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Perfluorinated Compounds in the Cape Fear Drainage Basin in North Carolina

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Concern over perfluorinated organic compounds (PFCs), e.g., perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), is due to a number of recent studies which show that the PFCs are persistent, bioaccumulative, and toxic in animals. Despite sustained interest in this topic, little information is available concerning the environmental distributions of the compounds. In this study, a new method was developed for the analysis of 10 target PFCs and its performance was examined in a systematic evaluation of surface water in the Cape Fear River Basin in North Carolina. One hundred samples from 80 different locations were collected during the spring of 2006. Detectable levels of the target PFCs were found in all samples, and were comparable to values reported previously, with maximum PFOS at 132 ng/L, PFOA at 287 ng/L, perfluorononanoic acid (C9) at 194 ng/L, and perfluoroheptanoic acid (C7) at 329 ng/L. In general, the lowest concentrations of the PFCs were found in the smallest tributaries while the highest levels were found in middle reaches of the Drainage Basin. Variability of PFC concentrations suggests a series of source inputs throughout the Basin. Seventeen sample sites (22%) had PFOS concentrations greater than 43 ng/L, a conservative safe water concentration estimated to be protective of avian life. In addition, a total of 26 sites (32%) had PFOA concentrations above 40 ng/L.

Introduction

Increasing worldwide attention is being focused on a group of persistent organic compounds known as the perfluorinated compounds (PFCs). Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) are probably the two best known PFCs, but there are a great number of other structurally related compounds which share the unique physical and chemical characteristics of this class of materials. Concern over these compounds is in part due to a number of recent studies that have indicated serious health effects associated with PFOS and PFOA in various animal models (*1*, *2*). Consequently, this has led to voluntary cessation of the production of PFOS in the United States and reductions in factory emissions of PFOA and its residuals in finished products (*3*). There are still many companies worldwide which produce and/or use a wide range of different PFCs in a great variety of products (*4*). While most residents tested in the industrialized countries have detectable levels of many PFCs in their blood (*5*), the routes of exposure and the associated risks are largely unknown.

A series of studies in Japan has suggested a relationship between PFOS and PFOA levels in water supplies and in the blood of residents living in some of the most heavily industrialized areas of that country (*6*, *7*). Likewise, in the United States, PFOA in human blood was found to be correlated to the consumption of contaminated well water and homegrown fruits and vegetables in one particularly contaminated area (*8*). Other studies have documented that the PFCs are ubiquitous in aquatic food webs and that they tend to be concentrated in the fish that may be eaten by humans (*9*, *10*).

Although mounting evidence indicates the importance of aquatic systems in the global transport of many of the PFCs (*11*, *12*), there are still few data that have been published describing PFC distributions in the aqueous environment. In the small number of studies which have been published, many aspects of the collection and analysis procedures are poorly described. Few contain adequate detail on the performance characteristics (i.e., precision and accuracy) of the methods employed, making it difficult to interpret the data. In a recent worldwide interlaboratory study (*13*), only 31% of the participating laboratories demonstrated substantial agreement in the analysis of an aqueous PFOS sample. The need for more rigorous standardized testing procedures for the PFCs will increase as our understanding of the issue increases (*14*, *15*).

This study was undertaken to establish a new method for the collection and analysis of 10 PFCs in surface water and to provide the details on the performance characteristics that are needed for interpretation of the resulting data. This method was applied in a pilot-scale evaluation of the Cape Fear River Basin in North Carolina to demonstrate its utility and to provide preliminary information about the PFCs in this watershed.

Materials and Methods

Standards and Reagents. Potassium salts of perfluorobutane sulfonate (PFBS, 98% purity), perfluorohexane sulfonate (PFHS, 93%), and perfluorooctane sulfonate (PFOS, 93%) were provided by 3M Company (St. Paul, MN). Perfluorohexanoic acid (C6, 97%), perfluoroheptanoic acid (C7, 99%), perfluorooctanoic acid (C8 or PFOA, 96%), perfluorononanoic acid (C9, 97%), and perfluorodecanoic acid (C10, 98%) were purchased from Sigma-Aldrich (St. Louis, MO). Perfluoroundecanoic acid (C11, 96%), and perfluorododecanoic acid (C12, 96%) were purchased from Oakwood Products (West Columbia, SC). $^{18}O_2$-Ammonium perfluorooctane sulfonate (18O-PFOS) was purchased from Research Triangle Institute (Research Triangle Park, NC). 1,2-$^{13}C_2$-labeled PFOA (13C-PFOA) was purchased from Perkin-Elmer Life and Analytical Sciences (Boston, MA). Deionized (DI) water, HPLC-grade methanol, and ammonium acetate were determined to be free of PFCs prior to use.

Water Collection. One hundred water samples were collected from 80 different sites (more than 10% duplicates) in the Cape Fear River Basin in central North Carolina on 6 different dates during the spring of 2006 (Figure 1). Sample sites were subjectively selected to reflect water quality throughout the Basin. The Cape Fear is the largest drainage basin within North Carolina with an area of 23 700 km^2. The Haw and Deep Rivers originate in the north central part of the state and their confluence

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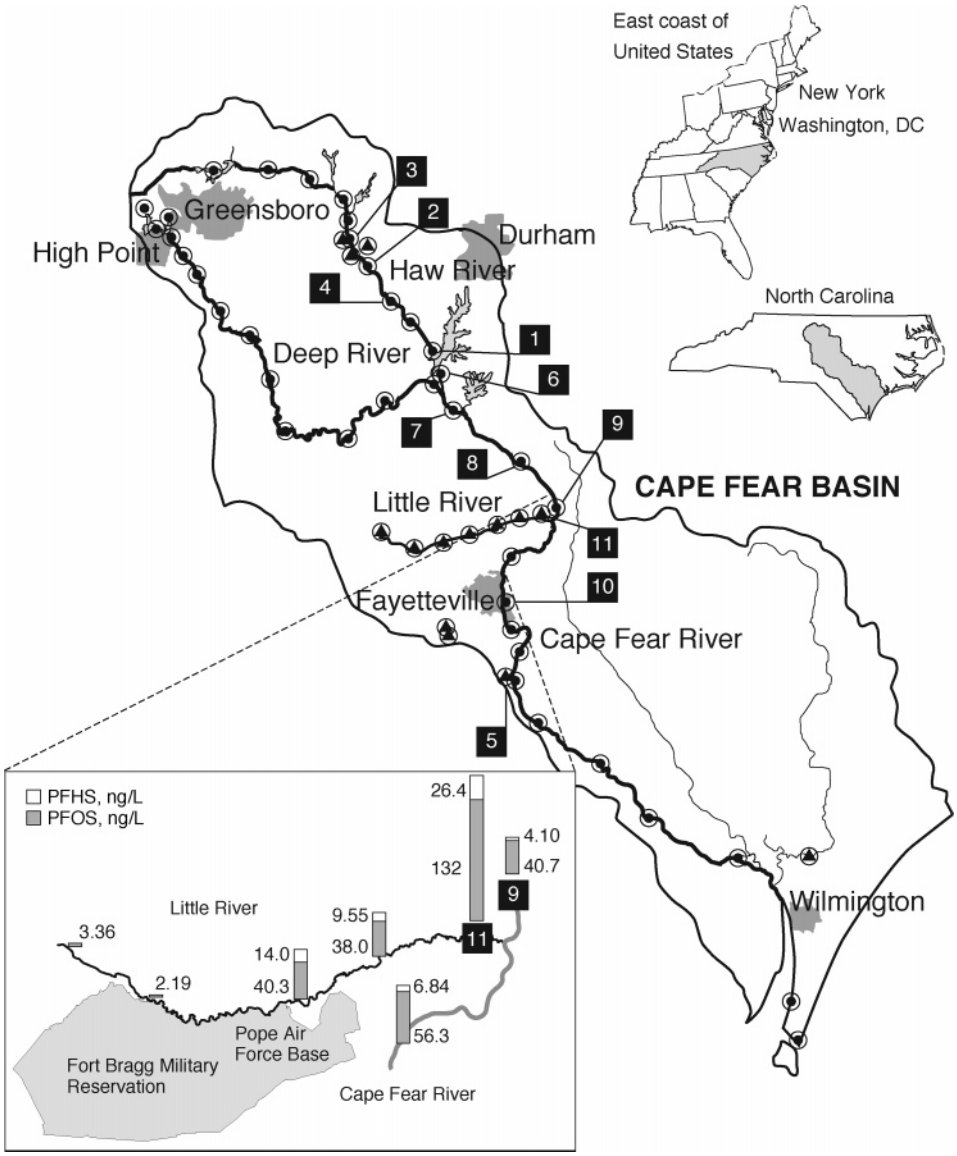

FIGURE 1. Cape Fear River Drainage Basin, North Carolina. The solid circles and triangles represent sampling locations on the main stream and tributaries, respectively. Eleven numbered locations along the watershed show the sites with the highest total PFC concentrations measured in this survey (See Table 3).

forms the Cape Fear River. The Little River joins the Cape Fear River just north of Fayetteville. Local water authorities estimate that as many as 1.7 million residents obtain drinking water from surface water resources within this basin. While the watershed is principally rural and agricultural in nature, possible sources of PFCs include use of fire-fighting foams, metal-plating facilities, textile and paper production, and other industries found within this basin.

Samples were collected in pre-cleaned (methanol rinsed) 1 L high-density polyethylene (HDPE) bottles (Nalge Nunc International, Rochester, NY) using either a Kemmerer stainless steel sampler, an open water grab sampler (Wildlife Supply Company, Buffalo, NY), or a homemade dip sampler. All samples were collected approximately 15−30 cm below the surface of the water. Samples were returned to the laboratory and stored at room temperature for no longer than 3 days prior to analysis.

Field Quality Assurance Sample Preparation. On each sampling date, a 1 L bottle was filled with deionized (DI) water and carried into the field as a field blank. Independent quality control (QC) samples were spiked with known levels of the PFCs (typically at two different levels) and transported to the field each day. These field blanks and QC samples were returned to the laboratory and analyzed at the same time as the field samples.

Solid-Phase Extraction (SPE). Oasis HLB Plus (225 mg) cartridges (Waters Corporation, Milford, MA) were conditioned with 10 mL of methanol and DI water at a flow rate of approximately 10 mL/min. Water samples were divided into two 500 mL aliquots and spiked with 100 μL of a 100 pg/μL solution (10 ng) of the internal standards (^{13}C-PFOA and ^{18}O-PFOS), and then loaded onto the pre-conditioned cartridges at a flow rate of 10 mL/min with a positive pressure pump (Sep-Pak Concentrator, Waters Corporation). The cartridge was then washed with 10 mL of DI water and dried completely by purging with nitrogen gas. The target analytes were eluted from the cartridge with 2 mL of methanol at a flow rate of 1 mL/min. The eluate was reduced in volume to 500 μL with a TurboVap II nitrogen evaporator at 60 °C (Caliper Life Sciences, Hopkinton, MA). Finally, a 200 μL aliquot of this reduced eluate was mixed with 50 μL of 2 mM ammonium acetate to match the initial HPLC mobile phase conditions.

TABLE 1. Method Performance Characteristics

	recovery[a]				precision[b]				accuracy[c]			
	10 ng/L, $N = 5$		100 ng/L, $N = 5$		intra, ng/L, $N = 6$		inter, ng/L, $N = 4$		5 ng/L, $N = 4$		50 ng/L, $N = 4$	
compound	% recovery	RSD[d]	% recovery	RSD	mean	RSD	mean	RSD	% accuracy	RSD	% accuracy	RSD
C12	55.3	0.100	59.8	0.098	3.56	0.096	46.4	0.058	80.3	0.160	101	0.045
C11	66.9	0.086	78.4	0.100	27.6	0.051	49.6	0.044	90.3	0.069	103	0.038
C10	84.6	0.088	90.1	0.048	76.5	0.069	51.6	0.080	102	0.064	102	0.050
C9	92.4	0.035	97.4	0.018	147	0.041	52.7	0.043	103	0.120	105	0.039
C8	96.5	0.019	101	0.007	197	0.026	50.5	0.019	96.2	0.003	99.5	0.013
C7	91.1	0.024	104	0.027	60.3	0.047	48.4	0.034	96.2	0.043	98.4	0.012
C6	90.1	0.026	95.6	0.035	12.4	0.054	49.2	0.111	103	0.064	101	0.064
PFOS	95.1	0.033	96.5	0.018	30.9	0.031	48.9	0.048	92.0	0.048	94.6	0.011
PFHS	92.8	0.024	102	0.038	7.15	0.052	48.2	0.044	94.1	0.029	97.2	0.036
PFBS	83.2	0.028	93.0	0.054	2.50	0.041	48.2	0.108	95.3	0.051	96.3	0.092

[a] Matrix matched recovery. [b] Intra-day variation of samples from a location and inter-day variation of spiked samples. [c] Percent accuracy using deionized water spiked with target compounds (measured value/spiked amount). [d] Relative standard deviation.

Instrumental Analysis. Samples were analyzed using an Agilent 1100 high-performance liquid chromatograph (HPLC, Agilent Technology, Palo Alto, CA) coupled with an API 3000 triple quadrupole mass spectrometer (Applied Biosystems, Foster City, CA).

The HPLC consisted of a membrane degasser, binary high-pressure gradient pumps, an auto-sampler, and column heaters. A Wakopak Fluofix-II 120E column (5 μm), 3.0 $\times$ 100 mm (Wako Pure Chemical Industries, Osaka, Japan) containing a fluorinated stationary phase was used for the analysis at 40 °C. Samples (10 μL) were injected using a gradient mobile phase consisting of mixture of 2 mM ammonium acetate and methanol at a flow rate of 200 μL/min. The gradient program was optimized for the separation of all analytes and matrix interferences (Table S1, Supporting Information).

The API 3000 was operated in the electro-spray ionization (ESI) mode using multiple reaction monitoring (MRM). The operational parameters are described in Table S1 (Supporting Information). Ionization and collision cell parameters were optimized for each individual analyte. The MRM transitions for each analyte are indicated in Table S2 (Supporting Information).

Quantitation. Six-point calibration curves were produced for each analytical batch by spiking blank DI water with varying amounts of the target PFCs and fixed levels of the two internal standards (^{18}O-PFOS and ^{13}C-PFOA) such that the quantifiable range for this study was from 1 to 500 ng/L. Curves were prepared by plotting the area ratio of analytes to internal standards versus the concentration of the PFC standards. Quantitation was performed with the Analyst 1.4.1 software (Applied Biosystems) using a quadratic "1/x" weighted regression fit with a coefficient of correlation greater than 0.99.

In a separate series of experiments, the instrumental quantitation limit (IQL) and lower limit of quantitation (LLOQ) of the method were calculated by using a series of solvent standards and fortified DI water samples (0.01−250 pg/μL and 0.01−250 ng/L, respectively). The IQL was determined to be 0.5 pg on column and the method LLOQ was determined to be 0.2 ng/L for all PFCs. At these levels the signal-to-noise ratio was at least 10:1 with precision of ±15% and accuracy of 100% ± 20%.

Recoveries and QC Values. Recoveries were calculated based on a matrix matched method (details in Supporting Information). The intra-day precision was calculated based on analysis of the 6 replicated samples collected from a single location on a single day. The inter-day precision was determined by comparing DI water spiked with 50 ng of PFC mixture on 4 different days. The relative standard deviations (RSD), or coefficient of variation, were calculated from these measurements. Accuracy was calculated by analyzing low and high (5 and 50 ng/L) QC spikes into DI water on 4 different days. The QC samples were treated with the same procedure as the other samples and calibrated by the standard curves described above.

Statistical Analyses. All statistical analyses were performed using SAS/STAT software (SAS Institute, Cary, NC) with the level of significance set at 0.05. If duplicate samples were collected at any given location, mean values were used in all subsequent analyses.

Results and Discussion

Method Validation. None of the field blanks were determined to have measurable PFC contamination. The recovery, precision, and accuracy for the 7 perfluorinated carboxylates and 3 sulfonates targeted in this method are listed in Table 1. Recoveries for most compounds ranged from 80% to 104%. The C11 and C12 acids had lower recoveries but excellent overall precision with RSDs no higher than 10%. The greatest variance was found for the inter-day C6 acid at a concentration of 50 ng/L (11% RSD). The accuracy of spiked samples was 80−105% with less than 16% RSD. None of the duplicate samples taken from 8 different locations on 5 different days had significant variation either within-day or between-day analyses (p values > 0.1, paired t-test).

Several aspects of this method provided enhanced accuracy and precision. The use of a positive-pressure dual piston pump, Sep-Pak Concentrator, allowed a relatively large volume of water to be run through the SPE cartridge without filtration at a steady flow rate and pressure in an automated manner, thereby contributing to reproducible SPE loading and overall sample consistency. Most surface water samples were found to contain complex organic materials which coeluted from the SPE cartridge and were present as interferences in the final eluate. To minimize this interference, a Fluofix-II column with a bonded fluorinated stationary phase was used to separate these organic interferences from the target PFCs (Figure S1, Supporting Information). The combination of the HLB cartridge and the Fluofix analytical column provided excellent accuracy and precision for the measurement of PFCs in surface water.

Low levels of background contamination in the analytical instrumentation will also contribute to low LOQs and improved accuracy and precision. Some researchers have suggested that all HPLC fittings and parts containing polytetrafluoroethylene (PTFE) should be replaced with stainless steel and/or polyetheretherketone (PEEK) materials to avoid potential PFC contamination (*16*, *17*). While this may be necessary for ultralow-level determinations, any potential

TABLE 2. Summary of Measurements

compound	mean ng/L	median ng/L	GM[a] ng/L	max. ng/L	min. ng/L	% above LOQ[b]	% ND[c]
C12	2.17	1.95	1.93	4.46	< LOQ	19.0	53.2
C11	10.4	5.67	6.25	52.1	< LOQ	43.0	17.7
C10	22.1	13.2	8.35	120	< LOQ	62.0	15.2
C9	33.6	5.70	9.73	194	< LOQ	74.7	10.1
C8	43.4	12.6	16.2	287	< LOQ	82.3	7.6
C7	38.7	14.8	14.0	329	< LOQ	55.7	32.9
C6	7.38	5.14	5.41	23.0	< LOQ	44.3	45.6
PFOS	31.2	28.9	20.0	132	< LOQ	97.5	0
PFHS	7.29	5.66	5.73	35.1	< LOQ	73.4	1.3
PFBS	2.58	2.46	2.34	9.41	< LOQ	39.2	38.0

[a] Geometric mean. [b] Limit of quantitation (1 ng/L, samples below this level were excluded from the calculation of mean and GM). [c] Not detected, less than 0.05 ng/L.

contamination was eliminated in this study by flushing the entire HPLC system (degasser, pumps, tubing, and valves) with 100% methanol for more than 3 days as well as by avoiding injection of more than 1 ng of any specific PFC on column at any time.

PFC Concentrations in Surface Water. The PFOS and PFOA were found to be above the LOQ (1 ng/L for all compounds) in 97.5% and 82.3% of the samples, respectively (Table 2). Of the other compounds, the C7−10 acids and PFHS were the most prevalent, being found above the LOQ in more than 50% of samples. The median concentrations were all below 30 ng/L for each compound, with PFOS levels at 28.9 ng/L, PFOA at 12.6 ng/L, the C7 acid at 14.8 ng/L, and the C10 acid at 13.2 ng/L. However, the peak levels of each compound (see Table 3 and discussion below) were relatively high when compared with previously published data. For example, maximum PFOS was measured at 132 ng/L, PFOA at 287 ng/L, the C10 acid at 120 ng/L, the C9 acid at 194 ng/L, and the C7 acid at 329 ng/L. As all data were found to be log-normally distributed, Spearman's correlation analysis was conducted indicating that the carboxylates were strongly correlated with each other and that PFOS was correlated with the C8 and C9 acids, PFHS, and PFBS (Table S3, Supporting Information). A significant correlation was also found between PFBS and the C6−C9 acids. These correlations suggest common sources among these groupings.

Different PFC profiles were observed at each sampling location along the entire length of the watershed (Figure S2, Supporting Information). Figure 2 shows plots of the PFOA and PFOS concentrations from the mouth of the Cape Fear River up into the headwater tributaries more than 400 river km inland. These plots reveal that lower concentrations of the PFCs were found in the smallest upland tributaries and the broad lowland costal sections of the river. The highest

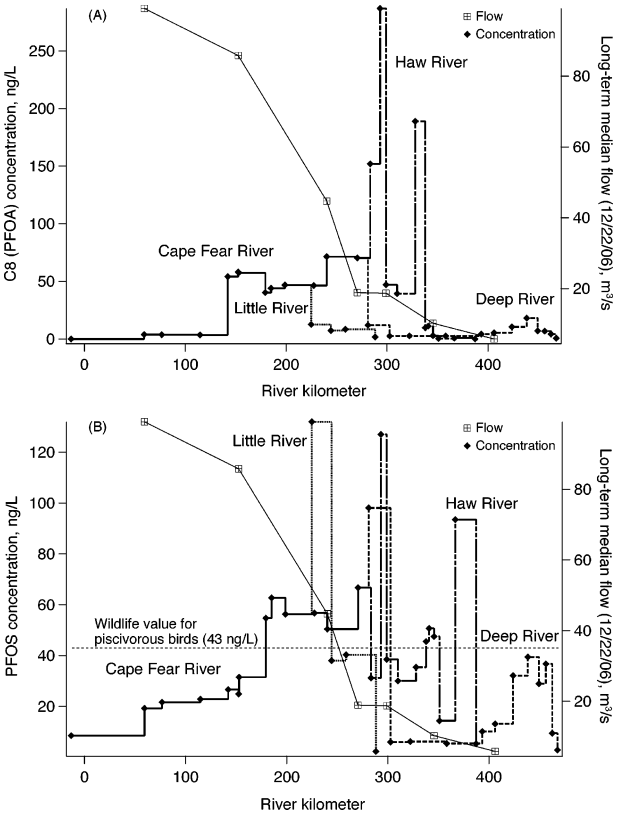

FIGURE 2. Concentrations of PFOA (A) and PFOS (B) vs river km. The Haw and Deep River join at river kilometer 277 to form the Cape Fear River. River kilometer 0 is the mouth of the Cape Fear River near Wilmington, NC.

concentrations were found in the middle reaches of the Cape Fear River and its two major tributaries (the Haw and Deep Rivers). Figure 2 also shows the long-term median flow rate of the main streams. Together these data indicate that the highest concentrations and the greatest degree of variation tend to occur in the low-volume, middle and upper reaches of these rivers. Source inputs in these areas apparently have a greater influence here than in the downstream costal areas with substantially greater water volume. It is of great interest to determine if this decline in PFC concentration is due to dilution, biological uptake, or sequestration in sediments or other abiotic pools.

Table 3 lists the measured concentrations of each PFC at the eleven sampling locations (Figure 1) with the highest aggregate (sum of all target compounds) PFC levels. The maximum concentrations of the C8, 9, 10, 11, and 12 acids

TABLE 3. Measured Concentrations at the Eleven Sites with the Highest Total Concentrations of PFCs in the Cape Fear River Basin[a] (See Figure 1 for locations)

no.	river	C12 (ng/L)	C11 (ng/L)	C10 (ng/L)	C9 (ng/L)	C8 (ng/L)	C7 (ng/L)	C6 (ng/L)	PFOS (ng/L)	PFHS (ng/L)	PFBS (ng/L)	total (ng/L)
1	Haw River	***4.46***	***52.1***	***120***	***194***	***287***	118	21.7	127	8.43	***9.41***	942
2	Haw River	3.20	28.7	112	157	200	66.8	14.5	33.4	7.87	2.61	626
3	Haw River	3.29	27.6	109	157	191	59.2	13.7	36.4	9.49	3.04	609
4	Haw River	1.98	20.0	88.2	151	201	58.2	13.2	31.5	7.49	2.88	574
5	tributary to Cape Fear	2.26	15.0	19.6	71.2	58.6	***329***	***23.0***	30.0	3.36	ND	531
6	Haw River	1.18	8.87	31.0	72.1	152	58.3	13.5	31.2	7.70	ND	376
7	Cape Fear River	< LOQ	3.34	13.2	34.8	70.3	24.0	7.84	66.7	5.59	ND	227
8	Cape Fear River	1.14	6.39	17.2	35.7	71.5	26.9	9.35	50.4	4.82	ND	223
9	Cape Fear River	1.23	6.75	17.1	38.0	72.7	23.7	7.05	40.7	4.10	ND	211
10	Cape Fear River	< LOQ	7.55	19.3	31.2	46.8	13.9	4.62	56.3	6.84	2.12	189
11	Little River	< LOQ	< LOQ	2.17	2.24	12.6	3.38	3.23	***132***	***26.4***	3.20	185

[a] Italicized values show maximal concentrations of each compound.

as well as PFBS were found at sampling point 1 in Figure 1. Peak levels of PFOS and PFHS were found in the Little River at sampling point 11. The highest levels of the C6 and C7 acids were found in a small tributary of the Cape Fear River at sampling point 5. These data indicate the presence of many different PFC sources within the Basin. Further evaluation of these areas could be undertaken to identify the various sources.

Comparison to Other Findings. In general, these results are similar to PFOS and PFOA levels measured in 9 major freshwater lakes and rivers throughout New York State (*18*). In that study, median PFOS levels were all below 7 ng/L except Lake Onondaga (a listed Superfund site) where it was found to be 756 ng/L. Median PFOA levels ranged from 14 to 49 ng/L with a high value of 173 ng/L. In the Cape Fear River Basin, median PFOS was 28.9 ng/L with a maximum of 132 ng/L, and median PFOA was 12.6 ng/L with a maximum of 287 ng/L. One difference noted between these two studies is that the New York State effort measured only PFOS, PFOA, and PFHS with a 4 target compound method. In the Cape Fear Basin, all 10 of the target compounds were routinely quantified, with an average of 6 compounds being above LOQ at each location.

Another study examined the impact of a fluorochemical production facility on the Tennessee River in Alabama (*19*). In that study, PFOS and PFOA levels remained below 55 and 25 ng/L, respectively, before the discharge site of the fluorochemical plant. After a 10 km mixing distance downstream of the discharge, the PFOS and PFOA concentrations remained fairly constant, averaging 114 ng/L and 394 ng/L, respectively, for the remaining 55 km of the river that was studied. The authors pointed out that this pattern was consistent with a single source that influenced the main body of the river for a considerable distance after the input. In contrast, the current study revealed evidence of many unidentified sources of PFCs in the Cape Fear Basin leading to much greater overall variability in water concentrations (Figures 2 and S2).

Comparing these results with a nationwide survey in Japan (*20*, *21*), the PFOS and PFOA levels from the present study were at least 3.5−6 times higher than all of the Japanese regions surveyed except the heavily industrialized area around Osaka, where the peak levels of PFOS were found to be 526 ng/L and PFOA was as high as 67 000 ng/L. The authors determined that the PFOA source was a water reclamation facility which receives waste from a number of industrial facilities operating in the area. The elevated PFOS concentrations were found in a tributary draining the Osaka International Airport with the concentrations as high as 526 ng/L (roughly 500 times higher than typical background concentrations in that study). The authors noted that use of fire-fighting foams at airports has been known to cause PFC contamination of ground and surface waters (*22*, *23*) and they speculate that this may be the source of contamination here as well. In light of these findings, it is interesting to note that the highest PFOS concentration measured in the current study (132 ng/L) was from the Little River which runs along the northern boundary of Fort Bragg and Pope Air Force Base (Figure 1). The highest PFHS concentration (26.4 ng/L) was also recorded at this location. In Figure 1 both compounds increase to their maximum concentration as the Little River flows along the northern boundary of this military reservation and it makes its confluence with the Cape Fear River. According to the NC Department of Environment (*24*), the Base is permitted to pump 30 300 kL of wastewater per day into the Little River in this area. This finding is consistent with past or current use of PFOS-containing materials in this area.

Another recent study measured PFCs in the Rhine River and some of its tributaries in Germany (*25*). In general, the median levels of PFOA and PFOS on the Cape Fear were higher than most of the sampling locations on the main body of the Rhine River. One exceptionally contaminated tributary to the Rhine was identified in an area that had received surface application of organic wastes containing PFC material. Further testing of finished drinking water supplies coming from this highly contaminated area showed little evidence of effective removal of the PFCs by conventional activated carbon filters. Like the Japanese work discussed above, this study underscores the worldwide nature of this issue, and it also shows how the systematic application of an effective collection and analysis method can be used to trace and identify PFC sources within a watershed.

Exposure Aspects. A U.S. EPA Great Lakes Initiative methodology (*26*) was used to estimate an avian wildlife value for PFOS of approximately 43 ng/L (*17*). PFOS concentrations below this level are estimated to be protective of trophic level IV bird species which consume aquatic organisms at equilibrium with PFOS in the water. Because of uncertainties in the estimate, the authors (*17*) consider this value to be "probably overly conservative, possibly by 50−100 fold." It is interesting to note that 17 (22%) of the sampling sites in this study had PFOS concentrations above this 43 ng/L threshold (Figure 2B). The New York State study (*18*) and a recent Korean study (*27*) also found limited areas where this threshold was exceeded.

While this study only measured *surface water*, a health-based guidance level recommended by the State of New Jersey for PFOA in *drinking water* provides a reference point for interpretation of some of the data from the current study. The State of New Jersey Department of Environmental Protection has recommended that PFOA levels in *drinking water* not exceed 40 ng/L in order to be protective of both non-cancer effects and cancer at the one in one million risk level (*15*). In the current study, 26 sites (32%) had PFOA levels above 40 ng/L. While no drinking water measurements were made in this study, these findings indicate the potential for exposures above this threshold if PFOA is not effectively removed by drinking water treatment plants using the Cape Fear River and its tributaries as source water. The removal of all the PFCs by water treatment processes should be evaluated.

In conclusion, this method for 10 target PFCs in surface water specifically identifies the key performance characteristics (accuracy, precision, and sensitivity) that are needed to design and conduct sampling surveys which will adequately document surface water quality. This pilot study of the Cape Fear Drainage Basin found ample evidence of potential sources of PFCs, with PFOS and PFOA being the most prevalent compounds identified. The C7, C9, and C10 acids and PFHS were also commonly detected, suggesting other sources of these materials as well. In general, the indication of a wide variety of PFC sources indicates that much further work will be required to evaluate this river system and the potential impacts on drinking water sources, wildlife species, and potential human exposures. This study contributes to the growing body of data that suggests that PFC contamination in the waterways of the industrialized world is pervasive and as yet poorly characterized.

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Supporting Information Available

Tables showing LC/MS/MS conditions, mass transitions of each analyte, and Spearman's correlation coefficients between analytes. Additional Figures showing representative chromatograms and summaries of all measurements made at each location. This material is available free of charge via the Internet at http://pubs.acs.org.

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