implications for the area's source water. We would support actions identified by NCDEQ to ensure proper regulation and management of the dischargers for the protection of the river and its users. If additional information or assistance is needed, please contact me.

Sincerely,

James R. Flechtner, PE
Executive Director

Copy: Jay Zimmerman, Director NCDWR
Julie Grzyb, NPDES Permitting Supervisor
Jessica Godreau, PWS Section Chief

Enclosure

Environmental
Quality

ROY COOPER
*Governor*

MICHAEL S. REGAN
*Secretary*

June 9, 2017

Mr. James Flechtner, PE
Executive Director
Cape Fear Public Utility Authority
235 Government Center Drive
Wilmington, N.C. 28403

Dear Mr. Flechtner:

Thank you for your June 7 letter regarding the presence of poly-fluoroalkyl substances present in the Lower Cape Fear River. We certainly understand the public concerns surrounding this issue and are working with the EPA and others to better understand the chemical compound and any potential impacts it may have.

It iss important that people know that drinking water from the Cape Fear Public Utility Authority and other utilities supplying consumers in the Lower Cape Fear Region meets all state and federal drinking water standards. Thank you for reinforcing that message with your customers and the media in the recent articles on this topic.

The EPA is the sole agency responsible for establishing drinking water standards nationwide. The federal agency has extensive resources necessary to determine the nature, extent and potential impacts of chemicals such as GenX. As such, the North Carolina Department of Environmental Quality is awaiting guidance from the EPA that will provide our agency with the information needed to begin developing regulatory limits for GenX.

We recognize that the regulatory process can sometimes take considerable time. While we are awaiting guidance from the EPA, staff in DEQ will be working with Chemours to assess waste streams containing GenX and determine if the company can reduce the amount of the chemical compound being discharged to the river. I am also working closely with staff and health experts at the N.C. Department of Health and Human Services to stay abreast of any new developments from the numerous interested stakeholders so we will can take swift action to address public health concerns.

Our No. 1 priority in DEQ is to protect public health and the environment. That is the mission that guides us. Please feel free to reach out to me at Sheila.Holman@ncdenr.gov or 919-707-8619 if you have questions, concerns or suggestions. I look forward to working with you.

Sincerely,

Sheila Holman
Assistant Secretary for the Environment

State of North Carolina | Environmental Quality
217 West Jones Street | 1601 Mail Service Center | Raleigh, North Carolina 27699-1601
919 707 8600

# Perfluoroalkyl ether carboxylic acids: Occurrence in the Cape Fear river watershed and fate in drinking water treatment processes

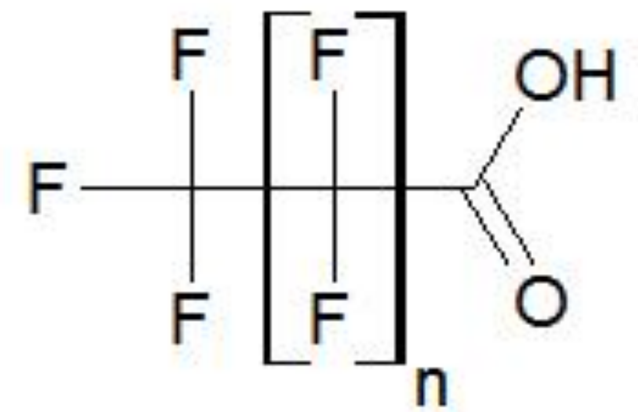
Mei Sun, Elisa Arevalo, Leigh-Ann Dudley, Andrew Lindstrom, Mark Strynar, Detlef Knappe

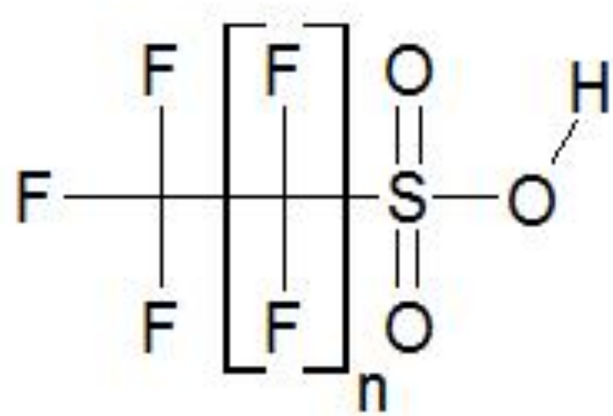
NC STATE UNIVERSITY

Wilmington, April 19, 2017

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

# Perfluoroalkyl acids are organic compounds in which all C-H bonds are replaced with C-F bonds.

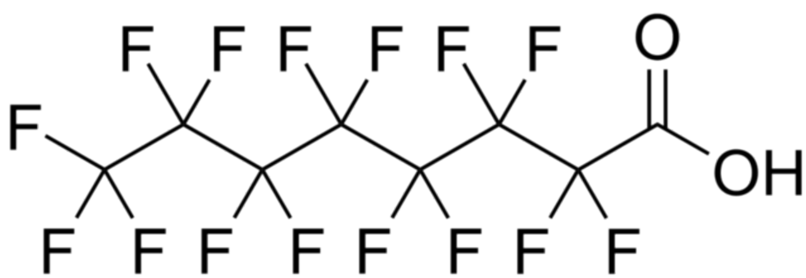


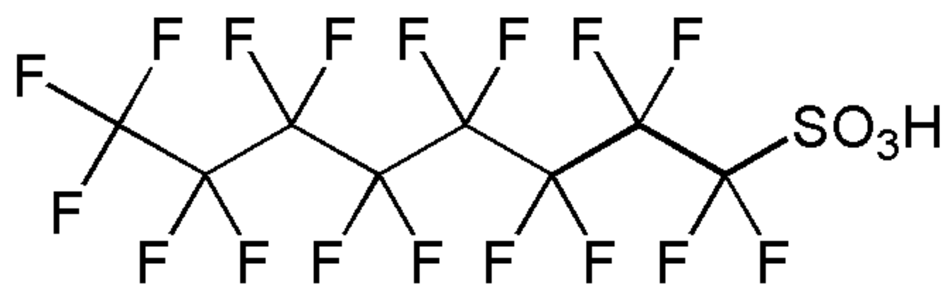


Long-chain PFASs:

PFCAs: $C_nF_{2n+1}COOH$, $n \geq 7$

PFSAs: $C_nF_{2n+1}SO_3H$, $n \geq 6$





# Long-chain PFASs have long half-lives in humans

- Half-lives in humans
  - PFOA: 3.8 years
  - PFOS: 5.4 years
  - PFBS: 4 months
- Toxicokinetic differences for PFOA
  - 17-19 days in mice
  - 4 hours in female rats



## To protect the public from adverse health effects, health based guidelines have been established

| | |
|---|---|
| EPA Health Advisory (chronic exposure) → | PFOS + C8: 70 ng/L |
| New Jersey guidance level (C8) and recommended MCL (C9) → | C8: 40 ng/L<br>C9: 13 ng/L |

# Are PFASs a concern in US drinking water?

Six PFASs were included in the third Unregulated Contaminant Monitoring Rule (UCMR3)

| Compound | MRL (ng/L) |
|---|---|
| Perfluoroheptanoic acid (PFHpA, C7) | 10 |
| Perfluorooctanoic acid (PFOA, C8) | 20 |
| Perfluorononanoic acid (PFNA, C9) | 20 |
| Perfluorobutanesulfonic acid (PFBS) | 90 |
| Perfluorohexanesulfonic acid (PFHxS) | 30 |
| Perfluorooctanesulfonic acid (PFOS) | 40 |

Samples collected from January 2013 – December 2015
Public Water Systems (PWSs) serving >10,000 people

# At first glance, UCMR3 data suggest low PFAS detection frequency

**UCMR3 requires monitoring for six PFASs in US drinking water.**
**Monitoring began in 2013, and latest data release was January 2017.**

| PFAS | MRL (ng/L) | Occurrence (%) | Max. Concentration (ng/L) | Locations with high concentrations |
|---|---|---|---|---|
| C7 | 10 | 0.64 | 410 | Saipan, PA, NY, DE, CO |
| C8 | 20 | 1.03 | 349 | PA, MN, Saipan, DE, WV |
| C9 | 20 | 0.05 | 56 | NJ, DE, PA, MA, NY |
| PFBS | 90 | 0.05 | 370 | GA, Saipan, CO, AL, PA |
| PFHxS | 30 | 0.56 | 1,600 | Saipan, AZ, DE, CO, PA |
| PFOS | 40 | 0.79 | 7,000 | Saipan, DE, CO, PA, WA |

36,972 samples from 4,920 PWSs
PFAS detects: 599 samples (1.6%) from 198 PWSs (4.0%)
Of samples with PFAS detects: 23.4% derived from surface water

Some drinking water samples had PFOA+PFOS levels well above the HAL

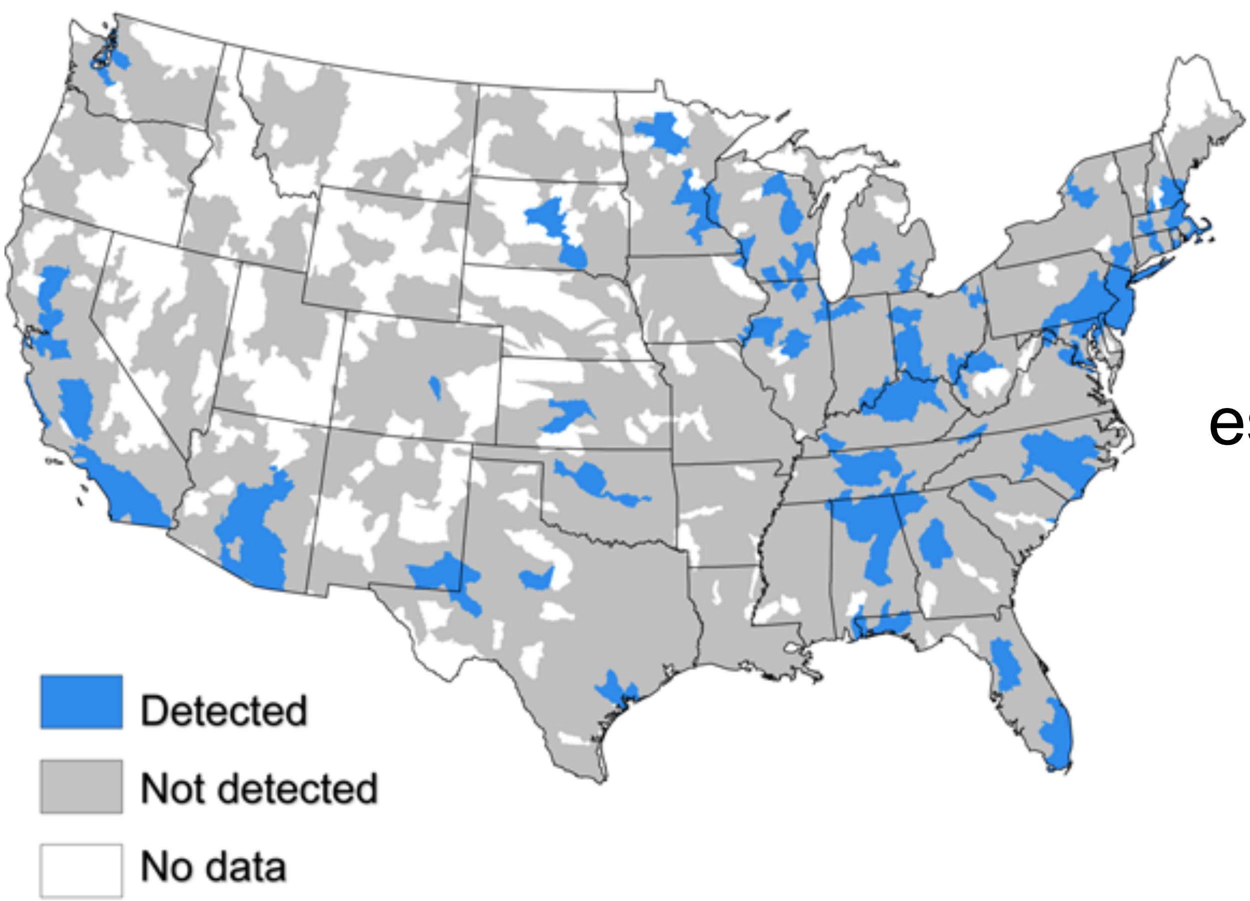
# UCMR3 Data for North Carolina: PFAS detection frequency higher than for entire US

| Compound | MRL (ng/L) | NC Detects |
|---|---|---|
| Perfluoroheptanoic acid (PFHpA, C7) | 10 | 29 (max. 60 ng/L) |
| Perfluorooctanoic acid (PFOA, C8) | 20 | 10 (max. 30 ng/L) |
| Perfluorononanoic acid (PFNA, C9) | 20 | 0 |
| Perfluorobutanesulfonic acid (PFBS) | 90 | 0 |
| Perfluorohexanesulfonic acid (PFHxS) | 30 | 5 (max. 110 ng/L) |
| Perfluorooctanesulfonic acid (PFOS) | 40 | 8 (max. 90 ng/L) |

1,320 samples from 151 PWSs in NC
PFAS detects: 43 samples (3.3%) from 20 PWSs (13.2%)
Of samples with PFAS detects: 79% derived from surface water

# Elevated PFAS levels affect a sizeable number of US residents

Hydrological units with detectable PFASs

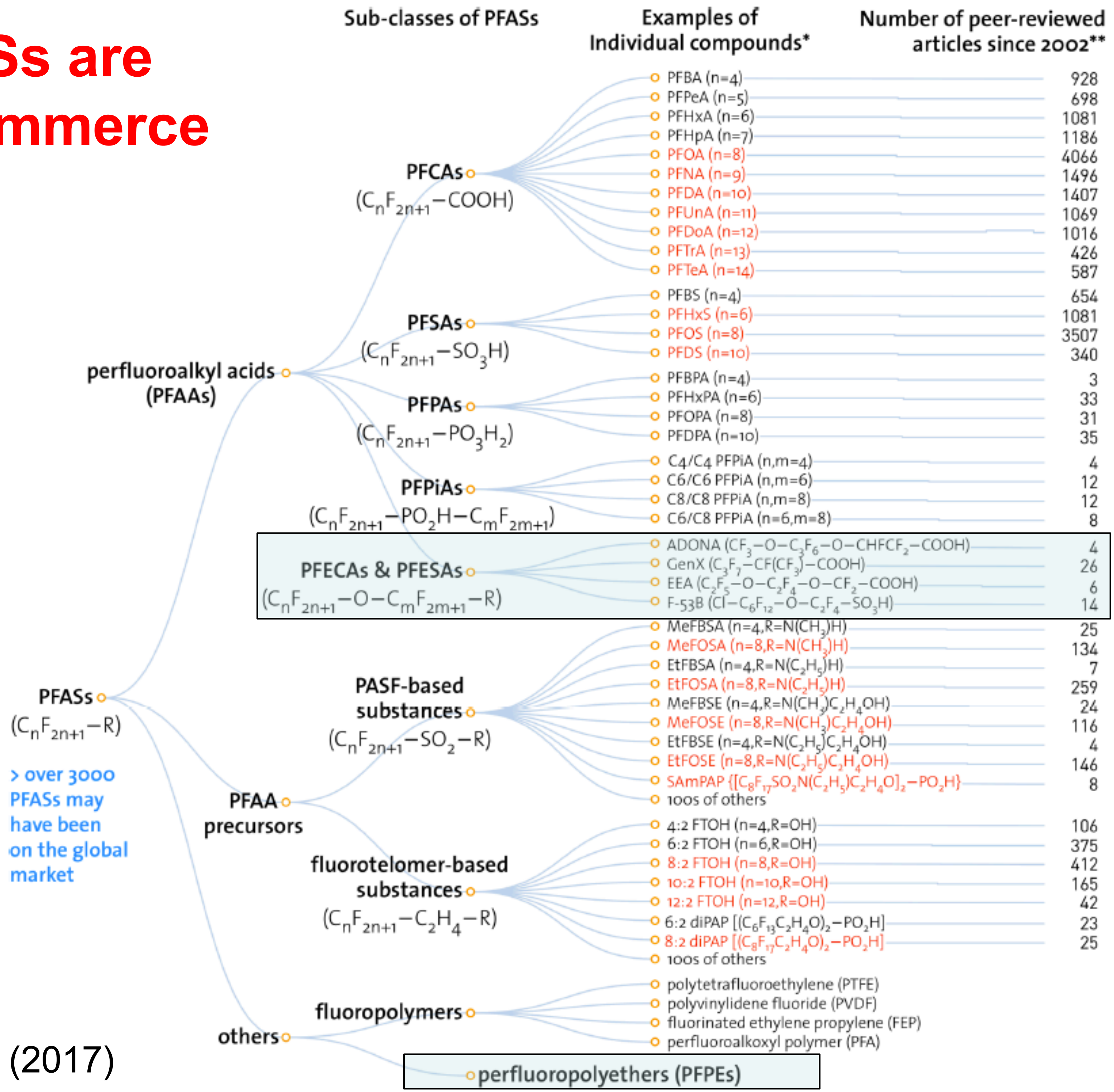



PFOS+PFOA levels estimated to exceed the 70 ng/L HAL in the drinking water of 6 million US residents

Hu et al. ES&T Letters (2016)

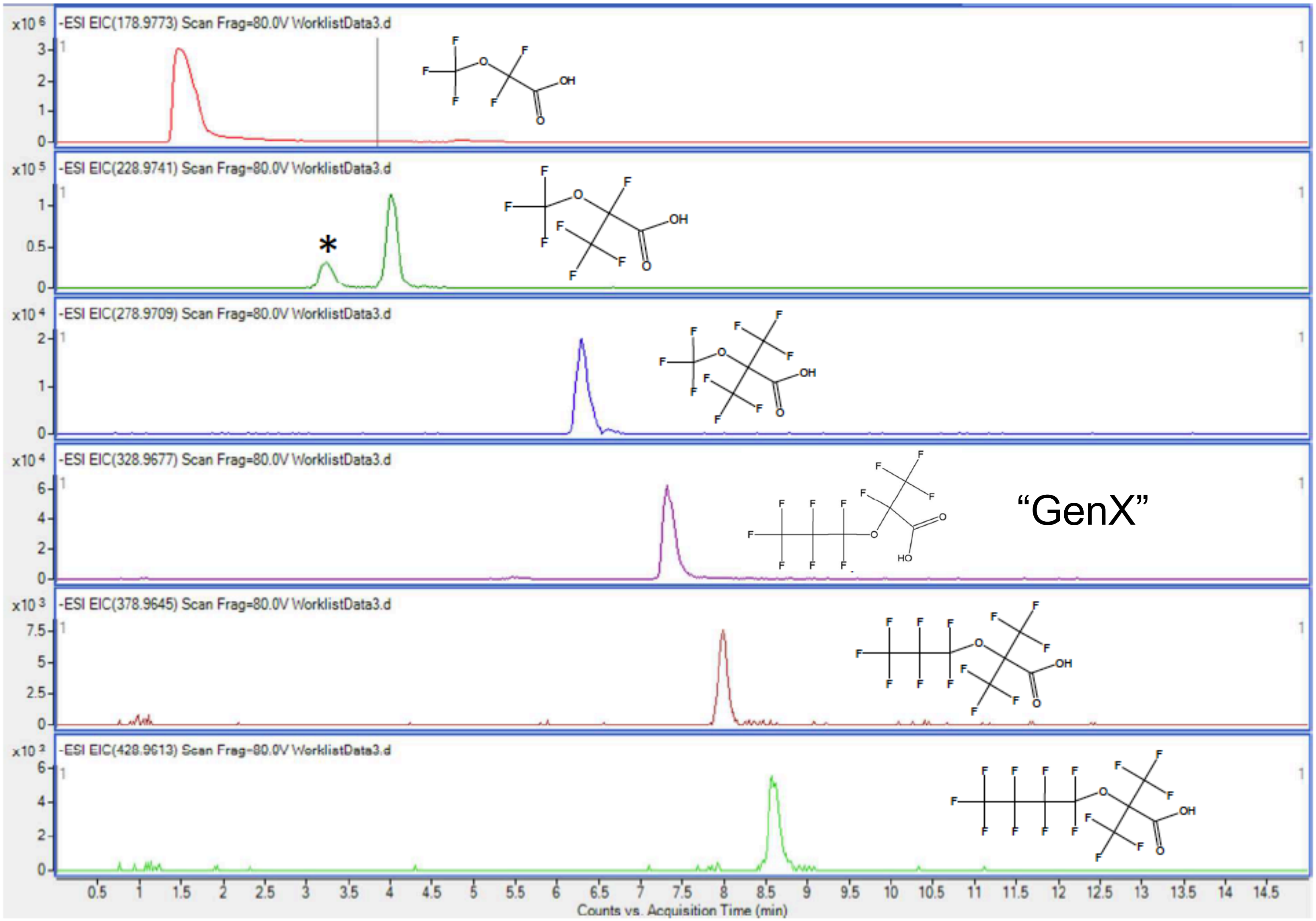
**…but are we seeing the complete picture?**

# Many PFASs are used in commerce



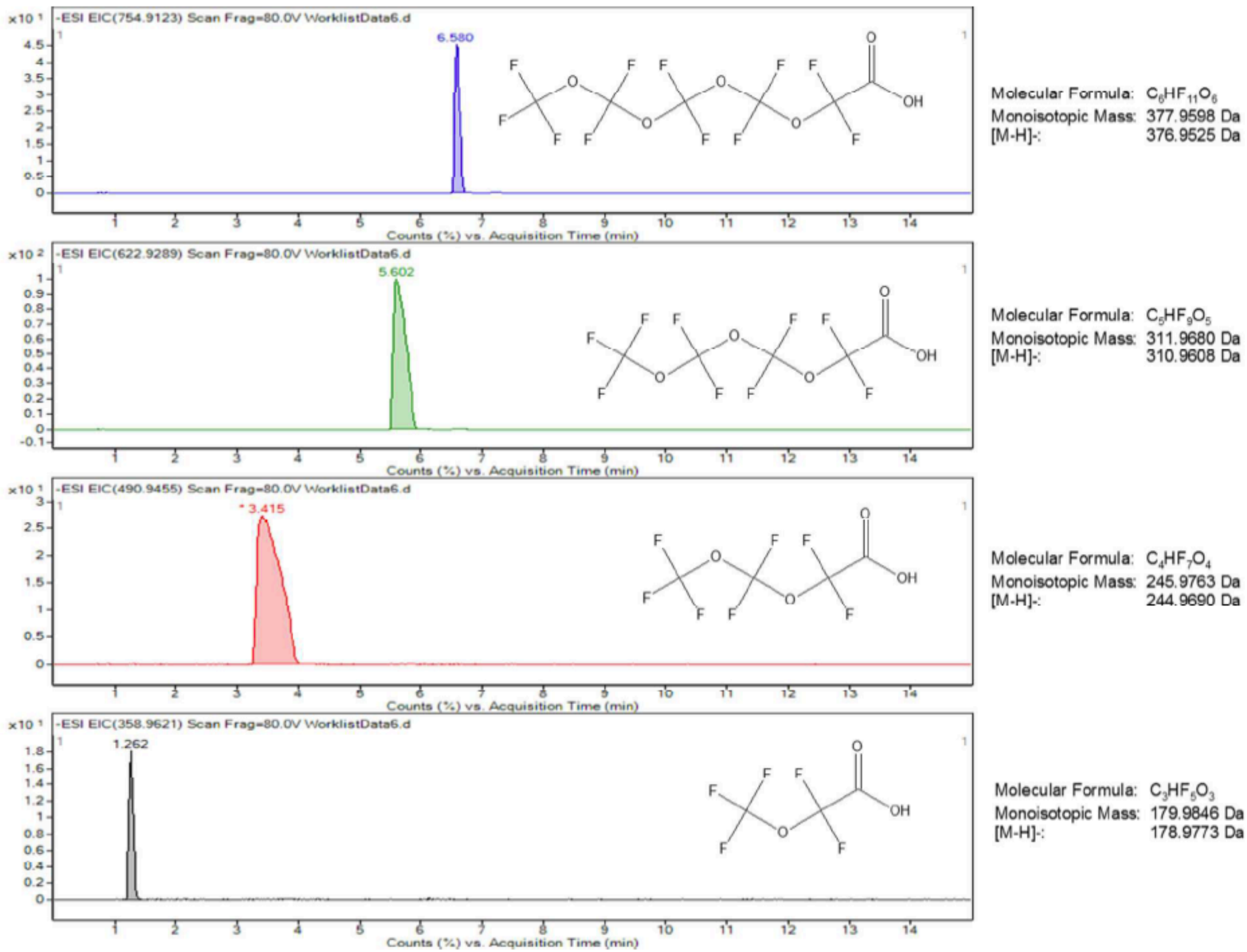

Wang et al. ES&T (2017)

# Two series of PFECAs were recently discovered in the Cape Fear River



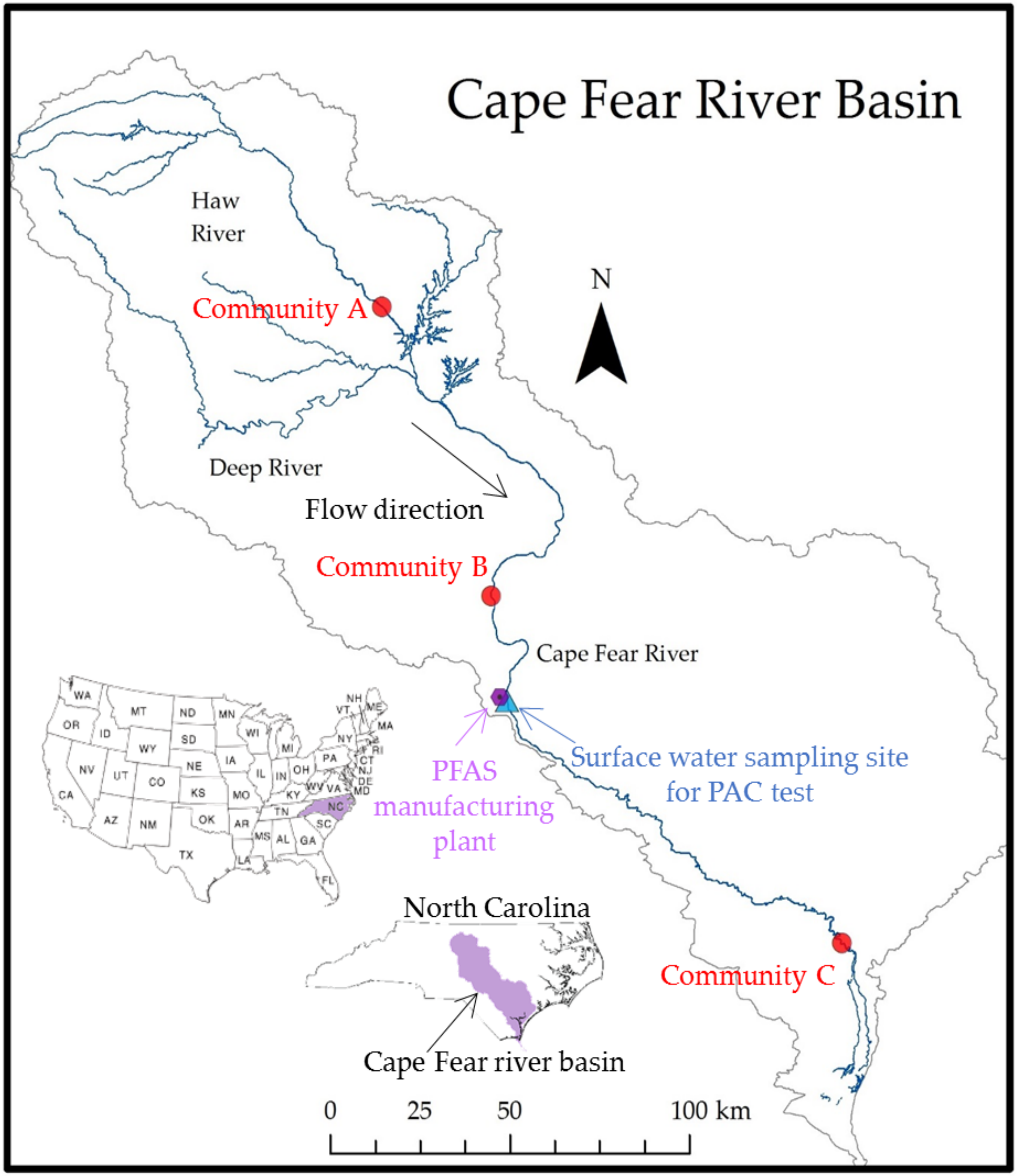

Strynar et al. ES&T (2015)

# Two series of PFECAs were recently discovered in the Cape Fear River




Strynar et al. ES&T (2015)

# Study Design




- Largest watershed in NC
- Supplies ~1.5M people with drinking water

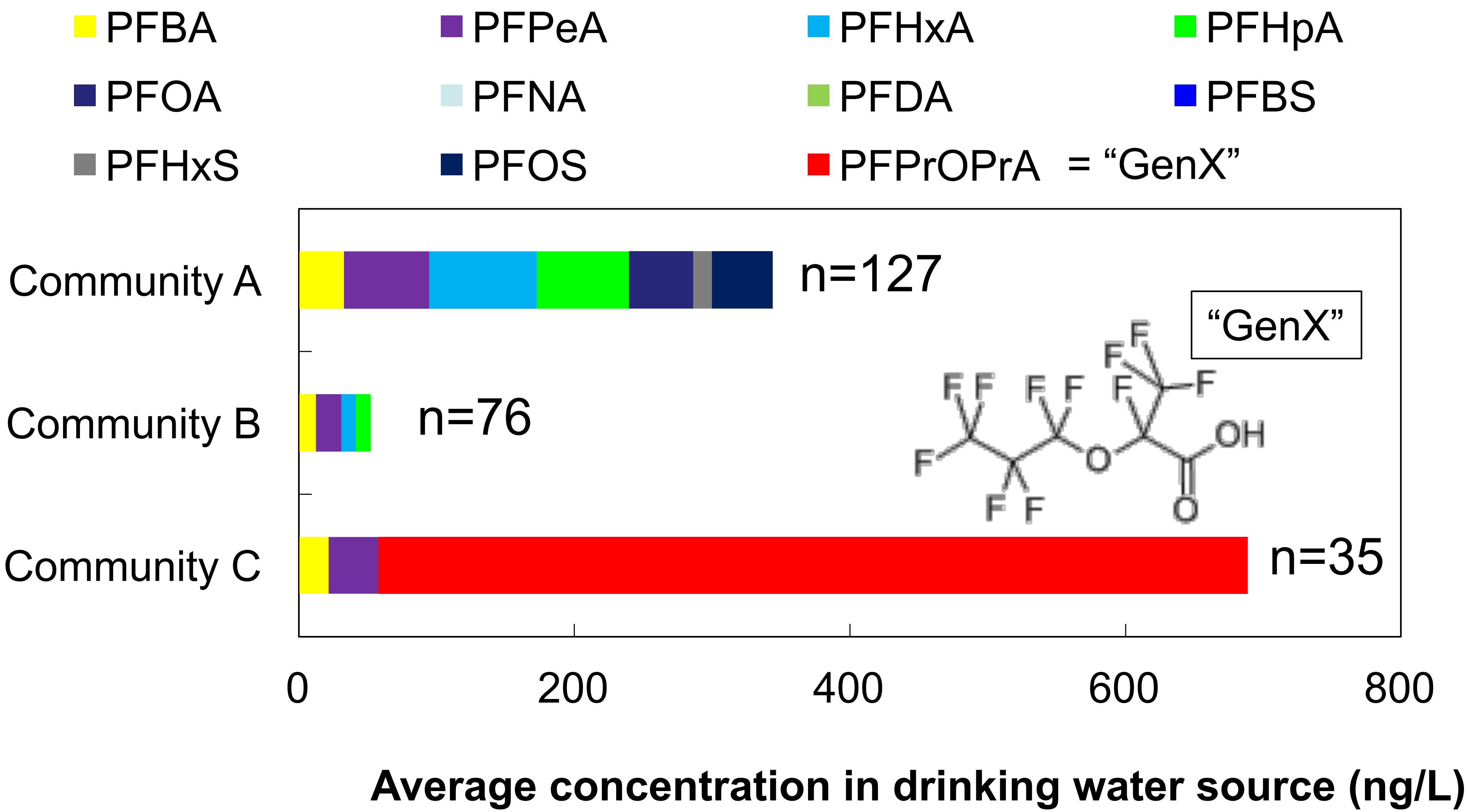
# Sampling Protocol

- Samples collected in 1-L HDPE bottles
- Two sampling approaches
  - Daily composite samples of source water at three drinking water treatment plants
  - Grab samples to track PFAS fate in drinking water treatment plant
- No preservative
- Storage at room temperature
- Analysis within 7 days of sample collection

# PFAS Analytical Method

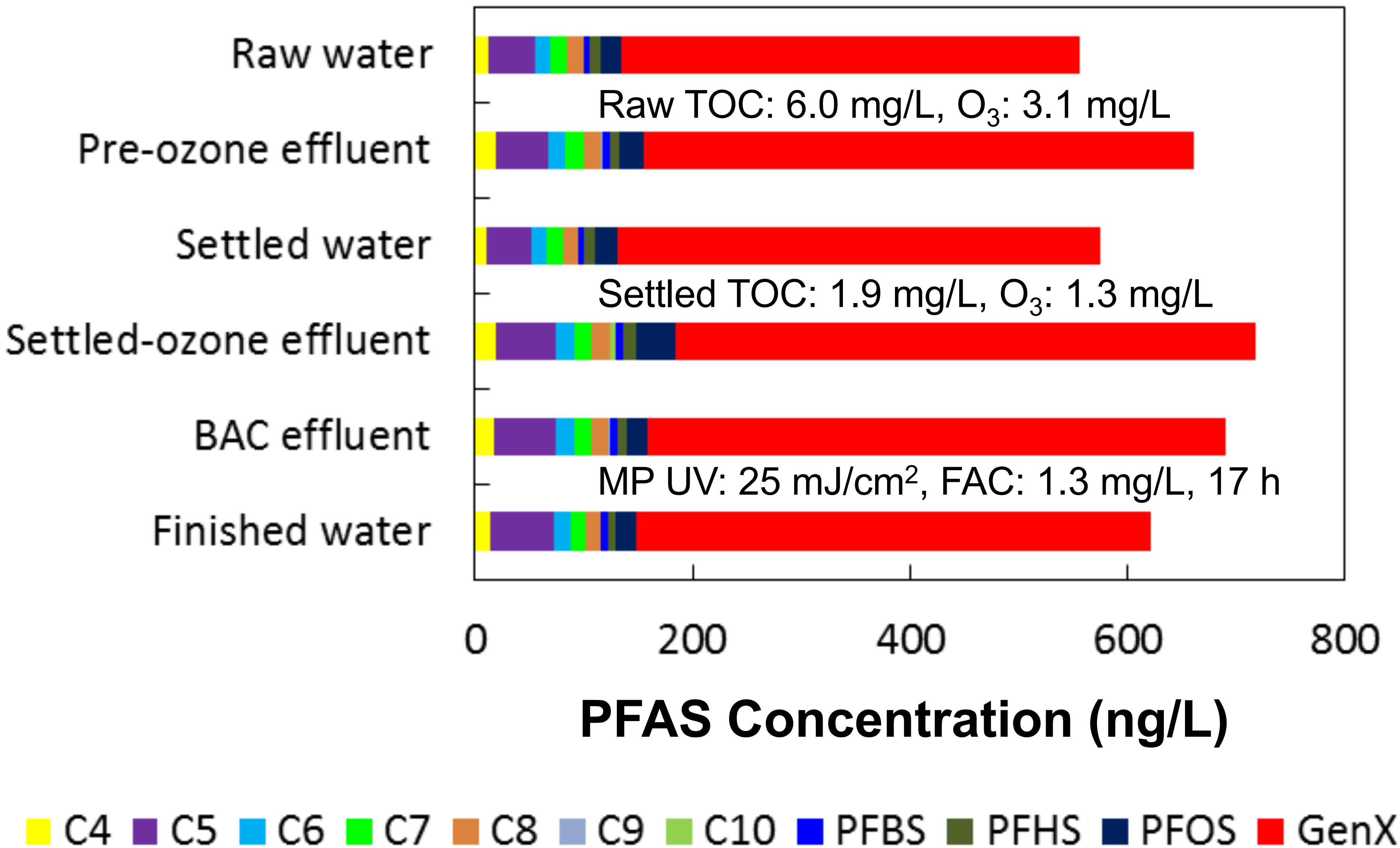
- PFAS concentrations measured by LC-MS/MS
- Large-volume direct injection (900 µL)
- Sample and standard preparation:
  - filtration with a 0.45-µm glass fiber filter
  - addition of mass-labeled internal standards
  - addition of formic acid
- Calibration curves ranged from 10 - 750 ng/L
- Limit of quantitation was 10 ng/L for all PFASs except C10 and PFOS (25 ng/L)

# PFAS Occurrence in the CFR Watershed

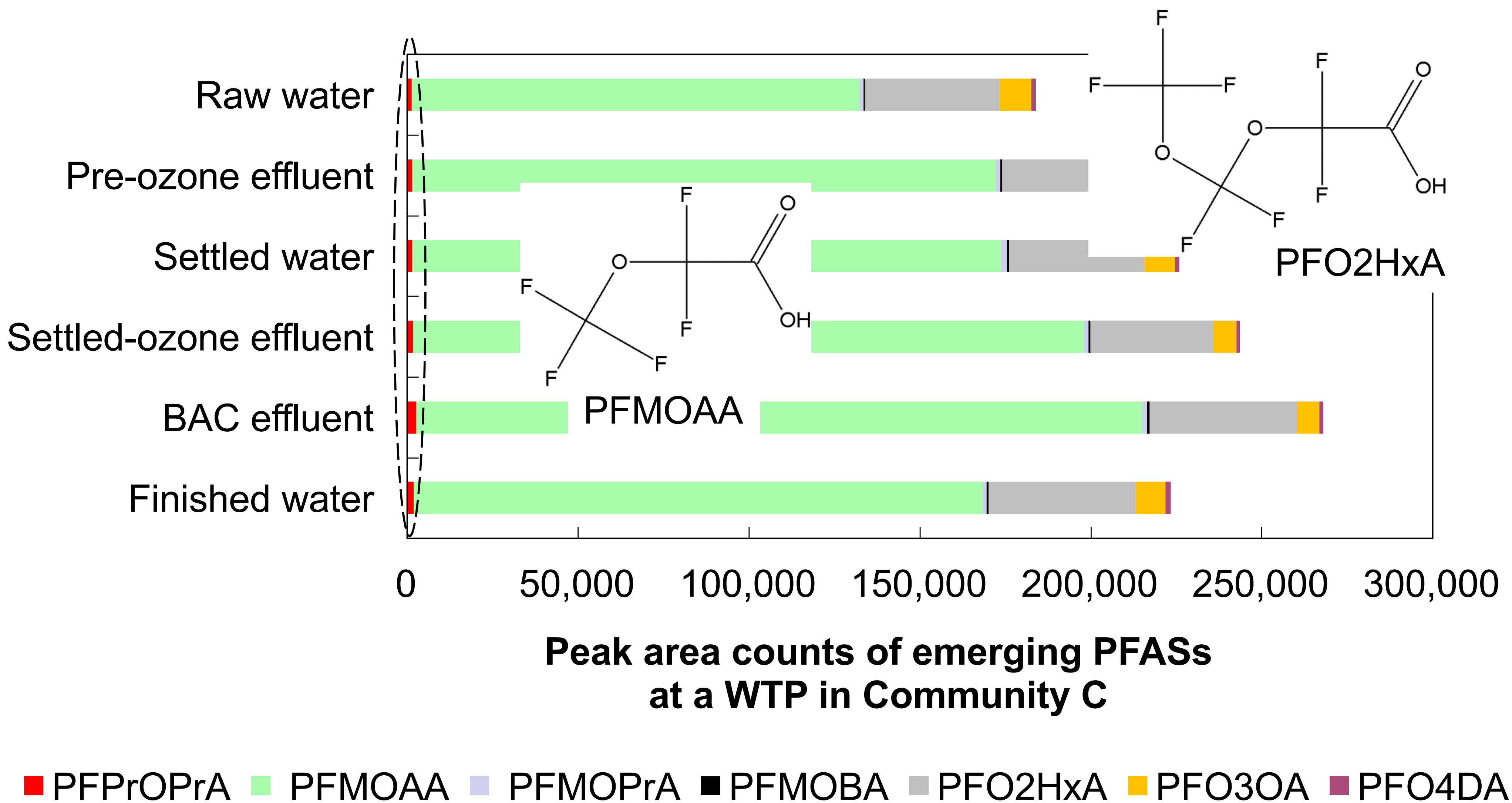



Sun et al. (2016) ES&T Letters

# No measurable PFAS removal by conventional and advanced treatment



# Recently discovered perfluoroalkyl ether carboxylic acids occur at substantially higher concentrations than traditional PFASs and GenX




Sun et al. (2016) ES&T Letters

# What about activated carbon?

**PAC:** thermally activated, wood-based

**PAC Doses:** 30, 60, 100 mg/L

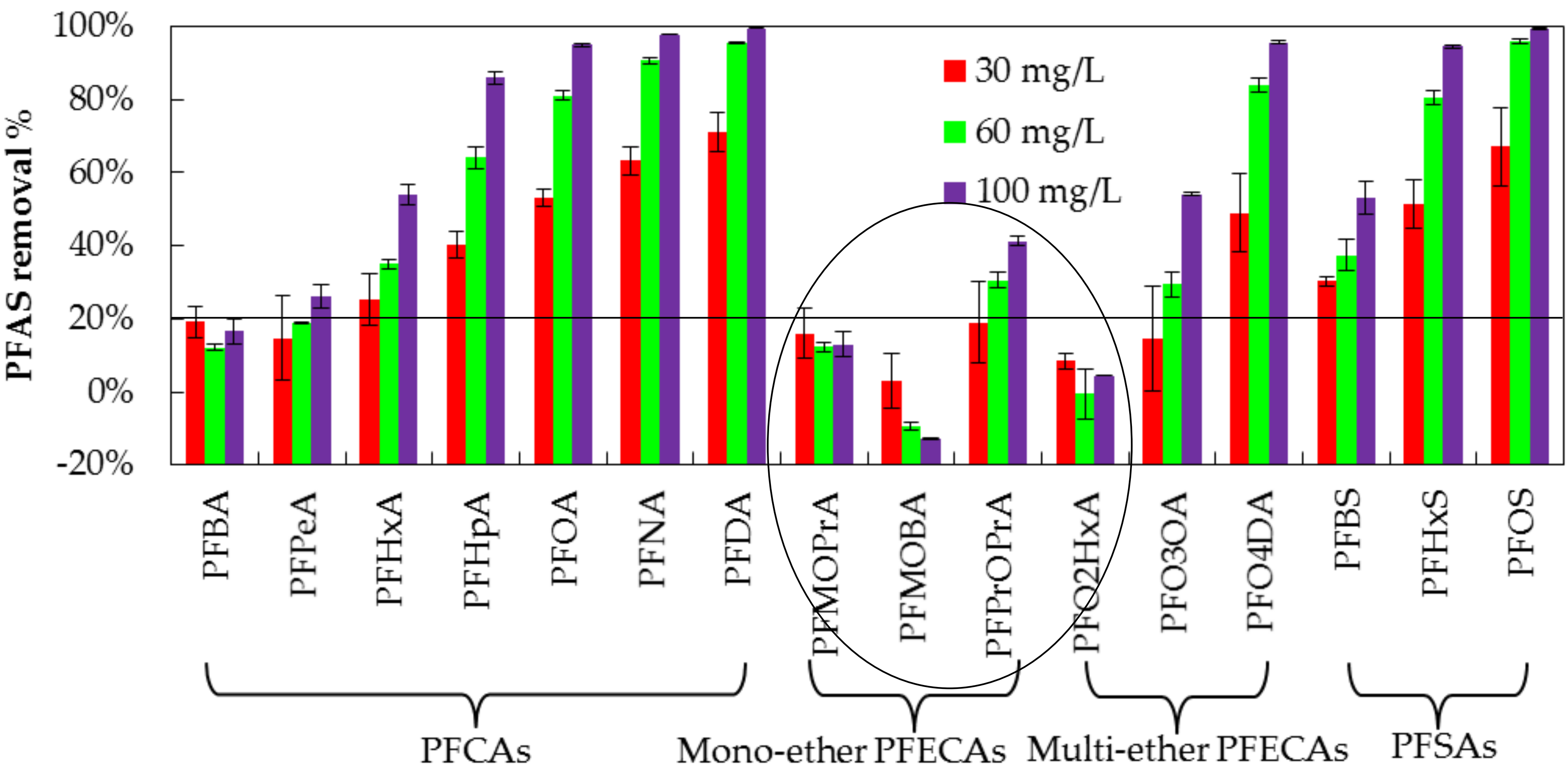
**Contact time:** 60 minutes

**Water:** Cape Fear River (TOC: 9.0 mg/L)

**PFECAs:** Native levels

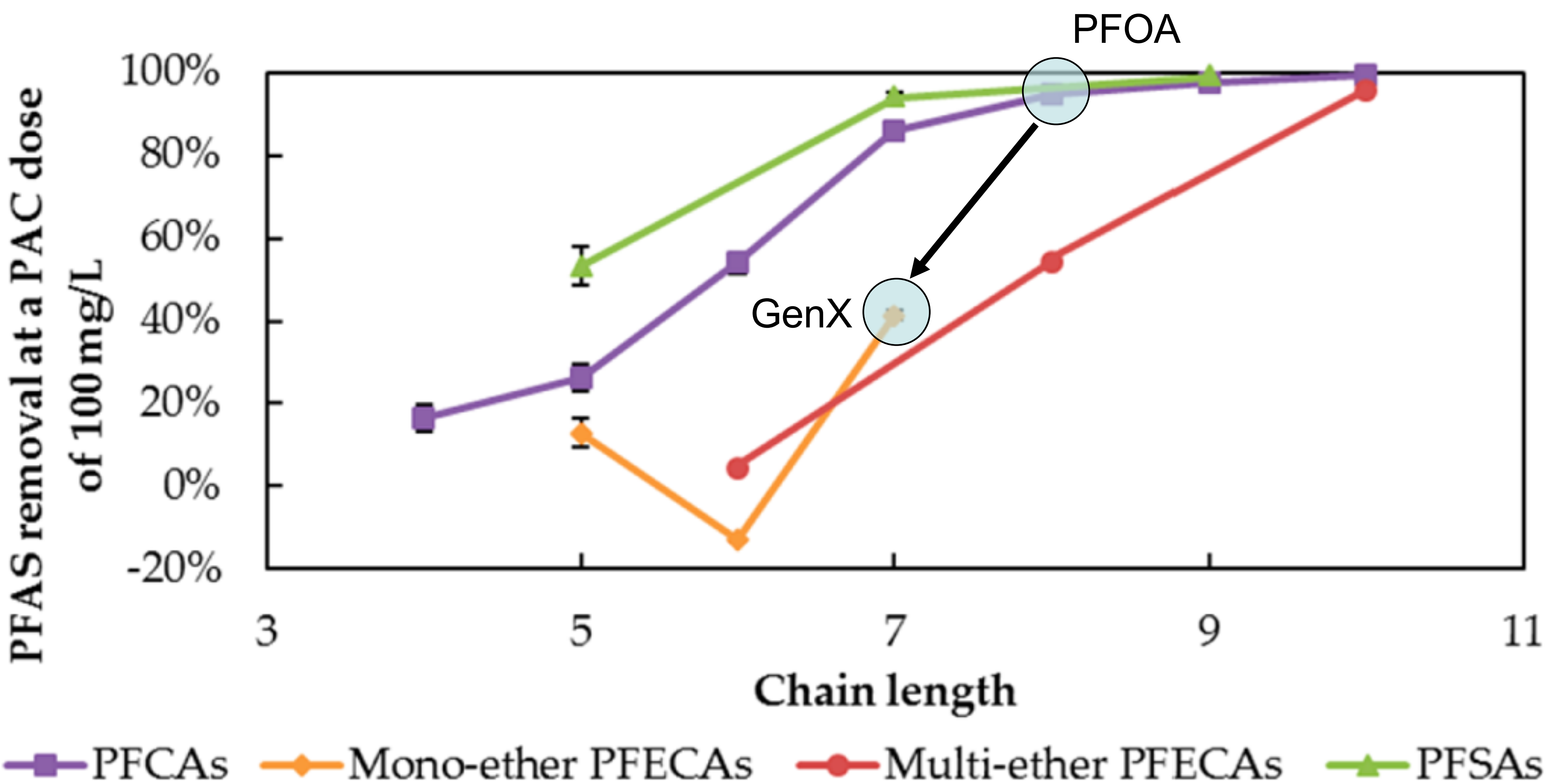
**PFCAs and PFSAs:** Spiked at 1000 ng/L

# Adsorbability of PFASs varies greatly. The PFECAs that were present at the highest concentrations were essentially non-adsorbable




Sun et al. (2016) ES&T Letters

# PFAS adsorbability: PFSA>PFCA>PFECA

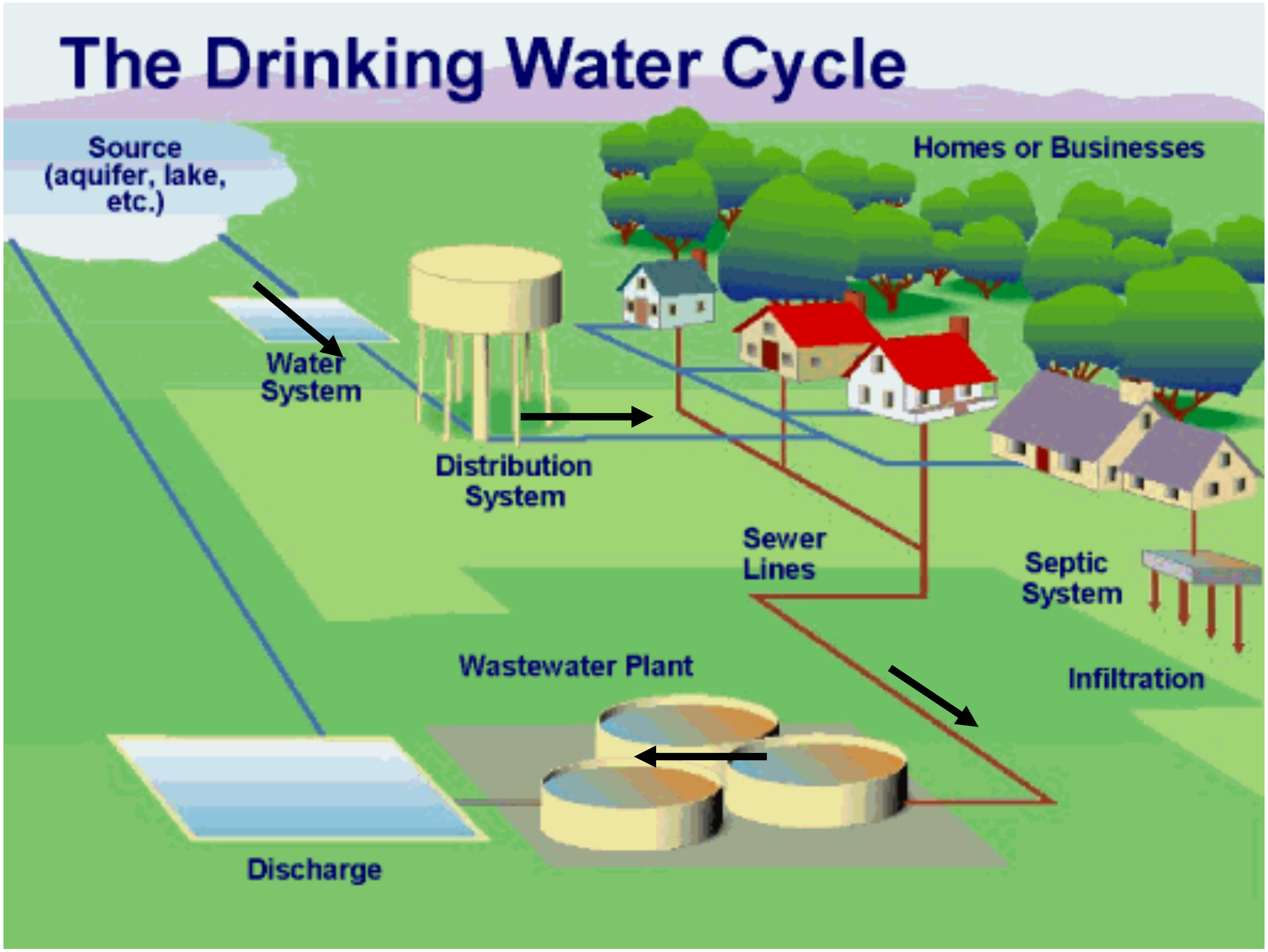



Sun et al. (2016) ES&T Letters

# Proposed sampling plan

1,4-Dioxane and PFAS Fate in Urban Water Cycle

**Objective 1:** Determine fate of 1,4-dioxane and perfluoroalkyl substances (PFASs) in the urban water cycle




Identify residence times/water ages at suitable sampling points to trace a parcel of water through the water/wastewater system

**Objective 2:** Determine fate of 1,4-dioxane and PFASs during aquifer storage and recovery (ASR)

Sample monthly for one ASR cycle (ASR and monitoring wells)

- Recharge
- Storage
- Recovery

| Laboratory | Biweekly | Monthly |
|---|---|---|
| Cape Fear Public Utilities Authority | Temperature, pH, turbidity, specific conductance, dissolved oxygen, redox potential, residual chlorine (during recharge) | Total organic carbon, trihalomethanes |
| NCSU | Nitrate, nitrite, ammonium, sulfate, chloride, bromide, fluoride | 1,4-dioxane, PFASs, dissolved organic carbon, $UV_{254}$ absorbance |

**Objective 3:** Determine possible association of 1,4-dioxane and PFASs with biosolids

Measure 1,4-dioxane and PFAS concentrations in aqueous and solid phases of biosolids. Determine partition coefficients.

# Target Audiences for Results

- CFPUA staff
  - Data expected to illustrate treatment/ operational challenges associated with PFASs and 1,4-dioxane
  - Demonstrate need for source control – eliminate PFASs and 1,4-dioxane at upstream NPDES discharge locations
- North Carolina DEQ
  - Raise awareness about treatment challenges with emerging contaminants
  - Expand scope of current 1,4-dioxane working group to start looking at possibilities for controlling PFAS sources

# Acknowledgments


- National Science Foundation (Award #1550222)
- North Carolina Urban Water Consortium
- Adam Pickett, Chris Smith, Michael Richardson, Ben Kearns at participating utilities


NC STATE UNIVERSITY

Environmental Science & Technology LETTERS

Letter

pubs.acs.org/journal/estlcu

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

Mei Sun,*[,†,‡] Elisa Arevalo,[‡] Mark Strynar,[§] Andrew Lindstrom,[§] Michael Richardson,[∥] Ben Kearns,[∥] Adam Pickett,[⊥] Chris Smith,[#] and Detlef R. U. Knappe[‡]

[†]Department of Civil and Environmental Engineering, University of North Carolina at Charlotte, Charlotte, North Carolina 28223, United States

[‡]Department of Civil, Construction, and Environmental Engineering, North Carolina State University, Raleigh, North Carolina 27695, United States

[§]National Exposure Research Laboratory, U.S. Environmental Protection Agency Research, Triangle Park, North Carolina 27711, United States

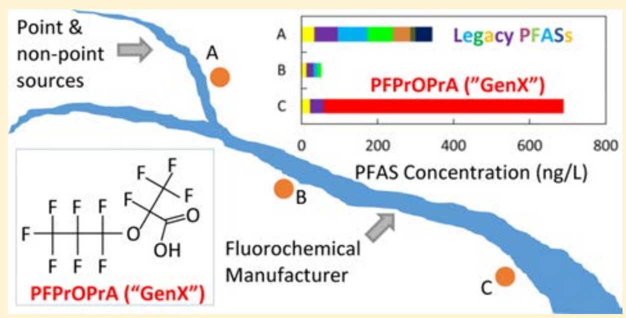
[∥]Cape Fear Public Utility Authority, Wilmington, North Carolina 28403, United States

[⊥]Town of Pittsboro, Pittsboro, North Carolina 27312, United States

[#]Fayetteville Public Works Commission, Fayetteville, North Carolina 28301, United States

*Supporting Information*

**ABSTRACT:** Long-chain per- and polyfluoroalkyl substances (PFASs) are being replaced by short-chain PFASs and fluorinated alternatives. For ten legacy PFASs and seven recently discovered perfluoroalkyl ether carboxylic acids (PFECAs), we report (1) their occurrence in the Cape Fear River (CFR) watershed, (2) their fate in water treatment processes, and (3) their adsorbability on powdered activated carbon (PAC). In the headwater region of the CFR basin, PFECAs were not detected in raw water of a drinking water treatment plant (DWTP), but concentrations of legacy PFASs were high. The U.S. Environmental Protection Agency's lifetime health advisory level (70 ng/L) for perfluorooctanesulfonic acid and perfluorooctanoic acid (PFOA) was exceeded on 57 of 127 sampling days. In raw water of a DWTP downstream of a PFAS manufacturer, the mean concentration of perfluoro-2-propoxypropanoic acid (PFPrOPrA), a replacement for PFOA, was 631 ng/L ($n$ = 37). Six other PFECAs were detected, with three exhibiting chromatographic peak areas up to 15 times that of PFPrOPrA. At this DWTP, PFECA removal by coagulation, ozonation, biofiltration, and disinfection was negligible. The adsorbability of PFASs on PAC increased with increasing chain length. Replacing one $CF_2$ group with an ether oxygen decreased the affinity of PFASs for PAC, while replacing additional $CF_2$ groups did not lead to further affinity changes.




## INTRODUCTION

Per- and polyfluoroalkyl substances (PFASs) are extensively used in the production of plastics, water/stain repellents, firefighting foams, and food-contact paper coatings. The widespread occurrence of PFASs in drinking water sources is closely related to the presence of sources such as industrial sites, military fire training areas, civilian airports, and wastewater treatment plants.[1] Until 2000, long-chain perfluoroalkyl sulfonic acids [$C_nF_{2n+1}SO_3H$; $n \geq 6$ (PFSAs)] and perfluoroalkyl carboxylic acids [$C_nF_{2n+1}COOH$; $n \geq 7$ (PFCAs)] were predominantly used.[2] Accumulating evidence about the ecological persistence and human health effects associated with exposure to long-chain PFASs[3,4] has led to an increased level of regulatory attention. Recently, the U.S. Environmental Protection Agency (USEPA) established a lifetime health advisory level (HAL) of 70 ng/L for the sum of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) concentrations in drinking water.[5,6] Over the past decade, production of long-chain PFASs has declined in Europe and North America, and manufacturers are moving toward short-chain PFASs and fluorinated alternatives.[7−10] Some fluorinated alternatives were recently identified,[8,11] but others remain unknown[12−14] because they are either proprietary or manufacturing byproducts.

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One group of fluorinated alternatives, perfluoroalkyl ether carboxylic acids (PFECAs), was recently discovered in the Cape Fear River (CFR) downstream of a PFAS manufacturing facility.[11] Identified PFECAs included perfluoro-2-methoxyacetic acid (PFMOAA), perfluoro-3-methoxypropanoic acid (PFMOPrA), perfluoro-4-methoxybutanoic acid (PFMOBA), perfluoro-2-propoxypropanoic acid (PFPrOPrA), perfluoro-(3,5-dioxahexanoic) acid (PFO2HxA), perfluoro(3,5,7-trioxaoctanoic) acid (PFO3OA), and perfluoro(3,5,7,9-tetraoxadecanoic) acid (PFO4DA) (Table S1 and Figure S1). The ammonium salt of PFPrOPrA is a known PFOA alternative[15] that has been produced since 2010 with the trade name "GenX". To the best of our knowledge, the only other published PFECA occurrence data are for PFPrOPrA in Europe and China,[15] and no published data about the fate of PFECAs during water treatment are available. Except for a few studies (most by the manufacturer),[16−20] little is known about the toxicity, pharmacokinetic behavior, or environmental fate and transport of PFECAs.

The strong C−F bond makes PFASs refractory to abiotic and biotic degradation,[21] and most water treatment processes are ineffective for legacy PFAS removal.[22−27] Processes capable of removing PFCAs and PFSAs include nanofiltration,[28] reverse osmosis,[25] ion exchange,[28,29] and activated carbon adsorption,[28,29] with activated carbon adsorption being the most widely employed treatment option.

The objectives of this research were (1) to identify and quantify the presence of legacy PFASs and emerging PFECAs in drinking water sources, (2) to assess PFAS removal by conventional and advanced processes in a full-scale drinking water treatment plant (DWTP), and (3) to evaluate the adsorbability of PFASs on powdered activated carbon (PAC).

## ■ MATERIALS AND METHODS

**Water Samples.** Source water of three DWTPs treating surface water in the CFR watershed was sampled between June 14 and December 2, 2013 (Figure S2). Samples were collected from the raw water tap at each DWTP daily as either 8 h composites (DWTP A, 127 samples) or 24 h composites (DWTP B, 73 samples; DWTP C, 34 samples). Samples were collected in 250 mL HDPE bottles and picked up (DWTPs A and B) or shipped overnight (DWTP C) on a weekly basis. All samples were stored at room temperature until they were analyzed (within 1 week of receipt). PFAS losses during storage were negligible on the basis of results of a 70 day holding study at room temperature. On August 18, 2014, grab samples were collected at DWTP C after each unit process in the treatment train [raw water ozonation, coagulation/flocculation/sedimentation, settled water ozonation, biological activated carbon (BAC) filtration, and disinfection by medium-pressure UV lamps and free chlorine]. Operational conditions of DWTP C on the sampling day are listed in Table S2. Samples were collected in 1 L HDPE bottles and stored at room temperature until they were analyzed. On the same day, grab samples of CFR water were collected in six 20 L HDPE carboys at William O. Huske Lock and Dam downstream of a PFAS manufacturing site and stored at 4 °C until use in PAC adsorption experiments (background water matrix characteristics listed in Table S3).

**Adsorption Experiments.** Adsorption of PFASs by PAC was studied in batch reactors (amber glass bottles, 0.45 L of CFR water). PFECA adsorption was studied at ambient concentrations (~1000 ng/L PFPrOPrA, chromatographic peak areas of other PFECAs being approximately 10−800% of the PFPrOPrA area). Legacy PFASs were present at low concentrations (<40 ng/L) and spiked into CFR water at ~1000 ng/L each. Data from spiked and nonspiked experiments showed that the added legacy PFASs and methanol (1 $ppm_v$) from the primary stock solution did not affect native PFECA removal. A thermally activated, wood-based PAC (PicaHydro MP23, PICA USA, Columbus, OH; mean diameter of 12 μm, BET surface area of 1460 $m^2/g$)[30] proven to be effective for PFAS removal in a prior study[29] was used at doses of 30, 60, and 100 mg/L. These doses represent the upper feasible end for drinking water treatment. Samples were taken prior to and periodically after PAC addition for PFAS analysis. PFAS losses in PAC-free blanks were negligible.

**PFAS Analysis.** Information about analytical standards and liquid chromatography−tandem mass spectrometry (LC−MS/MS) methods for PFAS quantification is provided in the Supporting Information.

## ■ RESULTS AND DISCUSSION

**Occurrence of PFASs in Drinking Water Sources.** Mean PFAS concentrations in source water of three DWTPs treating surface water from the CFR watershed are shown in Figure 1.

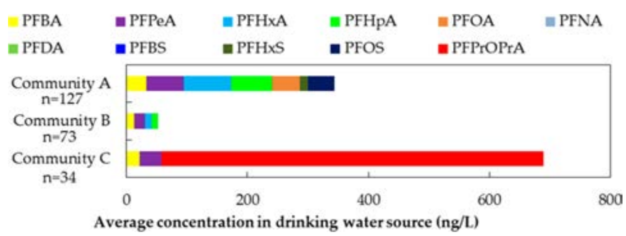


**Figure 1.** Occurrence of PFASs at drinking water intakes in the CFR watershed. Concentrations represent averages of samples collected between June and December 2013. Individual samples with concentrations below the quantitation limits (QLs) were considered as 0 when calculating averages, and average concentrations below the QLs were not plotted.

In communities A and B, only legacy PFASs were detected (mean ∑PFAS of 355 ng/L in community A and 62 ng/L in community B). Detailed concentration data are shown in Table S6 and Figure S3. In community A, PFCAs with four to eight total carbons, perfluorohexanesulfonic acid (PFHxS), and PFOS were detected at mean concentrations above the quantitation limits (QLs). During the 127 day sampling campaign, the sum concentration of PFOA and PFOS exceeded the USEPA HAL of 70 ng/L on 57 days. The mean sum concentration of PFOA and PFOS over the entire study period was 90 ng/L, with approximately equal contributions from PFOS (44 ng/L) and PFOA (46 ng/L). Maximum PFOS and PFOA concentrations were 346 and 137 ng/L, respectively. Similar PFOS and PFOA concentrations were observed in the same area in 2006,[31] suggesting that PFAS source(s) upstream of community A have continued negative impacts on drinking water quality. Also, our data show that legacy PFASs remain as surface water contaminants of concern even though their production was recently phased out in the United States. It is important to note, however, that among the PFCAs that were measured in both 2006 and 2013 (PFHxA to PFDA), the PFCA speciation shifted from long-chain (~80−85% $C_nF_{2n+1}COOH$; $n$ = 7−9) in 2006 to short-chain (76% $C_nF_{2n+1}COOH$; $n$ = 5−6) in 2013. In contrast, the PFSA speciation was dominated by PFOS in both 2006 and 2013.


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Relating total PFAS concentration to average daily streamflow (Figure S4) illustrated a general trend of low PFAS concentrations at high flow, and high concentrations at low flow, consistent with the hypothesis of one or more upstream point sources.

In community B, perfluorobutanoic acid (PFBA) and perfluoropentanoic acid (PFPeA) were most frequently detected with mean concentrations of 12 and 19 ng/L, respectively. Mean PFOA and PFOS concentrations were below the QLs, and the maximum sum concentration of PFOA and PFOS was 59 ng/L. Lower PFAS concentrations in community B relative to community A can be explained by the absence of substantive PFAS sources between the two communities, dilution by tributaries, and the buffering effect of Jordan Lake, a large reservoir located between communities A and B.

In community C (downstream of a PFAS manufacturing site), only mean concentrations of PFBA and PFPeA were above the QLs. The relatively low concentrations of legacy PFASs in the finished drinking water of community C are consistent with results from the USEPA's third unregulated contaminant monitoring rule for this DWTP.[32] However, high concentrations of PFPrOPrA were detected (up to ∼4500 ng/L). The average PFPrOPrA concentration (631 ng/L) was approximately 8 times the average summed PFCA and PFSA concentrations (79 ng/L). Other PFECAs had not yet been identified at the time of analysis. Similar to communities A and B, the highest PFAS concentrations for community C were also observed at low flow (Figure S4). Stream flow data were used in conjunction with PFPrOPrA concentration data to determine PFPrOPrA mass fluxes at the intake of DWTP C. Daily PFPrOPrA mass fluxes ranged from 0.6 to 24 kg/day with a mean of 5.9 kg/day.

**Fate of PFASs in Conventional and Advanced Water Treatment Processes.** To investigate whether PFASs can be removed from impacted source water, samples from DWTP C were collected at the intake and after each treatment step. Results in Figure 2 suggest conventional and advanced treatment processes (coagulation/flocculation/sedimentation, raw and settled water ozonation, BAC filtration, and disinfection by medium-pressure UV lamps and free chlorine) did not remove legacy PFASs, consistent with previous studies.[22−26] The data further illustrate that no measurable PFECA removal occurred in this DWTP. Concentrations of some PFCAs, PFSAs, PFMOPrA, PFPrOPrA, and PFMOAA may have increased after ozonation, possibly because of the oxidation of precursor compounds.[25] Disinfection with medium-pressure UV lamps and free chlorine (located between the BAC effluent and the finished water) may have decreased concentrations of PFMOAA, PFMOPrA, PFMOBA, and PFPrOPrA, but only to a limited extent. Small concentration changes between treatment processes may also be related to temporal changes in source water PFAS concentrations that occurred in the time frame corresponding to the hydraulic residence time of the DWTP.

Results in Figure 2 further illustrate that the PFAS signature of the August 2014 samples was similar to the mean PFAS signature observed during the 2013 sampling campaigns shown in Figure 1; i.e., PFPrOPrA concentrations (400−500 ng/L) greatly exceeded legacy PFAS concentrations. Moreover, three PFECAs (PFMOAA, PFO2HxA, and PFO3OA) exhibited peak areas 2−113 times greater than that of PFPrOPrA (Figure 2b).

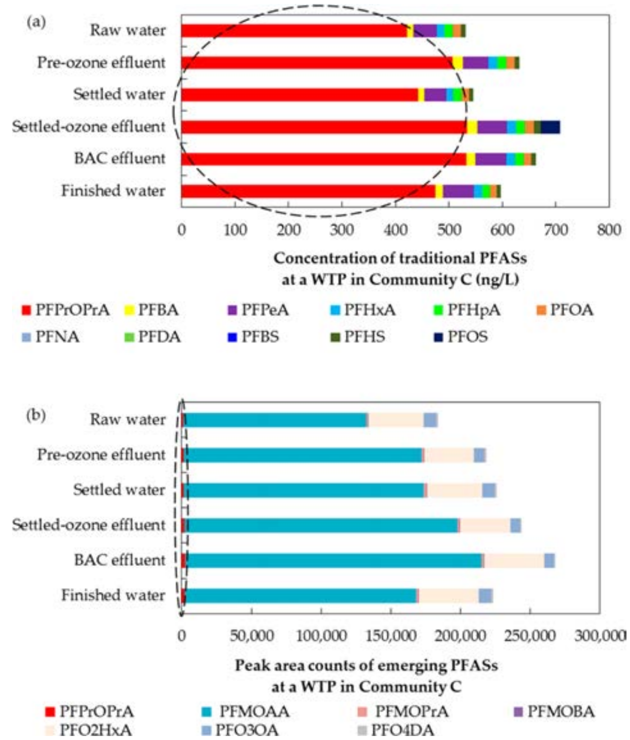


**Figure 2.** Fate of (a) legacy PFASs and PFPrOPrA and (b) PFECAs through a full-scale water treatment plant. Because authentic standards were not available for PFECAs other than PFPrOPrA, chromatographic peak area counts are shown in panel b. PFPrOPrA data are shown in both panels and highlighted with dashed ovals for reference. Compounds with concentrations below the QLs were not plotted.

The existence of high levels of emerging PFASs suggests a need for their incorporation into routine monitoring.

**Adsorption of PFASs by PAC.** PAC can effectively remove long-chain PFCAs and PFSAs, but its effectiveness decreases with decreasing PFAS chain length.[24,25,29] It is unclear, however, how the presence of ether group(s) in PFECAs impacts adsorbability. After a contact time of 1 h, a PAC dose of 100 mg/L achieved >80% removal of legacy PFCAs with total carbon chain lengths of ≥7. At the same PAC dose, removals were 95% for PFO4DA and 54% for PFO3OA, but <40% for other PFECAs. Detailed removal percentage data as a function of PAC contact time are shown in Figure S5. There was no meaningful removal of PFMOBA or PFMOPrA, and the variability shown in Figure S5 is most likely associated with analytical variability. PFMOAA could not be quantified by the analytical method used for these experiments; however, on the basis of the observations that PFAS adsorption decreases with decreasing carbon chain length and that PFECAs with one or two more carbon atoms than PFMOAA (i.e., PFMOPrA and PFMOBA) exhibited negligible removal (Figure 3), it is expected that PFMOAA adsorption is also negligible under the tested conditions.

To compare the affinity of different PFASs for PAC, PFAS removal percentages were plotted as a function of PFAS chain length [the sum of carbon (including branched), ether oxygen, and sulfur atoms] (Figure 3b). The adsorbability of both legacy and emerging PFASs increased with increasing chain length. PFSAs were more readily removed than PFCAs of matching chain length, a result that agrees with those of previous


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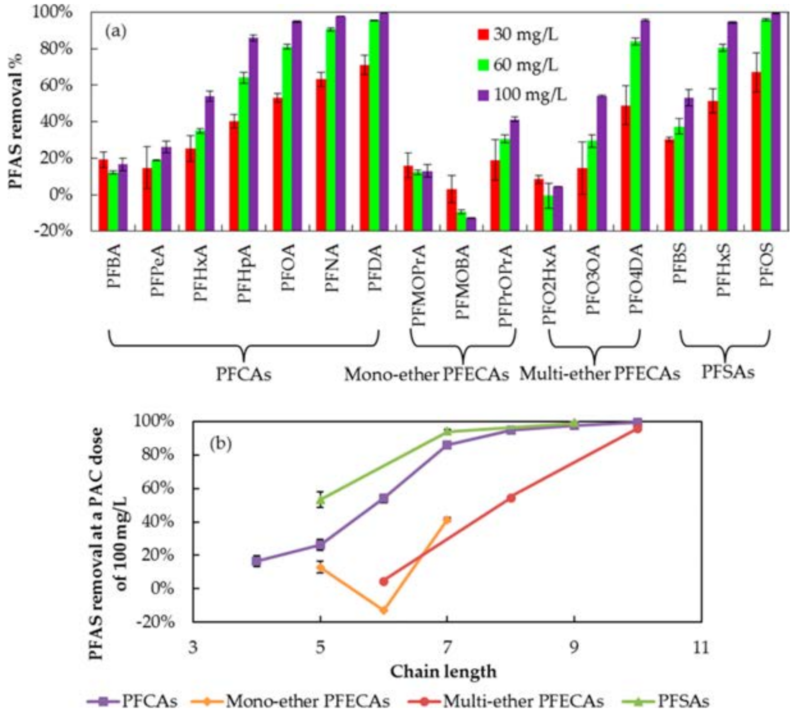


**Figure 3.** PFAS adsorption on PAC (a) at carbon doses of 30, 60, and 100 mg/L and (b) as a function of PFAS chain length. The PAC contact time in CFR water was 1 h. Legacy PFASs were spiked at ∼1000 ng/L, and the emerging PFASs were at ambient concentrations. Figures show average PFAS removal percentages, and error bars show one standard deviation of replicate experiments.

studies.[24,25,29] PFECAs exhibited adsorbabilities lower than those of PFCAs of the same chain length (e.g., PFMOBA < PFHxA), suggesting that the replacement of a $CF_2$ group with an ether oxygen atom decreases the affinity of PFASs for PAC. However, the replacement of additional $CF_2$ groups with ether groups resulted in small or negligible affinity changes among the studied PFECAs (e.g., PFMOBA ∼ PFO2HxA, PFPrOPrA ∼ PFO3OA). Alternatively, if only the number of perfluorinated carbons were considered as a basis of comparing adsorbability, the interpretation would be different. In that case, with the same number of perfluorinated carbons, PFCAs have an affinity for PAC higher than that of monoether PFECAs (e.g., PFPeA > PFMOBA) but an affinity lower than that of multi-ether PFECAs (e.g., PFPeA < PFO3OA).

To the best of our knowledge, this is the first paper reporting the behavior of recently identified PFECAs in water treatment processes. We show that PFECAs dominated the PFAS signature in a drinking water source downstream of a fluorochemical manufacturer and that PFECA removal by many conventional and advanced treatment processes was negligible. Our adsorption data further show that PFPrOPrA ("GenX") is less adsorbable than PFOA, which it is replacing. Thus, PFPrOPrA presents a greater drinking water treatment challenge than PFOA does. The detection of potentially high levels of PFECAs, the continued presence of high levels of legacy PFASs, and the difficulty of effectively removing legacy PFASs and PFECAs with many water treatment processes suggest the need for broader discharge control and contaminant monitoring.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.6b00398.

Six tables, five figures, information about PFASs, analytical methods, and detailed results (PDF)

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### Notes

The views expressed in this article are those of the authors and do not necessarily represent the views or policies of the USEPA.

The authors declare no competing financial interest.

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