Per- and poly-fluoroalkyl substances (PFAS) in river discharge: modeling loads upstream and downstream of a PFAS manufacturing plant in the Cape Fear watershed, North Carolina.

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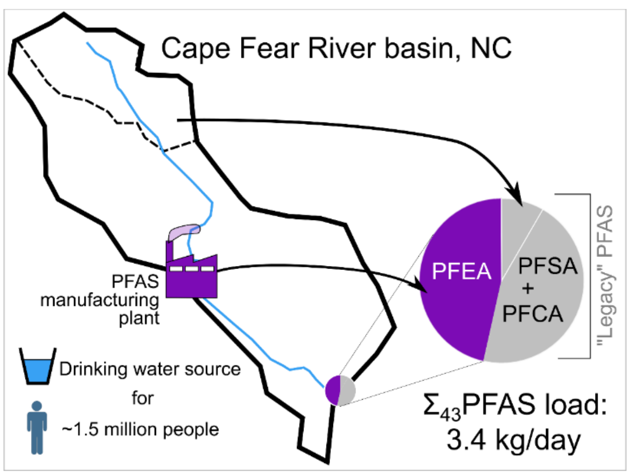
Highlights

- PFAS loads were calculated from data sets collected upstream and downstream of a PFAS plant
- Σ_{43}PFAS load was 459-17,300 g/day downstream, where 47% was PFEA from the plant
- PFAS load was estimated well by LOADEST downstream, but less so upstream near a WWTP
- Results indicate large input of legacy PFAS between upstream and downstream stations
- 1.5 million people might be exposed from drinking water drawn from the river.

Abstract

The Cape Fear River is an important source of drinking water in North Carolina, and many drinking water intakes in the watershed are affected by per- and polyfluoroalkyl substances (PFAS). We quantified PFAS concentrations and loads in river water upstream and downstream of a PFAS manufacturing plant that has been producing PFAS since 1980. River samples collected from September 2018 to February 2021 were analyzed for 13 PFAS at the upstream station and 43-57 PFAS downstream near Wilmington. Frequent PFAS sampling (daily to weekly) was conducted close to gauging stations (critical to load estimation), and near major drinking water intakes (relevant to human exposure). Perfluoroalkyl acids dominated upstream while fluoroethers associated with the plant made up about 47% on average of the detected PFAS downstream. Near Wilmington, Σ_{43}PFAS concentration averaged 143 ng/L (range was 40-377) and Σ_{43}PFAS load averaged 3,440 g/day (range was 459-17,300), with 17-88% from the PFAS plant. LOADEST was a useful tool in quantifying individual and total quantified PFAS loads downstream, however, its use was limited at the upstream station where PFAS levels in the river were affected by variable inputs from a wastewater treatment plant. Long-term monitoring of PFAS concentrations is warranted, especially at the downstream station. Results suggest a slight downward trend in PFAS levels downstream, as indicated by a decrease in flow-weighted mean concentrations and the best-fitting LOADEST model. However, despite the cessation of PFAS process wastewater discharge from the plant in November 2017, and the phase-out of PFOS and PFOA in North America, both fluoroethers and legacy PFAS continue to reach the river in significant quantities, reflecting groundwater discharge to the river and other continuing inputs. Persistence of PFAS in surface water and drinking water supply suggests that up to 1.5 million people in the Cape Fear watershed might be exposed.



Graphical abstract

1 Introduction

The presence of per- and polyfluoroalkyl substances (PFAS) in surface waters of urban watersheds has been widely documented (Munoz et al 2018, Zhang et al. (2013), Zhang et al. (2016), Bai and Son (2021), Juntilla et al (2019)) and is due to the influence of both point sources (industries, wastewater treatment plants, military bases) and diffuse sources (atmospheric deposition, groundwater inputs). Two-thirds of the drinking water in the United States comes from rivers and streams (USGS 2018, Dieter et al. 2018), and PFAS contamination commonly impairs drinking water quality (Hu et al. 2016). Most conventional and advanced treatment processes do not remove PFAS efficiently, especially short-chain PFAS (Rahman et al. 2014), making it essential to quantitatively understand PFAS in rivers (sources, concentrations, loads, timing) for environmental regulation and for planning of water treatment plant upgrades.

Environmental studies monitoring PFAS contamination in urban watersheds typically report PFAS concentrations in surface waters, but PFAS load (riverine mass flux), the product of concentration and river discharge, may be better suited to assessing and managing PFAS sources. PFAS load can be used to quantify the mass of chemical passing monitoring stations and entering downstream waterbodies, such as reservoirs and estuaries. Accurately estimating loads is challenging as it requires continuous monitoring of river discharge and frequent co-located sampling of river water to capture the temporal variability in PFAS concentration (Lee et al. 2019).

Previous studies have highlighted the limitations of estimating PFAS loads from rivers. In some previous studies, PFAS load was based on the product of measured river PFAS concentration and long-term mean river discharge for the month of PFAS sampling, rather than measured discharge at the time and place of PFAS sampling (Ahrens et al. 2009, Pistocchi and Loos 2009, McLachlan et al. 2007). This could give rise to error from temporal differences in river discharge, and from the locations of PFAS sampling differing from the locations for the long-term average discharge values. Some recent studies have utilized "snapshot" or seasonal sampling campaigns rather than frequent and long-term monitoring of PFAS, e.g., Munoz et al. (2018), Labadie and Chevreuil 2011, Juntilla et al. (2019), Allinson et al (2012), Kim et al (2012), Nguyen et al (2017), Joerss et al. (2020), Sharma et al. (2016), Zhao et al. (2015). In some cases, the sources, locations, or methods for discharge values have not been fully clear.

To address the methodological challenges of characterizing the temporal variability in PFAS loads and river discharge, we used a sampling scheme with relatively frequent (daily to weekly) PFAS sampling conducted over a relatively long monitoring period (13 months at one station, 28 at another) for a significant list of PFAS analytes (13 at one station, 43-57 at another), including perfluoroalkylsulfonic acids (PFSA), perfluoroalkylcarboxylic acids (PFCA), per- and polyfluoroalkyl ether acids (PFEA), fluorotelomer sulfonates (FTS) and sulfonamides. Critical to load estimation, PFAS sampling was conducted in close proximity to continuous discharge gaging stations operated by the US Geological Survey (USGS 2021). In addition, PFAS data were collected at or very near drinking water intakes in the study area, providing relevance to PFAS exposure in the affected communities.

The study was undertaken in the Cape Fear River watershed in North Carolina, USA, where drinking water intakes have had elevated PFAS concentrations. One of the major sources of PFAS contamination in the watershed is the Fayetteville Works, a fluorochemical manufacturing facility that emitted PFAS to air (D'Ambro et al. 2021, Pétré et al. 2021) and through direct discharge of process wastewaters to the Cape Fear River (Sun et al. 2016a, Hopkins et al. 2018) for about 4 decades. Other distributed sources of PFAS are also present in the watershed (Nakayama et al. 2007), in particular in the Haw River sub-basin where PFSA and PFCA were detected from 2017-2019 at various water utilities (Herkert et al. 2020). The objectives of this study were to: 1) Quantify PFAS concentrations and loads in the Cape Fear River watershed, both upstream and downstream of the Fayetteville Works; 2) evaluate the persistence and impacts of PFAS contamination from the Fayetteville Works relative to other sources of PFAS, up to three years after cessation of direct wastewater discharge from Fayetteville Works; 3) identify implications for drinking water treatment and human exposure.

2 Material and Methods

2.1 Study area and sample collection

The Cape Fear River basin is the largest watershed of North Carolina, with a drainage area of 23,735 km^2. The Cape Fear River is formed by the confluence of the Haw and Deep Rivers just south of Jordan Lake (Figures 1, S1). About 1.5 million people obtain drinking water from surface water resources within the Cape Fear River basin (Cape Fear River Watch 2014). In particular, Jordan Lake is a drinking water source for residents in Cary and Apex, NC and the Haw River is a source for Pittsboro, NC. Recent sampling indicates that Pittsboro is among the highest in North Carolina for total PFAS in drinking water (NC PFAST Network 2021). Downstream, the Cape Fear River supplies drinking water for about 200,000 residents in the Wilmington area (Figure1). The Cape Fear Public Utility Authority (CFPUA) has reported elevated total quantified PFAS concentration up to 377 ng/L in their raw and finished water in 2019, despite the termination of direct discharge of PFAS process wastewater to the Cape Fear River from the Fayetteville Works in November 2017.

River water was collected for PFAS analysis at 13 locations in the Haw River watershed from June 2019 to July-August 2020 and at the Kings Bluff raw water intake in the Cape Fear River between 12 September 2018 and 1 February 2021 (28 months) (Figures 1, S1).

In the Haw River watershed, 28-42 water samples were collected at each station and 13 PFAS were targeted (Table 1). The sampling interval typically ranged from 6-8 days. Due to COVID-19, sample collection was reduced to three stations between April 14 and June 22, 2020: Bynum, Burlington Upstream, and Burlington Downstream (Figure S1). The latter two stations are located directly upstream and downstream of the Burlington wastewater treatment plant. The Bynum sampling station is adjacent to the water intake for the city of Pittsboro, NC, and about 40 km downstream of Burlington Downstream.

Water samples were collected in 1-liter pre-cleaned polyethylene bottles, either by wading into the middle of the channel to fill the bottle, or lowering a bucket from a bridge and then filling the bottle from the bucket (at the Cane Creek sites only, Figure S1). Details on PFAS analyses and quality assurance/quality control (QA/QC) protocols are provided in Texts S1 and S2.

The Kings Bluff sampling station is at the CFPUA water intake. It is located 88 km downriver of the Fayetteville Works and delivers water to the CFPUA's Sweeney Water Treatment Plant in Wilmington. At Kings Bluff, a total of 120 river water samples were collected by the utility and analyzed by a commercial lab (Text S1). The sampling interval typically ranged from 7-14 days, though samples were collected daily for 29 days during and after Hurricane Florence (September 14 to October 12, 2018). At least 43 PFAS were targeted during the 28-month period (Table 1) and an additional 14 PFAS, mostly PFEA, were targeted either from late 2019 or September 2020 onward (Dataset in SI), for a total number of 57 PFAS targeted during September-December 2020. Of these, a group of 20 PFEA is known to be specifically associated with the Fayetteville Works PFAS plant, as they are only present in the Cape Fear River in locations adjacent to or downstream from the plant (Geosyntec 2018). Initially, only 10 of these 20 were targeted (as part of the 43 PFAS targeted in total throughout the study), and the remaining 10 were subsequently added to the list of analytes in September 2020. The contribution of the PFAS associated with the plant to the total quantified PFAS at Kings Bluff was calculated by dividing the sum of the 10 site-related PFAS concentrations by the total quantified PFAS concentration summed over the 43 PFAS targeted during the entire study period at Kings Bluff, Σ_{43}PFAS (for consistency over the 28-month monitoring period, Σ_{43}PFAS was used for this calculation even during late 2020 when 57 PFAS were targeted). However, the calculation of the additional contribution of the 10 remaining compounds from September 2020 is presented in section 3.2.2.

2.2 River discharge

Daily river discharge data were obtained from three USGS gaging stations (Figure 1, Figure S1) located: 1) 1.5 km downstream of the PFAS sampling station Bynum (USGS02096960); 2) 500 m downstream of the PFAS sampling station Burlington Downstream (USGS 02096500), and 3) 200 m downstream of the PFAS sampling station Kings Bluff (USGS 02105769).

2.3 Concentration-discharge relationships

We plotted the PFAS concentration-discharge relationships at Bynum and Kings Bluff and compared them with historical PFAS levels reported at nearby locations in 2006 ("station #1" of Nakayama et al. 2007) and 2013 ("Communities A and C" of Sun et al. 2016a). The 2006 dataset targeted 10 PFAS and included only 1-2 samples per location, and thus represents a snapshot during low flow conditions (river discharge at Bynum on 19 April 2006, when the sample was collected, was 8.1 m^3/s). The 2013 dataset targeted 17 PFAS and included 127 samples collected during June-December 2013 in Community A (Haw River) upstream of Jordan Lake, and 34 samples collected during June-October 2013 in Community C (Kings Bluff). The 2013 dataset spans a range of flow conditions (4-266 m^3/s with a mean value of 31 m^3/s in Community A and 20-651 m^3/s with a mean value of 269 m^3/s in Community C).

To determine the relationship between discharge and PFAS concentration and how it may differ among years, we ran an interaction effects ANCOVA. This model allowed us to test whether concentration and discharge were correlated and also whether different years had distinct concentration-discharge relationships, including differences in the slope of the concentration-discharge relationship. ANCOVA outputs include an F statistic and an R^2 value indicating the overall fit of the model. Datasets for the Bynum and Kings Bluff stations were analyzed as separate models, and 2006 and 2021 data for Kings Bluff were left out of analyses due to small sample sizes ($n = 2$ and 5, respectively). Discharge data from the USGS gaging stations near Bynum and Kings Bluff were used. Discharge and concentration data were log-transformed to fit model assumptions of normality, and other model assumptions (i.e., equal variance, independence) were met.

2.4 PFAS load estimation

At each station, the instantaneous daily load (i.e., riverine export) of individual PFAS (g/day) was calculated as $L = QC$, where Q is the river discharge on the day of river PFAS sampling and C is the measured PFAS concentration in the river water. In addition, LOADEST (Runkel et al. 2004, Runkel 2013) was used to calculate the total PFAS load at a daily interval over the monitoring period. LOADEST develops a regression model for estimation of chemical load as a function of time and discharge, using a time series of daily river discharge and instantaneous chemical concentrations. Loads estimated by the model were validated against the observed loads to verify model performance. Model performance was evaluated based on the Load Bias (%) and the Nash-Sutcliffe Efficiency Index (Runkel 2013, Stenback et al. 2011). Load bias indicates the potential for bias, with a positive value indicates an overestimation of the model. According to Hirsh (2014), the Load Bias should be within ±10%. The Nash-Sutcliffe Efficiency Index provides a measure of model fit to the data and ranges from -∞ to 1, with value of 1 corresponding to a perfect fit. A value of 0 suggests the load estimates are as accurate as the mean, while a negative value suggests that the observed mean is a better estimate of load than the model (Runkel 2013).

LOADEST was executed for Σ43PFAS and the 19 most abundant individual PFAS at Kings Bluff, using daily river discharge data at the gaging station near Kings Bluff, and for Σ13PFAS (total quantified PFAS concentration summed over the 13 PFAS targeted at Bynum) and the main 10 individual PFAS at Bynum, using daily river discharge data from the gaging station at Bynum. LOADEST automatically selected the best-fit regression model from a list of nine pre-defined models, based on the minimum value of AIC (Akaike Information Criterion). Details on LOADEST are available in Runkel (2013).

3 Results and Discussion

3.1 Overview of PFAS concentrations

3.1.1 Haw River basin

Of the 13 PFAS analyzed in the Haw River, six constituted 88% of Σ_{13}PFAS: PFHxA (23.4%), PFPeA (15.8%), PFOA (14%), PFHpA (13.7%), PFBA (10.5%) and PFOS (10.5%). Tables S1 and S2 present a summary of the measured concentrations for all PFAS in the Haw River basin. Median concentrations were below 24 ng/L for all 13 PFAS, however peak levels were high and generally occurred during low flow conditions. Maximum concentrations of PFHxA, PFPeA, PFHpA, PFBA, PFOA, and PFOS were 416.8 ng/L, 274.1 ng/L, 235.9 ng/L, and 189.9 ng/L, 133.3 ng/L, and 110 ng/L respectively. PFOA, PFHpA, PFBS, PFHxA, PFHxS and PFNA were the most prevalent as they were found above the Method Detection Limit (MDL) in 99.3-100% of the water samples. PFOS, PFPeA, PFDA, PFBA were also frequently detected above the MDL in 93.2-96.1% of the samples. The fluorotelomer sulfonates 4:2 FTS and 6:2FTS were found above the MDL in 41.7% and 70.9% of the samples, respectively. GenX was found above the MDL in 57.0% of the samples, however, concentrations averaged only 0.1 ng/L and ranged from <MDL to 2.4 ng/L. MDLs ranged from 0.02 for GenX to 1.1 ng/L for PFOS.

On average, the composition profiles at the 13 sampling stations were similar, with Σ_{13}PFAS dominated by 75-80% PFCA and 19-24% PFSA. An exception was the Cane Creek samples (stations CC2, CC3 and CC4, Figure S1) where a higher proportion of PFOA and PFOS was observed (Figure 2), up to 34% and 43.6% of Σ_{13}PFAS, respectively. This may be due to runoff from areas of application of PFAS-contaminated biosolids along Cane Creek (NC DEQ 2020). Detected PFCA and PFSA indicate continuing inputs despite PFOS and PFOA production being phased out in the United States over a decade ago. There were strong positive correlations among all compounds, except for GenX and 4:2FTS, as illustrated by Spearman's correlation coefficients ranging from 0.02 to 0.96 (Table S4). This suggests that PFCA and PFSA in the Haw River originate from common (or similar) loading sources.

The highest Σ_{13}PFAS measured in the Haw River basin (1,197 ng/L, Table S1) was found at Burlington Downstream (Figure S1) in September 2019. The lowest Σ_{13}PFAS was found in samples collected in Jordan Lake and at station CC1, the most upstream station on Cane Creek (Figure S1). PFOA+PFOS at CC2, CC3 and CC4 was higher than the USEPA Health Advisory Level (HAL) of 70 ng/L for up to 53% of the sampling dates, reaching a maximum concentration of 181.5 ng/L. At the other sampling stations, PFOA+PFOS was below the USEPA HAL, except on July 12, 2020 when it reached 90.4 ng/L at Bynum. High concentrations of 6:2 FTS (48.8-72.4 ng/L) were found at Burlington Downstream and station H1 in

September and October 2019. This could reflect an input via an aqueous film-forming foam (AFFF) spill or partially degraded precursors in textile wastewater.

Σ_{13}PFAS at Burlington Downstream was 1.3 to 8.1 times higher than that at Burlington Upstream during 32 of the 40 sampling dates. This suggests a PFAS source between the two sampling points, likely the Burlington wastewater treatment plant. The PFAS input is most likely due to residential sources or industries (especially textile industry) that have used PFAS-containing chemicals and have discharge permits to the wastewater treatment plant. Concentrations of PFBA, PFDA, PFHpA, PFHxA, PFNA, PFOA, and PFPeA in samples collected at Burlington Downstream were generally higher than at Burlington Upstream (Figure S2). In contrast, perfluoroalkyl sulfonic acids (PFBS, PFHxS and PFOS) showed similar concentrations upstream and downstream from the wastewater treatment plant, suggesting these three compounds originate from further upstream in the Haw River watershed.

3.1.2 Cape Fear River at Kings Bluff

Of the 43 PFAS targeted throughout the sampling period at Kings Bluff, 32 were found to be above the MDL, with the three most abundant, PFMOAA, GenX, and PFO2HxA (Figure 2), accounting for 13.7%, 11.2%, and 9.7% of total quantified PFAS (Σ_{43}PFAS), respectively. The 19 most abundant PFAS constituted 99.6% of Σ_{43} PFAS at Kings Bluff: PFPeA, PFPeS, PFOA, PFOS, PFHxA, PFHxS, PFHpA, PFBA, PFBS, PFDA, PFNA, PEPA, PMPA, PFMOAA, PFO2HxA, PFO3OA, GenX, Nafion BP2, PFO4DA.

Most targeted chemicals had either high or very low detection frequencies (>62% for 17 PFAS and <4% for 24 PFAS). Only PFDA and Nafion BP2 had intermediate detection frequencies of 54.2% and 27%, respectively. FTS and sulfonamides were not detected, except on one sampling date each (October and November 2020, respectively). Σ_{43}PFAS ranged from 40 to 377 ng/L, with an average of 143 ng/L. Total concentration of targeted PFEA ranged from 12 to 274 ng/L. GenX was detected in all samples with concentrations from 3 to 76 ng/L (mean 14.8 ng/L), below the NC Health Goal of 140 ng/L (Table S3). PFOA+PFOS did not exceed the USEPA HAL of 70 ng/L, with a maximum concentration of 30 ng/L and a mean of 19.4 ng/L.

A Spearman's correlation analysis was conducted for the 19 most abundant PFAS found in the Cape Fear River at Kings Bluff (Table S5). There were strong positive correlations among all PFEA that are associated with Fayetteville Works. Chemicals in the PFCA or PFSA categories also exhibited a strong positive correlation with each other. There was generally no significant positive correlation between PFMOAA, PEPA and PMPA (associated with the Fayetteville works) and PFCA and PFSA, suggesting distinct sources. However, PFHxS, PFPeS and PFPeA showed significant positive correlations with several PFEA associated with the plant (GenX, Nafion BP2, PFO3OA, PFO4DA), suggesting that these PFAS may also originate from the Fayetteville Works.

3.2 Temporal variation and comparison with historical levels

3.2.1 Haw River

PFAS levels in the Haw River at Bynum were highest during the lower flow months of July-October (Figure S3). Σ_{13}PFAS ranged from 26 to 742 ng/L (mean=194 ng/L) at Bynum, and 62 to 729 ng/L (mean=219 ng/L) at Burlington Downstream.

There was a marked decrease in PFOS, PFOA, and PFDA concentrations in 2019-2020 compared to the 2006 and 2013 levels. Mean PFOS and PFOA levels at Bynum were each about 14 ng/L in 2019-2020, 3 times lower than the mean levels for 2013 samples (Sun et al. 2016a). The maximum PFOA concentration measured at Bynum was 32.1 ng/L in 2019-2020, lower than in 2006 and 2013 (287 ng/l and 137 ng/L, respectively). The same was true of maximum PFOS concentration at Bynum: it was 58.3 ng/L in 2019-2020, lower than in 2006 and 2013 (127 ng/l and 346 ng/L, respectively). The decrease in PFOA and PFOS concentrations is likely due to the phase-out of these compounds in North America. In contrast, mean PFHxA concentration at Bynum was 57.6 ng/L in 2019-2020, higher than in 2006 (21.7 ng/L) but lower than in 2013 (78 ng/L).

3.2.2 Cape Fear River

At Kings Bluff, PFAS concentrations were highest during low flow conditions in June-December 2019 (Figure 5b). On average, the PFEA known to be specifically associated with the Fayetteville Works constituted 46% of Σ_{43}PFAS at Kings Bluff; PFCA accounted for 36%, and PFSA 18%. Geosyntec (2018) found a similar contribution (52%) of PFEA related to Fayetteville Works based on sampling in summer 2018. Between September 2018 and September 2020, the relative contribution of PFEA associated with Fayetteville Works made up between 17% and 88% of Σ_{43}PFAS in the Cape Fear River at Kings Bluff (Figure 3). However, the PFEA contribution from Fayetteville Works was underestimated because 10 PFAS associated with the Fayetteville Works were not targeted during this period: Nafion Bp 4, Nafion Bp 5, Nafion Bp 6, NVHOS, Eve Acid, HydroEve acid, R-EVE, PES, PFECA-B, and PFO5DA. These compounds (and four others not specifically associated with the Fayetteville Works) were added to the list of analytes starting in September 2020 (except PFO5DA which was added in December 2019), increasing the total quantified PFAS concentration (i.e., Σ_{57}PFAS exceeded Σ_{43}PFAS by 13-80 ng/L). This increase was mostly due to Nafion BP4, Nafion BP5 and R-EVE. The additional analytes also increased both the mean and median contribution of PFEA associated with the Fayetteville Works by 14% (from 45% to 59% of Σ_{43}PFAS) during Sept. 2020 to Feb. 2021. PFEA averaged 47% of Σ_{43}PFAS for the entire study period (Sept. 2018 to Feb. 2021). While the estimate based on Σ_{57}PFAS might better reflect the actual contribution of the plant, other compounds are likely still unaccounted for. A recent non-targeted analysis conducted by Chemours identified a total of 257 unknown PFAS in their process wastewater samples and discharge samples from locations "that may reach the Cape Fear River" (The Chemours Company, 2020).

Concentrations of the main PFEA found at Kings Bluff (GenX, PFMOAA and PFO2HxA) generally followed the same temporal variations until mid-September 2020, but PFMOAA concentrations increased noticeably after that (Figure S4, CFPUA 2021). The causes of this increase are unclear and might be due to a process at or near the Fayetteville Works, the mobilization of PFMOAA from groundwater, or a combination of these and other factors.

It is possible that some PFAS reaching the river may become associated with river sediments and this may affect the PFAS concentrations in river water (Harfmann et al. 2021). In addition, semi-labile PFAS such as FTS and sulfonamides are precursor compounds and can transform during their transport in the river, forming PFCA and PFSA as terminal products (Liu and Mejia Avendaño, 2013). These processes merit further study in general; the extent of their influence on PFAS in the Cape Fear River is not fully known.

3.2.3 PFAS concentration relationships with river discharge

At both Bynum and Kings Bluff, total quantified PFAS concentration was negatively correlated with river discharge in each study year. Discharge and PFAS concentration were negatively correlated across years and sampling sites, indicating a diluting relationship (Figure 4). At Bynum, the concentration-discharge relationship was not significantly different among years. Discharge and year explained more than half of the variability in PFAS concentration at Bynum (Figure 4a; ANCOVA, $F(5, 164) = 41.74$, $R^2 = 0.55$). At King's Bluff, the slope of the concentration-discharge relationship was not significantly different among years, but the intercepts among years showed a decreasing trend over time, indicating that at a given discharge, PFAS concentrations were expected to be higher in 2013 and 2018 than in 2019 and 2020. Discharge and year explained 2/3 of the variability in PFAS concentration at King's Bluff (Figure 4b; ANCOVA, $F(7,141) = 43.77$, $R^2 = 0.67$).

Thus, the overall PFAS concentration differed among years, but the impact of discharge on PFAS concentration was remarkably similar across years. Also, for the mean discharge at Kings Bluff during the study period (409 m^3/s), the PFAS concentration given by each successive best-fit line is lower over time (Figure 4b). This decreasing trend is consistent with the flow-weighted mean concentrations calculated at Kings Bluff (Section 4.3).

3.3 Mass fluxes

At Kings Bluff, Σ_{43}PFAS load (i.e., the cumulative river export of 43 PFAS from the watershed) determined on the sampling dates ranged from 459 g/day to 17,300 g/day (mean 3,440 g/day). At Bynum, measured Σ_{13}PFAS load ranged from 28 to 949 g/day (mean 256 g/day). PFAS load generally increased with increasing river discharge (Figure S5). Despite the typically lower concentration during high flow, the highest PFAS mass transport occurred at high discharge due to the higher volume of water moving through the system. In particular, the Σ_{43}PFAS load at Kings Bluff was highest (6,500-17,300 g/day) during Hurricane Florence, with a cumulative load of 155 kg during 16-27 September 2018 (Figure 5c).

Statistical measures of model performance indicated that LOADEST models for Σ_{43}PFAS (Figure 5c) and 15 of the main 19 compounds at Kings Bluff (GenX, PFMOAA, PFOS, PFHxA, PFOA, PFPeA, PFO2HxA, PFHpA, PFMOPrA, PFHxS, PFBS, PFNA, PFO3OA, PFO4DA, PFPeS) were within acceptable limits, with a Load Bias between -4 and +4% and a Nash-Sutcliffe Efficiency Index of 0.7-0.9 (Excel file in the SI).

The equation of the best-fitting LOADEST model and regression coefficients for Σ_{43}PFAS are presented in the Appendix. The regression coefficients associated with the time variable are negative and small, suggesting a slight downward temporal trend in PFAS load. Other modeling results for individual PFAS including regression coefficients, performance metrics and annual loads are presented in the SI (Excel file). Even during the high flow in September-October 2018, the model estimated the PFAS load well. This suggests the possibility of predicting future PFAS river loads at Kings Bluff with the LOADEST model. While this may be reasonable for a time scale similar to the monitoring period (2-3 yr), extrapolation further into the future involves larger uncertainties due to potentially changing rates of PFAS inputs to the river from sources such as contaminated groundwater or waste-water treatment plants (such future changes would not be accounted for in a LOADEST model based on 2018-2021 data). Thus, continued collection of PFAS and discharge data may be important for updating the model and maintaining its predictive accuracy.

The total Σ_{43}PFAS load at Kings Bluff was 2,026 kg over the entire monitoring period (875 days, 12 September 2018 - 1 February 2021), including 667 kg in 2019 and 724 kg in 2020. The additional load due to the 14 additional PFAS targeted from September 2020 to February 2021 was 111 kg, indicating the importance of targeting as large a group of PFAS as possible in analyses. The load of most individual PFAS at Kings Bluff was higher in 2020 than in 2019 (Figure 6a), due to the higher river discharge (total river discharge was $9x10^4$ m^3 in 2020 and $7x10^4$ m^3 in 2019). However, the flow-weighted mean concentration (FWM, calculated as the total PFAS load for a given time period divided by the total discharge for this period) decreased from 109.8 ng/L in 2019 to 91.3 ng/L in 2020. The decrease in FWM concentration of individual PFAS (Figure 6b and Table S6) between 2019 and 2020 ranged from 2% to 38%, consistent with the general downward trend over time in concentration-discharge relationships at Kings Bluff (Figure 4b).

The load of PFEA associated with Fayetteville Works averaged 1,626 g/day at Kings Bluff. This load estimate falls within the range of a previous estimate of 1,300-2,000 g/day of PFAS load to the Cape Fear River from the Fayetteville Works between June 2019 and June 2020 (Geosyntec 2020a, 2019). The GenX load at Kings Bluff was 423 g/day on average (range 34-3,572 g/day), much lower than the average of 5,900 g/day reported by Sun et al. (2016a) in 2013. Even with the decreasing trend in PFAS concentration between 2013 and 2020, significant levels of PFEA in the Cape Fear River persist 3 years after the cessation of discharge of fluorochemical production process wastewater in November 2017. The continued presence of PFEA in the river is likely due at least in part to the discharge of PFAS-contaminated groundwater to the Cape Fear River and its tributaried. Pétré et al. (2021) showed that groundwater discharge to tributary streams of the Cape Fear River was a significant pathway for off-site migration of PFAS from the Fayetteville Works, with an estimated 32,000 g/year of PFAS discharged from groundwater to five small tributaries near the plant at baseflow. Stormwater runoff from the Fayetteville Works could also contribute to the presence of PFEA in the river; the role of PFAS desorption from river sediments should also be investigated (Harfmann et al. 2021; Saleeby et al. 2021).

LOADEST models did not perform as well at Bynum as at Kings Bluff for Σ_{13}PFAS (Figure S6) or individual PFAS, except for PFHxS, PFOA and PFOS (Excel file in SI). As mentioned in section 3.1.1, two of these compounds (PFOS and PFHxS) likely come from upstream sources in the Haw River basin and their loading at Bynum was not sensitive to discharge at the Burlington wastewater treatment plant. We estimated the PFAS load to the Haw river from the Burlington wastewater treatment plant by subtracting the PFAS load at the "Burlington Upstream" station from that at the "Burlington Downstream" station for the same 42 sampling days from 10 June 2019 to 20 July 2020. PFAS input to the Haw River from the wastewater treatment plant was highly variable during this time, from 9 to 444 g/day (mean value of 122 g/day). This variability in treatment plant effluent complicates the use of load estimation programs such as LOADEST, especially for 10 of the 13 PFAS targeted in this study whose loads in the Haw River are controlled partly by the wastewater treatment plant effluent.

The PFAS yields (kg/km^2yr) of the Cape Fear River at Kings Bluff and the Haw River at Bynum were calculated by dividing the respective annual PFAS load by the drainage area. The PFAS yield was 0.062 kg/km^2 yr at Kings Bluff (considering Σ_{43}PFAS) and 0.032 kg /km^2 yr^1 at Bynum (considering Σ_{13}PFAS). These numbers are 2-3 times lower than yields reported in the Rhone River or the Po River (Schmidt et al.

2019, Pistocchi and Loos 2009), but 5-300 times higher than yields reported for other watersheds in Europe and India (Pistocchi and Loos 2009, Sharma et al. 2016 Juntilla et al. 2019, Munoz et al. 2018) (Table S7).

PFAS loads between Bynum and Kings Bluff were compared using daily load estimates from LOADEST during the common monitoring period of the two stations (10 June 2019- 20 July 2020) and including only the 13 PFAS targeted at both Bynum and Kings Bluff (Table 1). Σ_{13}PFAS load at Kings Bluff was 1,024 g/day on average (Figure 7), 3.6 times higher than in Bynum (285 g/day). The mean river discharge at Kings Bluff was about four times higher than at Bynum. Thus, PFAS input to the Cape Fear River between Bynum and Kings Bluff was estimated to be 739 g/day, including a substantial input of “legacy” PFAS (558 g/day of PFCA+PFSA) and the PFEA input from the Fayetteville Works (181 g/day of GenX). The total PFEA input from the Fayetteville Works is not included in this comparison because GenX was the only PFEA considered. The total input from Fayetteville Works requires the fullest possible suite of PFAS measurements at Kings Bluff (section 3.2.2).

The average Σ_{43}PFAS load at Kings Bluff was 3,440g/day (over 28 months, 2018-2021) including 1,809 g/day of legacy PFAS (53%) and 1,626 g/day of PFEA (47%). If the 13-month Σ_{13}PFAS load estimate at Bynum (285 g/day) is applied over the 28-month monitoring period at Kings Bluff, the contribution from Bynum to the average PFAS composition at Kings Bluff can be estimated at 8.1% (Figure S7), with an average legacy PFAS input of 1,524 g/day (1,809-285) between Bynum and Kings Bluff. While 19 legacy PFAS were targeted at Kings Bluff and only 10 at Bynum, this cannot account for the large difference in legacy PFAS load at the two stations because concentrations of the additional 9 legacy PFAS targeted at Kings Bluff were always very low or <MDL. In other words, the results suggest a legacy PFAS input to the river of about 1500 g/day between Bynum and Kings Bluff, even recognizing that fewer PFAS were measured at Bynum.

3.4 Implications on exposure and water management

These results have significant implications for municipalities that draw their drinking water from the Haw or Cape Fear Rivers. PFAS are persistent compounds and generally do not degrade during hydrological transport. Furthermore, traditional drinking water treatment does not effectively remove PFAS, particularly short chain PFAS, and thus tap water and source water can have similar concentrations (Herkert et al. 2020). In some regions, drinking water exceeds food as the dominant source of PFAS ingestion exposure (Evans et al. 2020).

The Bynum sampling site is adjacent to the water intake for the city of Pittsboro, NC, and Σ_{13}PFAS concentrations at this site were up to 742 ng/L. The Kings Bluff sampling site is located at the river water intake for communities in the Wilmington area served by CFPUA, Brunswick County served by the County’s Northwest Water Treatment Plant, and Pender County served by the Pender County Utilities Surface Water Treatment Plant, with Σ_{57}PFAS concentrations up to 377 ng/L during the study period. These concentrations are higher than many state drinking water standards (Table S8, MassDEP 2020, DWQI 2017, 2018, EGLE 2020). For example, the state of Massachusetts established a maximum contaminant level (MCL) of 20 ng/L for the sum total of six PFAS (PFOA, PFOS, PFHpA, PFNA, PFHxS and PFDA). The results suggest a continuation of concern raised in earlier work (Sun et al. 2016b; Cape Fear River Watch 2014) over potential elevated PFAS exposure for up to 1.5 million people (about 14%

of North Carolina's population) in towns and cities utilizing the Haw and Cape Fear Rivers as sources of drinking water.

Kotlarz et al. (2020) collected blood samples from 344 residents of Wilmington in 2017 and 2018 to assess PFAS exposure. PFAS, including some fluoroethers, were detected in all samples. Levels of PFAS were higher in residents consuming water sourced from the Cape Fear River compared to other residents. In particular, PFOA and PFOS levels were ~ 2-3 times higher than levels measured in the US population as reported in NHANES (2015-2016). More recently, blood samples were collected from 49 individuals living in Pittsboro in 2019 and 2020. Preliminary results suggest that PFAS levels in this population were also elevated, and similar to levels reported by Kotlarz et al. (2020) (https://sites.nicholas.duke.edu/pfas). Taken together, these results suggest that towns located between Pittsboro and Wilmington that draw drinking water from the Cape Fear and Haw Rivers may have similar levels of exposure. Additional research and monitoring are needed to determine how many people are affected by elevated PFAS exposure in NC.

In addition, ecosystems health might be affected by the average PFAS load of 1,256 kg/yr reaching the Cape Fear estuary and the coastal ocean. Guillette et al. (2020) showed elevated PFAS levels in Cape Fear River striped bass and indicated that fish/seafood consumption is likely an important route of human exposure. NC coastal waters support an important commercial and sport fishery. Future work should address PFAS concentrations in the Cape Fear River estuary and coastal marine waters, including beaches and marine life, as PFAS distribution in seawater is influenced by river outflows and ocean currents (Wang et al. 2020).

Long-term monitoring of PFAS concentrations and river discharge is warranted. At Kings Bluff, the LOADEST model could be continually updated as new data become available and be used as a tool to determine the long-term trend in PFAS concentration and load in the river.

4 Conclusions

Results showed contrasting PFAS compositions in river water upstream and downstream of the Fayetteville Works PFAS plant in North Carolina, reflecting different PFAS sources: PFCA and PFSA dominated the PFAS profile in the Haw River at Bynum (near Pittsboro NC), while PFEA made up about half on average of the detected PFAS downstream in the Cape Fear River at Kings Bluff (near Wilmington NC).

PFAS concentration was negatively correlated with river discharge at both Bynum and Kings Bluff (Figure 4). Three indications of a downward trend in PFAS over time include: (1) decreases in the concentrations estimated at mean discharge and other typical discharges by best-fit regression lines (Figure 4), (2) declines in the FWM concentrations of most PFAS (Figure 6), and (3) a slight downward trend in PFAS load over time based on the best-fitting LOADEST models (Appendix). While the downward trend is encouraging, the rate is slow. Both PFEA and legacy PFAS continue to reach the river in significant quantities, and that seems likely to continue for years.

Persistent high PFEA at Kings Bluff, up to 3 years after the termination of process wastewater discharge to the river at the Fayetteville Works, likely reflects the importance of discharge of contaminated groundwater to the river and its tributaries (baseflow contribution). The occurrence and distribution of legacy PFAS indicate continuing inputs to the river system despite the phase out of PFOS and PFOA production over a decade ago in North America. The load estimation program LOADEST was a useful tool in quantifying individual and total quantified PFAS loads at Kings Bluff, however, its use was limited at the upstream Bynum station where PFAS levels in the river were affected by variable inputs from a wastewater treatment plant. On average, 3.4 kg/day of total quantified PFAS (1,256 kg/year) passed the Kings Bluff station on the Cape Fear River to enter coastal marine waters during the study period. Continued long-term monitoring of PFAS concentration is recommended. Persistence of PFAS in surface water and drinking water supply suggests that up to 1.5 million people in NC might be exposed, and raises technical and financial challenges for drinking water utilities that are faced with costly treatment upgrades.

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6 Appendix

In LOADEST, the regression equation of the best-fit model for Σ_{43}PFAS at Kings Bluff was:

$$\mathrm{Ln}(L) = a0 + a1\ \mathrm{Ln}Q + a2\ \mathrm{Ln}Q^2 + a3\ \mathrm{Sin}(2\pi\ dtime) + a4\ \mathrm{Cos}(2\pi\ dtime) + a5\ dtime + a6\ dtime^2$$

where ln is the natural logarithm; *L* is the Σ_{43}PFAS load, in kg per day; *Q* is the centered streamflow, in cubic feet per second; *dtime* is the centered decimal time in years from the beginning of the calibration period; sin ($2\pi T$) and cos ($2\pi T$) are periodic time functions that describe seasonal variability; a0, a1, a2, a3, a4, a5, and a6 are regression coefficients (constant over time, best fit values are below).

a0	a1	a2	a3	a4	a5	a6
0.9216	0.7088	-0.049	-0.1985	0.2555	-0.1805	-0.1867

Credit author Statement

Pétré M-A: Methodology, Formal analysis, Data Curation, Visualization Writing - Original Draft, **Genereux DP**: Conceptualization, Supervision, Writing - Review & Editing, **Salk KR**: Formal analysis, Writing - Review & Editing, **Ferguson PL:** Writing - Review & Editing, **Tait G:** Investigation, Resources, **Obenour DR:** Writing - Review & Editing, **Knappe DRU**; Writing - Review & Editing, **Stapleton HM**: Conceptualization, Writing - Review & Editing, Funding Acquisition, Supervision

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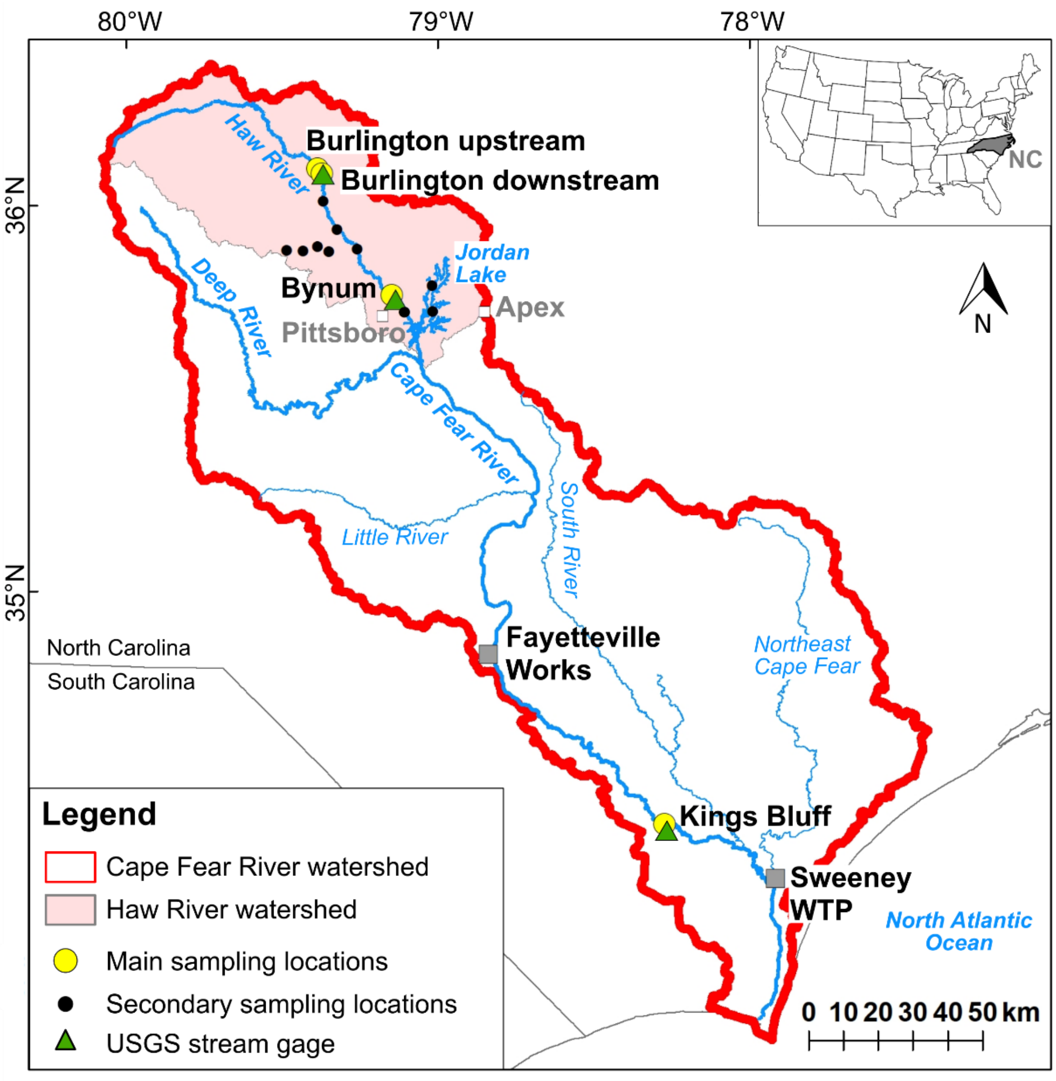

Figure 1 Study area and location of sampling sites in the Cape Fear River watershed, North Carolina (NC).

Table 1 Abbreviation and class of the 43 PFAS targeted in the Cape Fear River and the Haw River (bold font).

PFAS class	PFAS targeted
FTS	10:2 FTS, 8:2 FTS, **6:2 FTS**, **4:2 FTS**
Sulfonamides	NMeFOSAA, N-EtFOSE,NEtFOSAA,N-MeFOSE,NMeFOSA, EtFOSAm, PFOSA
PFCA	**PFPeA**, **PFOA**, **PFDA**, **PFHxA**, **PFBA**, **PFHpA**, **PFNA**, PFUdA, PFDoA, PFTDA, PFHxDA, PFTrDA
PFSA	**PFOS**, PFPeS, **PFHxS**, **PFBS**, PFHpS, PFDS, PFNS
PFEA	**GenX**, PMPA, PEPA, PFMOAA, PFO2HxA, PFO3OA,PFO4DA, Nafion Byproduct1, Nafion Byproduct2, PFO3ONS, PFO3UdS, PFECA-G, ADONA

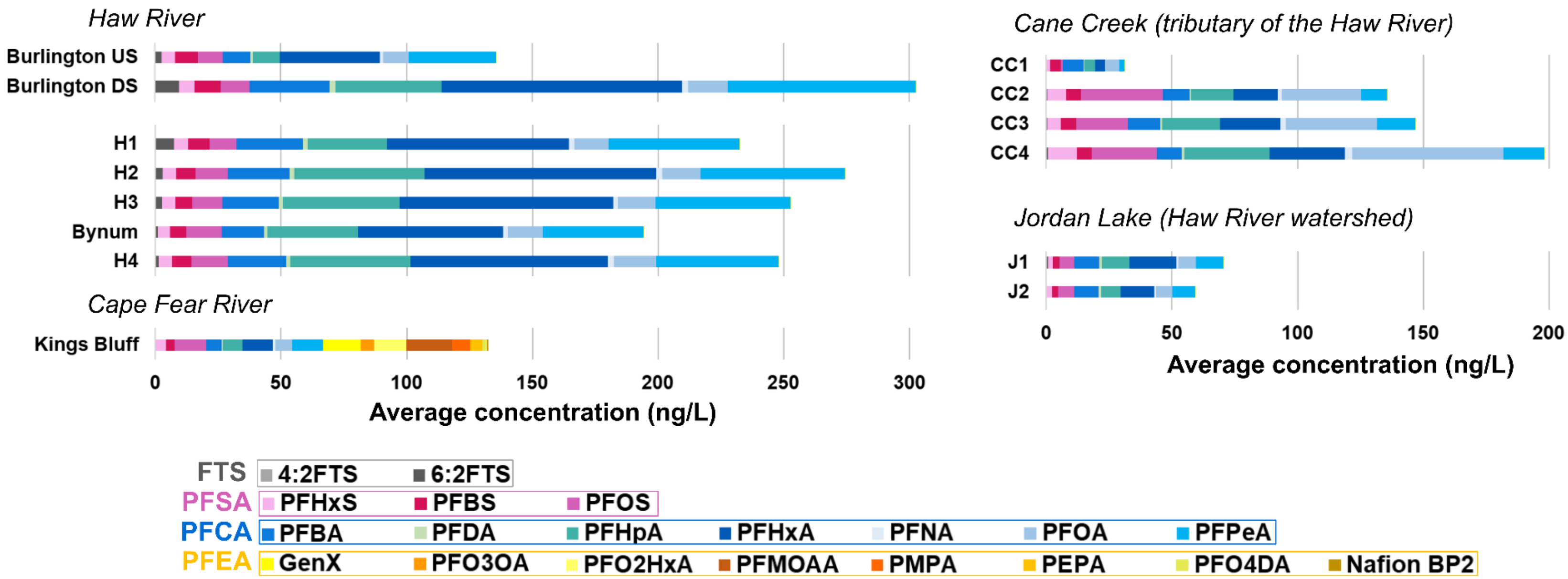

Figure 2 Average concentration of samples collected between 2019 and 2020 in the Haw River watershed and during 2018-2020 at Kings Bluff in the Cape Fear River watershed. Samples with concentrations <MRL were considered as zero when calculating average. GenX was the only PFEA targeted in the Haw River watershed and 4:2 FTS concentrations were always ≤0.2 ng/L.

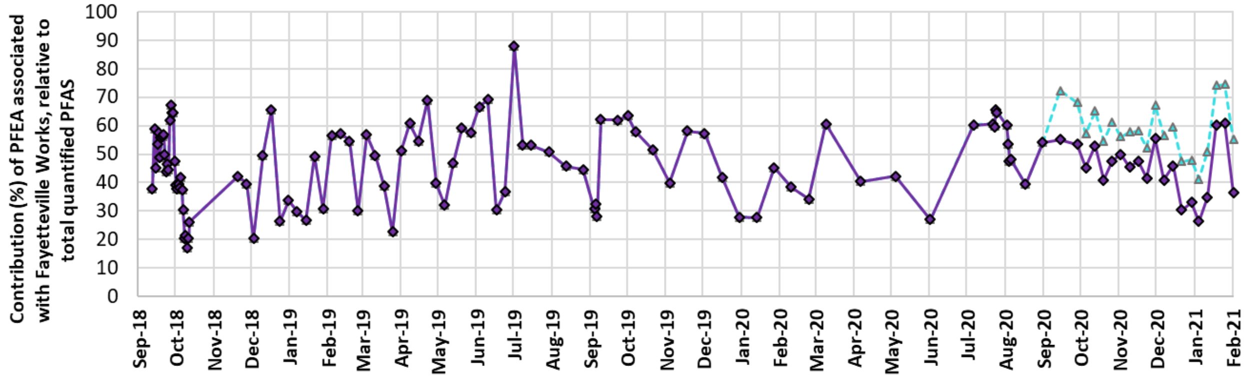

Figure 3 Estimated proportion (%) of PFEAs associated with the Fayetteville Works relative to the total quantified PFAS in the Cape Fear River at Kings Bluff. Ten PFEAs associated with the plant were targeted during the entire measurement period (solid line), and 20 (the original 10 plus 10 more) were targeted beginning in September 2020 (dashed line).

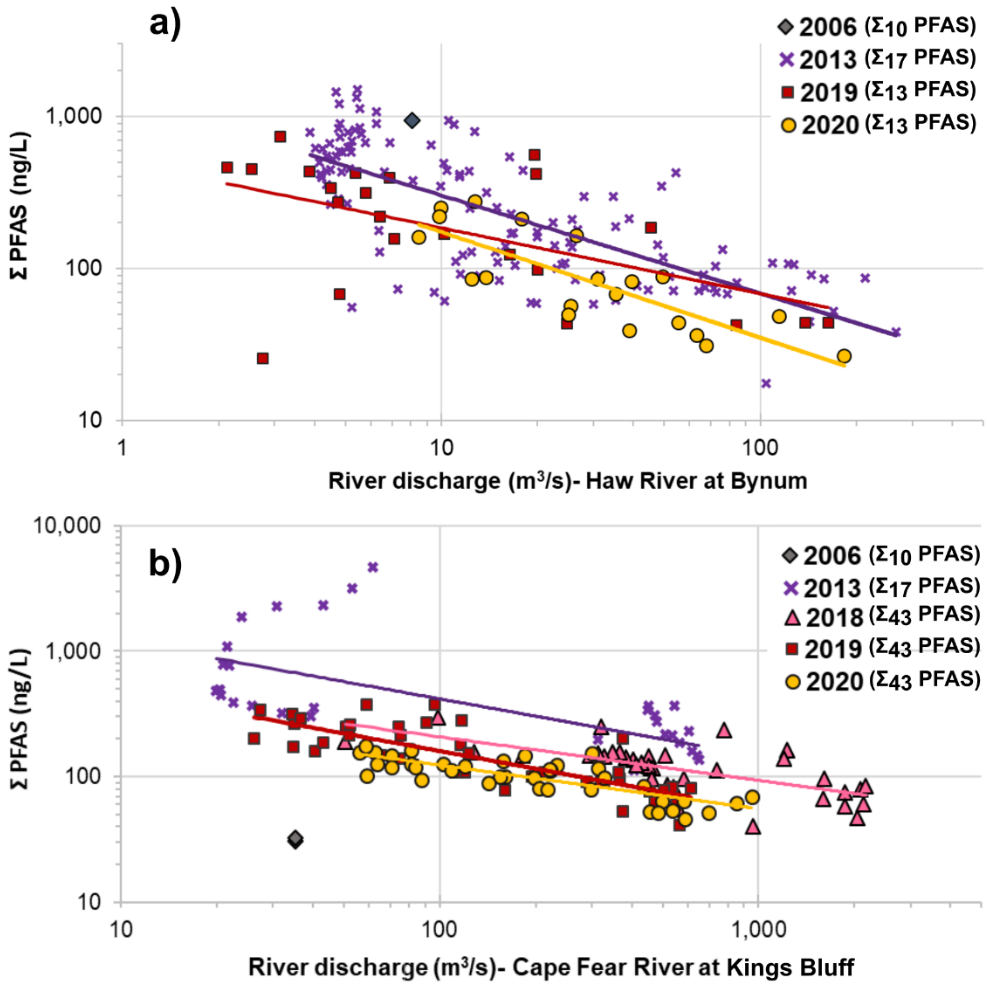

Figure 4 Concentration-discharge relationship at a) Bynum and b) Kings Bluff in 2006 (Nakayama et al. 2007), 2013 (Sun et al. 2016), and 2018-2020 (this study).

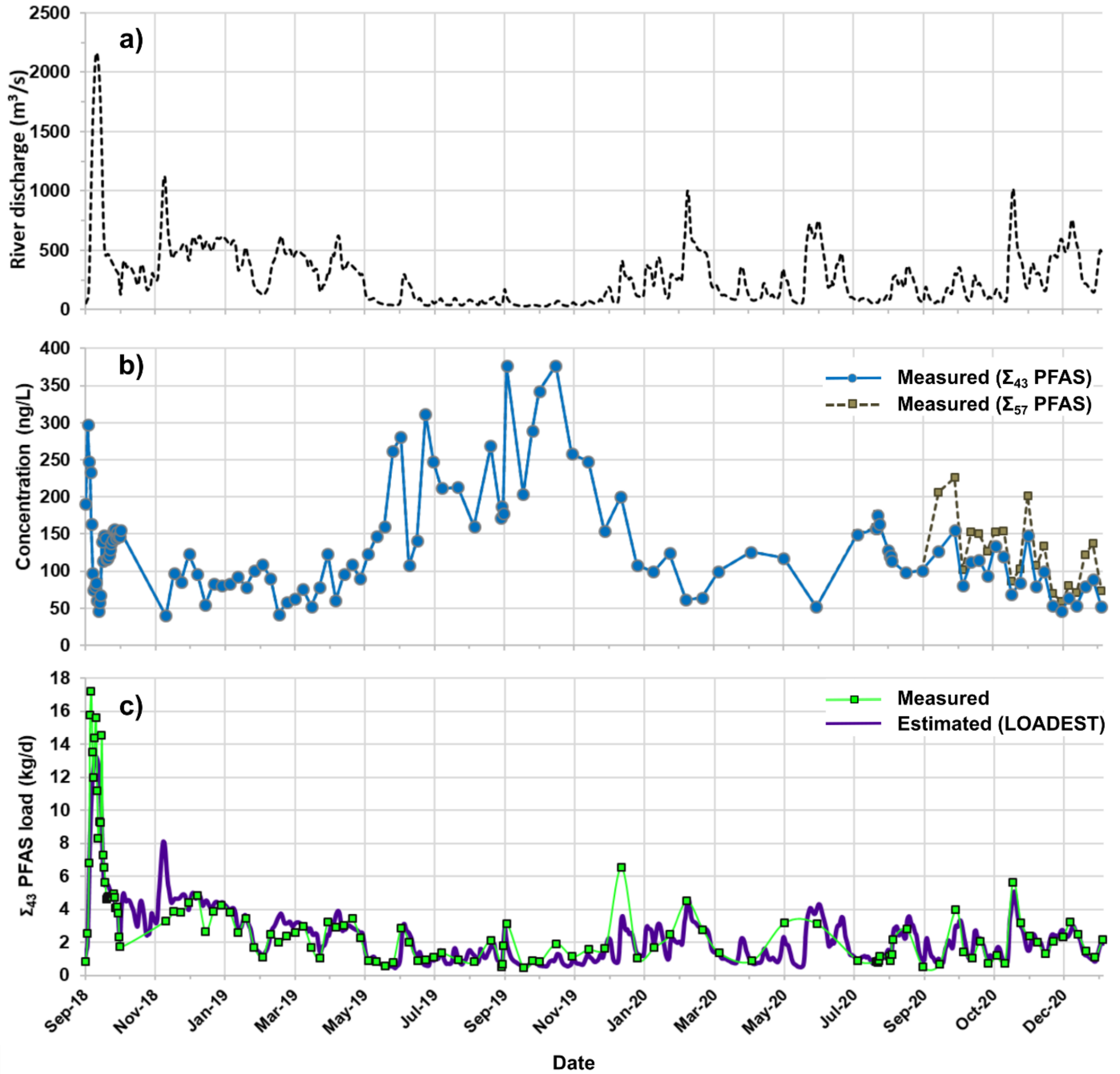

Figure 5 a) River discharge (m^3/s) in the Cape Fear River at Kings Bluff, b) Σ_{43}PFAS concentration (ng/L) and Σ_{57}PFAS concentration (ng/L) and c) Observed and estimated Σ_{43}PFAS load (kg/d) in the Cape Fear River at Kings Bluff.

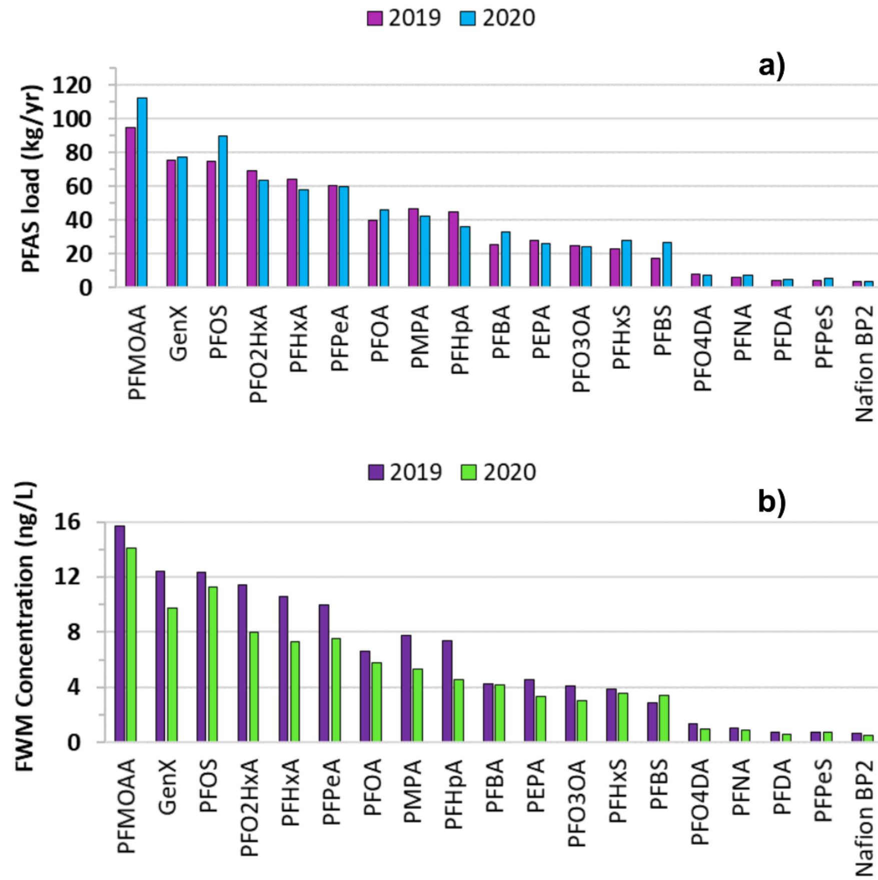

Figure 6 a) LOADEST estimated PFAS load and b) flow weighted mean concentration (FWM) for the main 19 PFAS found in the Cape Fear River at Kings Bluff in 2019 and 2020.

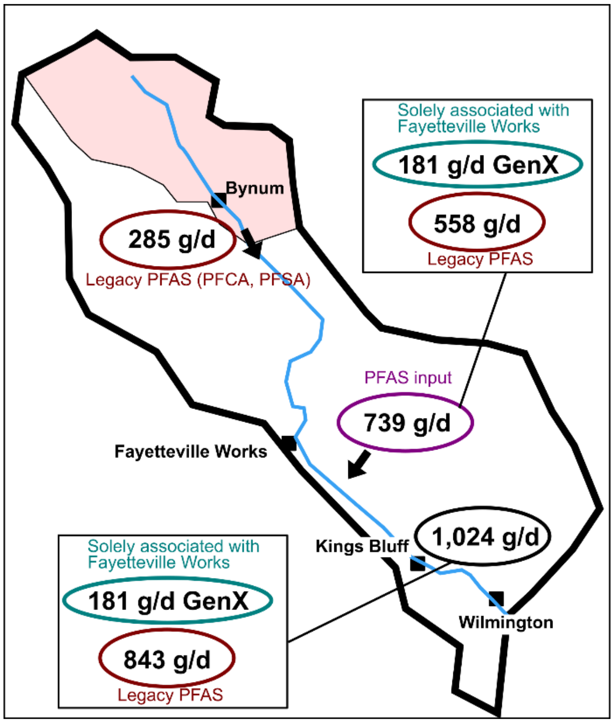

Figure 7 Average Σ₁₃PFAS river export (g/day) at Bynum and Kings Bluff from 10 June 2019 to 20 July 2020, considering the 13 PFAS targeted at Bynum. See Table 1 for the list of PFAS.

Supplementary Material for

Per- and poly-fluoroalkyl substances (PFAS) in river discharge: modeling loads upstream and downstream of a PFAS manufacturing plant in the Cape Fear watershed, North Carolina.

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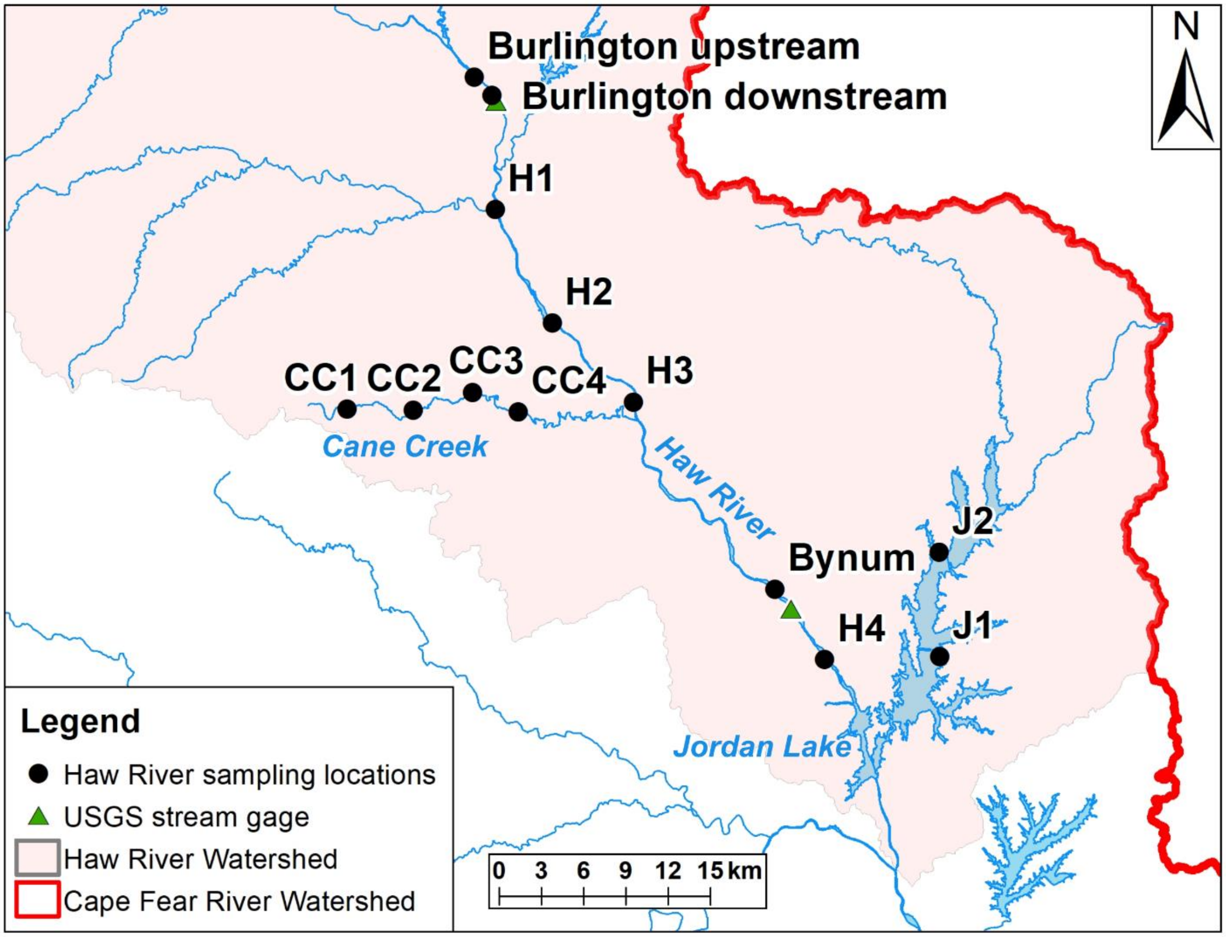


Figure S2 Sampling sites and stream gages in the Haw River basin.

Text S1 Chemicals and standards/ extraction and analysis

Water samples collected in the Haw River watershed were processed as in Herkert et al. (2020). Samples were stored in a 4°C refrigerator until analysis, and were filtered under vacuum using a glass fiber filter . Laboratory blanks (800 mL of LC-MS water) were processed in each batch of water samples. All samples were spiked with an isotopically labelled GenX [2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)-13C3-propanoic acid] and a mix of isotopically labelled PFAAs from Wellington Laboratories (MPFAC-MXA). This mix includes, Perfluoro-n-[1,2,3,4-13C4]butanoic acid, Perfluoro-n-[1,2-13C2]hexanoic acid, Perfluoro-n-[1,2,3,4-13C4]octanoic acid, Perfluoro-n-[1,2,3,4,5-13C5]nonanoic acid, Perfluoro-n-[1,2-13C2]decanoic acid, Perfluoro-n-[1,2-13C2]undecanoic acid, Perfluoro-n-[1,2-13C2]dodecanoic acid, Sodium perfluoro-1-hexane[18O2]sulfonate, and Sodium perfluoro-1-[1,2,3,4-13C4]octanesulfonate .

Samples were extracted for PFAS using a Thermo Scientific™ Dionex™ AutoTrace™ 280 Solid-Phase Extraction (SPE) instrument. Water extracts were analyzed in electrospray negative mode on an Agilent

1260 Infinity II LC system coupled to an Agilent 6460A triple quadrupole mass spectrometry (LC-MS/MS).

Water samples collected in the Cape Fear River at Kings Bluff were taken by the CFPUA from both the Lower Cape Fear Water & Sewer Authority (LCFWSA) tap and the Kings Bluff tap, which come from each of the pump stations at Lock and Dam 1. The containers used to collect samples were 250 mL high-density polyethylene (HDPE) bottles with TRIZMA preservation in them. Water samples were put on ice at the time of collection and were kept on ice until analysis at Gel analytical in Charleston, South Carolina. PFAS were determined in water samples following the EPA Method 537 by solid phase extraction and liquid chromatography/tandem mass spectrometry (LC/MS/MS).

Text S2 Quality Assurance and Quality control

Laboratory processing blanks were included in every batch of samples. Method detection limits (MDL) were determined for each batch of samples and were calculated using three times the standard deviation of laboratory processing blanks. MDLs ranged from 0.02 for GenX to 1.1 ng/L for PFOS among the batches. Average recoveries for labelled PFAAs were 74%.

Table S1 Statistics of PFAS concentrations (ng/L) in river water collected in the Haw River watershed (considering all 13 sampling stations).

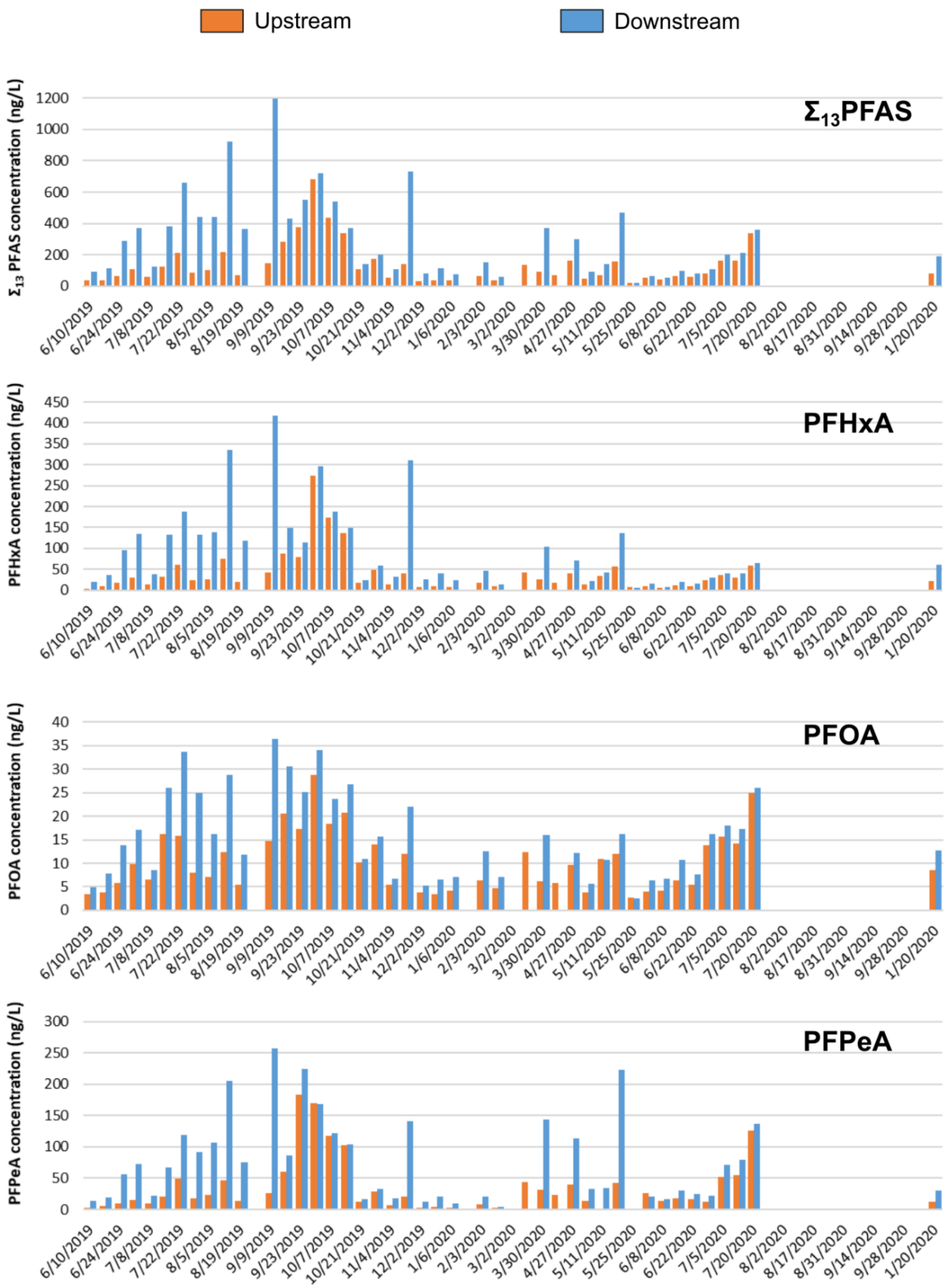
	Min	25th percentile	Median	Mean*	75th percentile	Max
4:2FTS	<MDL	<MDL	<MDL	0.1	<MDL	2.3
6:2FTS	<MDL	<MDL	0.3	2.4	1.3	72.4
GenX	<MDL	<MDL	0.1	0.1	0.1	2.4
PFBA	<MDL	4.7	9.2	17.0	18.1	189.9
PFBS	<MDL	2.4	4.2	6.6	7.8	70.8
PFDA	<MDL	0.5	0.9	1.3	1.7	7.2
PFHpA	<MDL	6.6	13.0	28.0	33.5	235.9
PFHxA	<MDL	12.1	23.2	49.6	50.2	416.8
PFHxS	<MDL	2.5	4.1	5.2	6.9	24.6
PFNA	<MDL	0.8	1.4	1.8	2.4	11.8
PFOA	0.7	6.7	12.5	18.7	23.7	133.3
PFOS	<MDL	6.9	10.5	13.6	16.4	110.8
PFPeA	<MDL	7.6	14.9	34.0	42.2	274.1
ΣPFAS	<MDL	<MDL	42.4	104.5	139.0	1196.5

*arithmetic mean

Table S2 Statistics of PFAS concentrations (ng/L) in the Haw River at the Bynum sampling station.

	Min	25th percentile	Median	Mean*	75th percentile	Max
4:2FTS	<MDL	<MDL	<MDL	0.1	<MDL	1.6
6:2FTS	<MDL	0.1	0.4	1.0	1.2	5.8
GenX	<MDL	<MDL	0.1	0.1	0.2	1.7
PFBA	<MDL	2.7	10.2	16.8	25.8	67.9
PFBS	<MDL	2.3	4.7	6.4	7.9	21.3
PFDA	0.3	0.5	1.1	1.4	1.7	6.3
PFHpA	2.5	5.6	12.5	36.1	53.8	166.2
PFHxA	<MDL	11.1	29.9	57.6	89.4	276.9
PFHxS	1.7	3.1	4.4	4.8	6.0	11.0
PFNA	0.5	0.9	1.4	2.0	2.4	11.8
PFOA	4.9	7.3	11.6	13.8	19.4	32.1
PFOS	6.0	8.6	11.1	14.1	17.0	58.3
PFPeA	<MDL	9.4	26.2	40.1	59.4	169.8
ΣPFAS	25.9	49.4	124.7	194.2	276.0	742.2

*arithmetic mean


Upstream
Downstream
Σ_{13}PFAS
Σ_{13} PFAS concentration (ng/L)
PFHxA
PFHxA concentration (ng/L)
PFOA
PFOA concentration (ng/L)
PFPeA
PFPeA concentration (ng/L)
6/10/2019
6/24/2019
7/8/2019
7/22/2019
8/5/2019
8/19/2019
9/9/2019
9/23/2019
10/7/2019
10/21/2019
11/4/2019
12/2/2019
1/6/2020
2/3/2020
3/2/2020
3/30/2020
4/27/2020
5/11/2020
5/25/2020
6/8/2020
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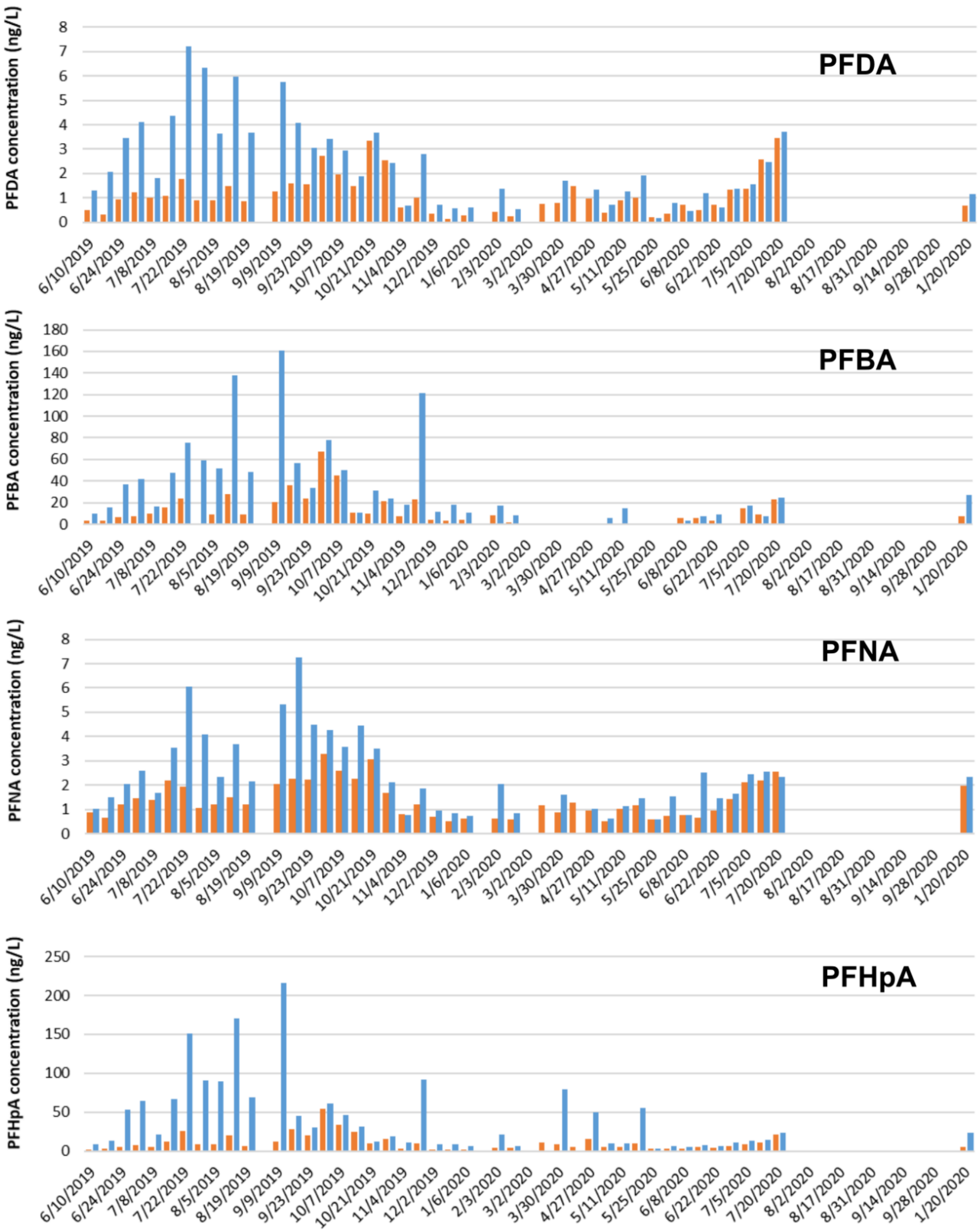
7/20/2020
8/2/2020
8/17/2020
8/31/2020
9/14/2020
9/28/2020
1/20/2020


PFDA
PFDA concentration (ng/L)
PFBA
PFBA concentration (ng/L)
PFNA
PFNA concentration (ng/L)
PFHpA
PFHpA concentration (ng/L)

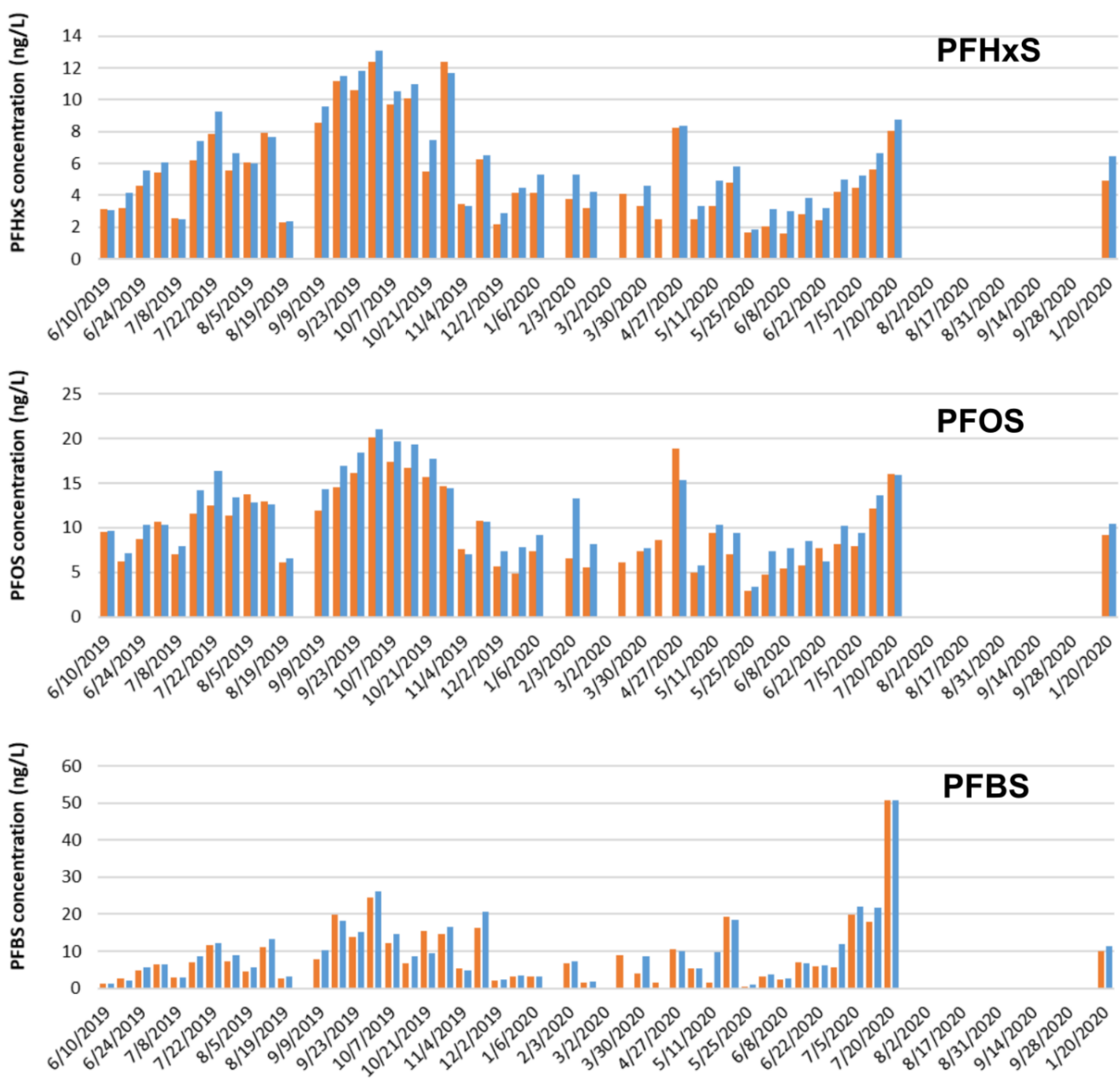


Figure S2 PFAS concentrations (ng/L) in the Haw River for selected targeted PFAS and Σ_{13}PFAS at stations "Burlington upstream" and "Burlington downstream".

Table S3 Statistics of PFAS concentrations in water collected in the Cape Fear River at Kings Bluff.

	Min	25th percentile	Median	Mean*	75th percentile	Max
PFMOAA	<MDL	7.8	14.6	18.2	24.2	63.0
PFOS	<MDL	9.5	12.6	12.5	15.1	21.4
GenX	3.1	7.8	11.3	14.8	18.7	76.0
PFPeA	<MDL	6.1	9.2	12.2	16.2	45.1
PFHxA	2.5	5.7	8.6	12.0	15.2	45.5
PFO2HxA	<MDL	5.3	8.4	12.9	14.8	57.7
PFOA	<MDL	5.2	6.7	6.7	8.0	12.1
PMPA	<MDL	4.0	6.0	7.2	9.5	64.9
PFBA	<MDL	4.2	5.7	6.1	7.8	18.3
PFHpA	1.7	3.3	5.3	7.8	10.1	30.2
PFHxS	<MDL	3.2	4.0	4.1	4.7	9.4
PFO3OA	<MDL	2.6	4.0	5.4	6.2	43.4
PFBS	1.4	2.4	3.3	3.5	4.3	10.3
PEPA	<MDL	<MDL	2.4	4.8	6.9	25.7
PFO4DA	<MDL	<MDL	1.5	1.7	2.3	14.6
PFNA	<MDL	0.9	1.1	1.1	1.4	2.5
PFDA	<MDL	<MDL	0.7	0.6	1.0	1.9
PFPeS	<MDL	<MDL	0.7	0.6	0.8	5.7
NafionBP2	<MDL	<MDL	<MDL	0.6	1.4	6.1

*arithmetic mean

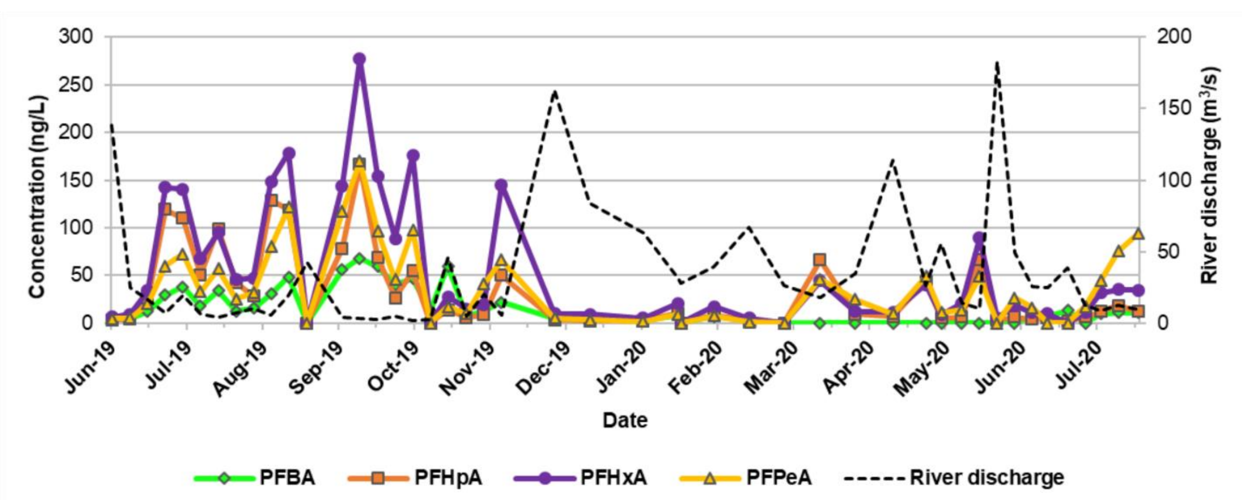


Figure S3 PFAS concentration (ng/L) at Bynum for the four most abundant PFAS in the Haw River basin. River discharge (m^3/s) at the USGS gage station "Haw River at Bynum" (USGS02096960) is also shown.

*Table S4 Spearman correlation coefficients for the 13 PFAS detected in the Haw River at Bynum. ***p<.001, **p<.01, *p<.05, ns=not significant (p>.05). Shaded values show significant correlations.*

	4:2FTS	6:2FTS	GenX	PFBA	PFBS	PFDA	PFHpA	PFHxA	PFHxS	PFNA	PFOA	PFOS	PFPeA
4:2FTS	1	0.23^{ns}	0.23^{ns}	0.44**	0.44**	0.31*	0.3^{ns}	0.31*	0.49***	0.36*	0.4**	0.27^{ns}	0.18^{ns}
6:2FTS		1	0.02^{ns}	0.38*	0.35*	0.48**	0.44**	0.51***	0.5***	0.47**	0.49**	0.41**	0.48**
GenX			1	0.09^{ns}	0.16^{ns}	0.16^{ns}	0.18^{ns}	0.18^{ns}	0.14^{ns}	0.1^{ns}	0.05^{ns}	0.05^{ns}	0.22^{ns}
PFBA				1	0.57***	0.64***	0.62***	0.68***	0.66***	0.68***	0.59***	0.28^{ns}	0.58***
PFBS					1	0.75***	0.57***	0.63***	0.81***	0.73***	0.8***	0.54***	0.65***
PFDA						1	0.7***	0.74***	0.81***	0.94***	0.86***	0.81***	0.71***
PFHpA							1	0.96***	0.75***	0.68***	0.76***	0.47**	0.9***
PFHxA								1	0.8***	0.73***	0.78***	0.51***	0.92***
PFHxS									1	0.85***	0.92***	0.7***	0.75***
PFNA										1	0.89***	0.8***	0.7***
PFOA											1	0.78***	0.76***
PFOS												1	0.46**
PFPeA													1

*Table S5 Spearman correlation coefficients for the main 19 PFAS found in the Cape Fear River at Kings Bluff. ***p<.001, **p<.01, *p<.05, ****p<.05, ns=not significant (p>.05). Shaded values show significant correlations.*

	GenX	NafionBP2	PFBA	PFBS	PFDA	PFHpA	PFHxA	PFHxS	PFMOAA	PEPA	PMPA	PFNA	PFO2HxA	PFO3OA	PFO4DA	PFOA	PFOS	PFPeA	PFPeS
GenX	1.00	0.72***	0.44***	0.46***	0.34***	0.38***	0.4***	0.58***	0.66***	0.4***	0.65***	0.2*	0.86***	0.83***	0.82***	0.2*	0.33***	0.48***	0.49***
NafionBP2		1.00	0.33***	0.41***	0.31**	0.34***	0.33***	0.54***	0.56***	0.32***	0.45***	0.17^{ns}	0.64***	0.65***	0.69***	0.22*	0.34***	0.41***	0.48***
PFBA			1.00	0.49***	0.63***	0.65***	0.73***	0.59***	0.24*	0.43***	0.12^{ns}	0.67***	0.4***	0.51***	0.56***	0.56***	0.55***	0.8***	0.52***
PFBS				1.00	0.44***	0.54***	0.6***	0.71***	0.53***	0.21*	0.31**	0.47***	0.47***	0.44***	0.4***	0.57***	0.54***	0.62***	0.82***
PFDA					1.00	0.73***	0.74***	0.54***	0.05^{ns}	0.26**	0.09^{ns}	0.79***	0.23*	0.34***	0.45***	0.7***	0.75***	0.7***	0.51***
PFHpA						1.00	0.97***	0.68***	0.16^{ns}	0.27**	0.16^{ns}	0.73***	0.37***	0.41***	0.47***	0.8***	0.73***	0.87***	0.64***
PFHxA							1.00	0.74***	0.21*	0.28**	0.17^{ns}	0.77***	0.41***	0.46***	0.52***	0.83***	0.76***	0.94***	0.67***
PFHxS								1.00	0.52***	0.29**	0.35***	0.59***	0.64***	0.64***	0.68***	0.68***	0.77***	0.76***	0.77***
PFMOAA									1.00	0.26**	0.38***	0.08^{ns}	0.75***	0.71***	0.57***	0.18^{ns}	0.27**	0.35***	0.45***
PEPA										1.00	0.15^{ns}	0.25**	0.34***	0.45***	0.4***	0.17^{ns}	0.24*	0.31**	0.23*
PMPA											1.00	-0.03^{ns}	0.58***	0.49***	0.47***	0.05^{ns}	0.11^{ns}	0.2*	0.33***
PFNA												1.00	0.22*	0.32***	0.4***	0.8***	0.8***	0.74***	0.49***
PFO2HxA													1.00	0.89***	0.77***	0.27**	0.37***	0.5***	0.51***
PFO3OA														1.00	0.85***	0.33***	0.44***	0.57***	0.51***
PFO4DA															1.00	0.37***	0.49***	0.64***	0.49***
PFOA																1	0.86***	0.76***	0.6***
PFOS																	1	0.72***	0.62***
PFPeA																		1	0.68***
PFPeS																			1

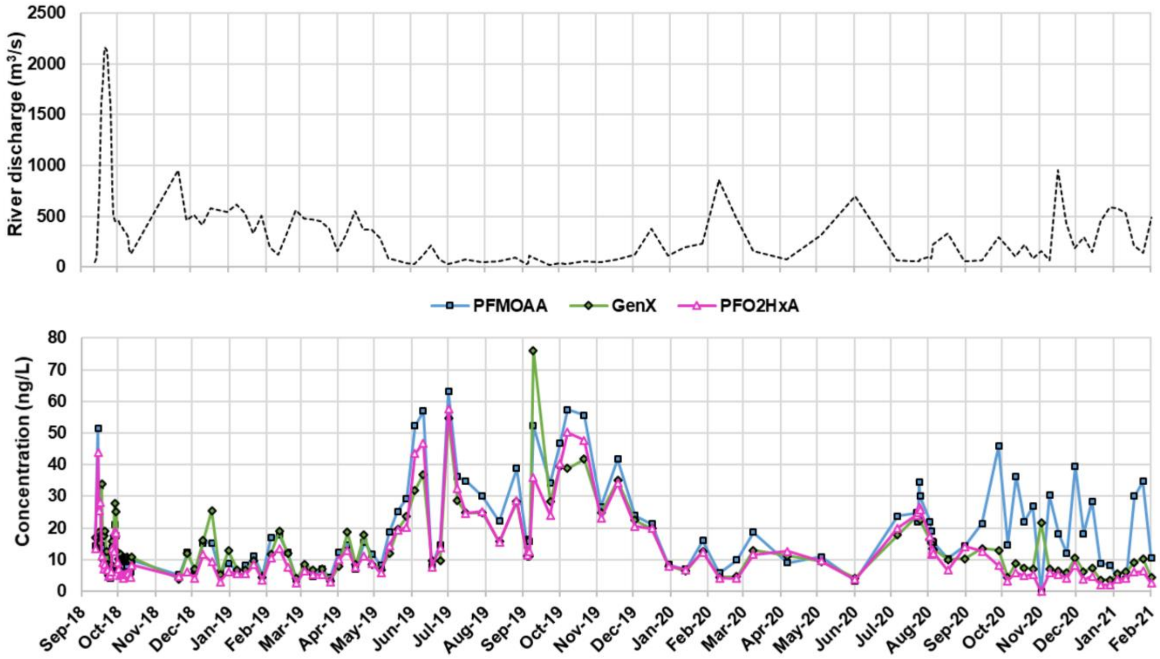


Figure S4 Cape Fear River discharge (m^3/s) at USGS gage station Lock and Dam #1 (top) and concentration (ng/L) of the three most abundant PFEA detected in the Cape Fear river at Kings Bluff.

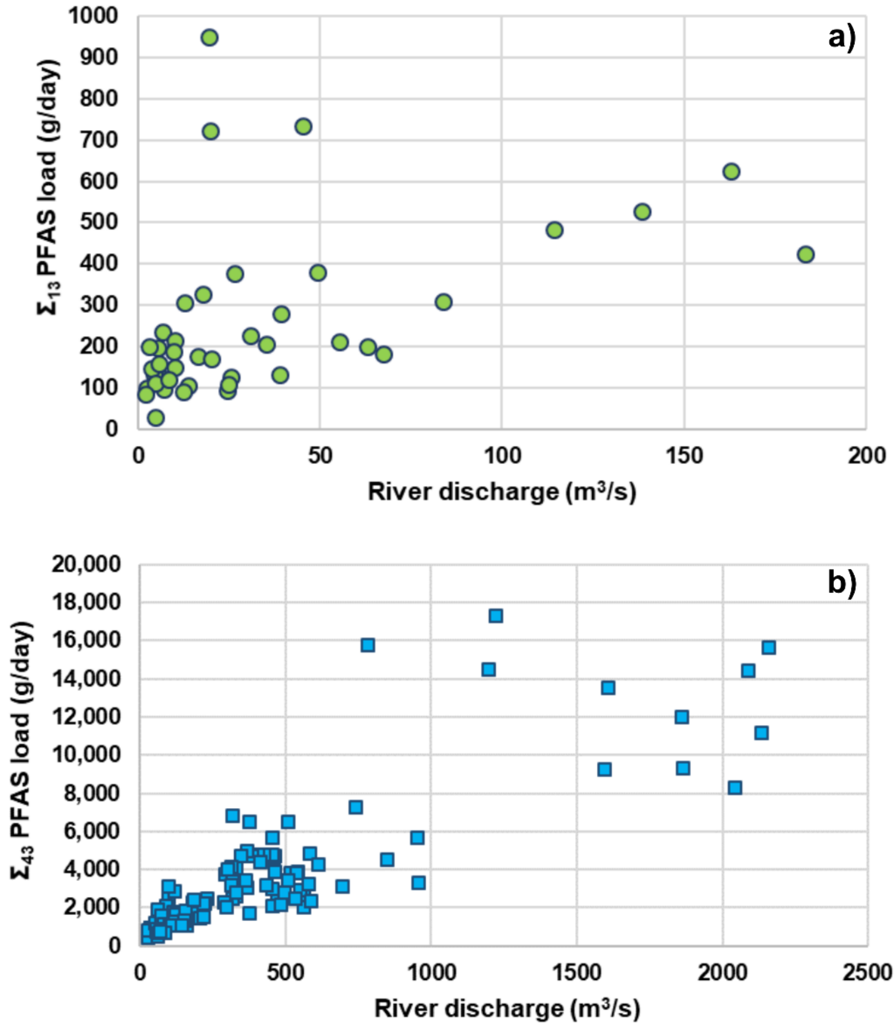


Figure S5 Relationship between PFAS export load and river discharge a) in the Haw River at Bynum and b) in the Cape Fear River at Kings Bluff.

Table S6 Flow-weighted mean (FWM) concentration for the main 19 PFAS detected in the Cape Fear River at Kings Bluff in 2019, 2020, and the entire monitoring period (Sept.2018 - Feb.2021).

	FWM concentration (ng/L)		
	2019	**2020**	**2018-2021**
Σ_{19}PFAS	109.8	91.3	98.7
Σ_{43}PFAS	109.8	91.3	98.7
Σ_{57}PFAS	107.5	102.7	104.1
PFMOAA	15.7	14.1	13.6
GenX	12.4	9.7	10.9
PFOS	12.3	11.3	11.5
PFO2HxA	11.4	8.0	8.7
PFHxA	10.6	7.3	9.0
PFPeA	10.0	7.5	9.0
PFOA	6.6	5.8	6.1
PFMOPrA	7.7	5.3	6.0
PFHpA	7.4	4.6	6.0
PFBA	4.2	4.1	4.8
PFMOBA	4.6	3.3	3.9
PFO3OA	4.1	3.0	3.6
PFHxS	3.8	3.6	3.6
PFBS	2.9	3.4	3.0
PFO4DA	1.3	1.0	1.2
PFNA	1.0	0.9	1.0
PFDA	0.7	0.6	0.7
PFPeS	0.7	0.7	0.7
Nafion BP2	0.6	0.5	0.6

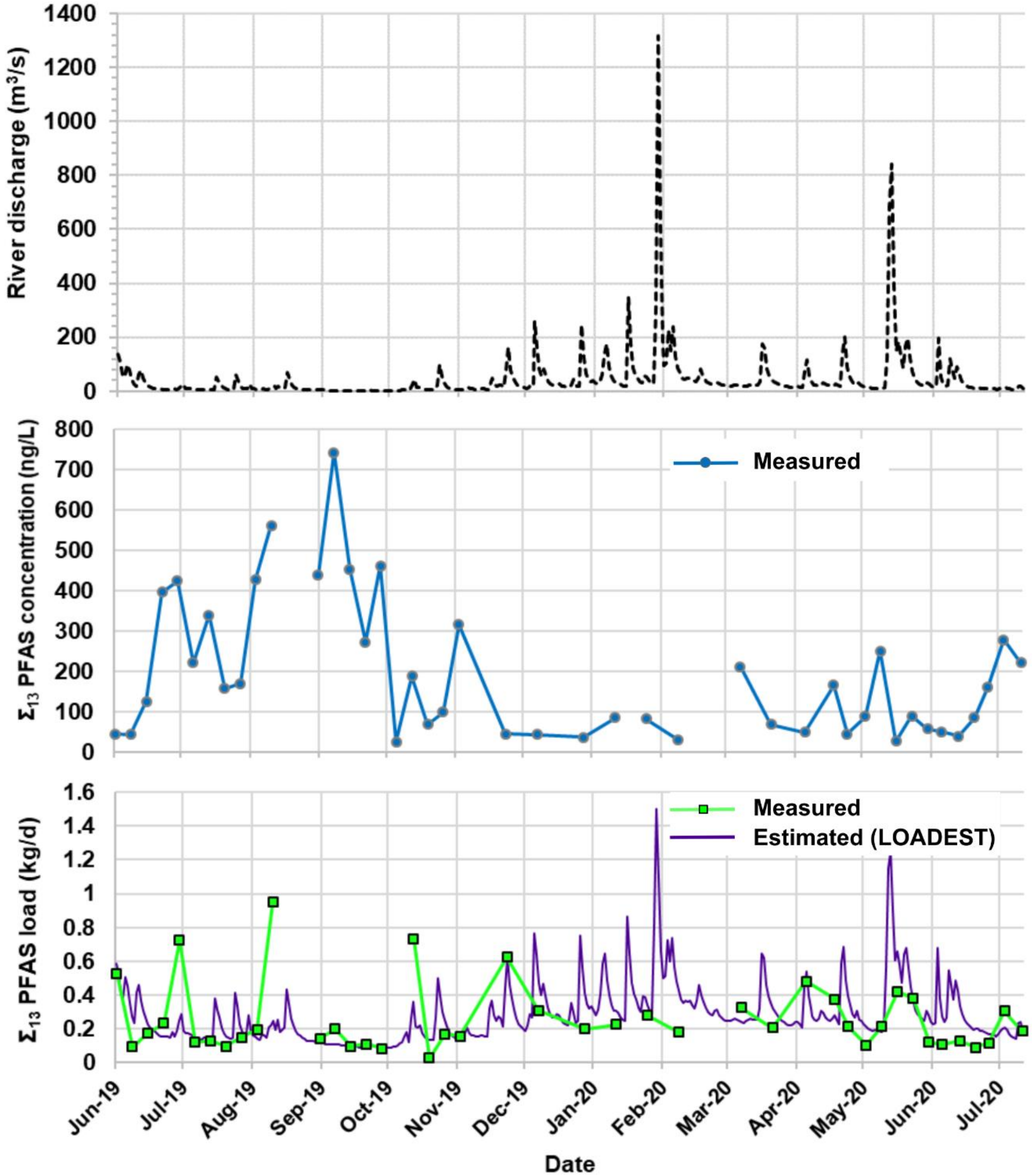


Figure S6 a) River discharge (m^3/s) in the Haw River at Bynum, b) Σ_{13}PFAS concentration (ng/L) and c) observed and estimated Σ_{13}PFAS load (kg/d) in the Haw River at Bynum.

Table S7 Summary of PFAS yield (kg/km²yr) in the Haw River and Cape Fear River watersheds and in recent studies.

Location	ΣPFAS	Yield (kg/km² yr)	Reference
Cape Fear River at Kings Bluff	43	6.2×10^{-2}	This study
Haw River at Bynum	13	3.2×10^{-2}	This study
Georgia Branch (tributary of the Cape Fear River)	29	1	Pétré et al. (2021)
Rhone River		0.1	Schmidt et al. (2019)
Po River		0.1	Pistocchi et al. (2009)
Ganges		2×10^{-4}	Sharma et al. (2016)
Rhine River		6×10^{-3}	Pistocchi et al. (2009)
Vantaanjoki	10	4.7×10^{-3}	Juntilla et al (2019)
Seine River	16	6.9×10^{-3}	Munoz et al. (2018)

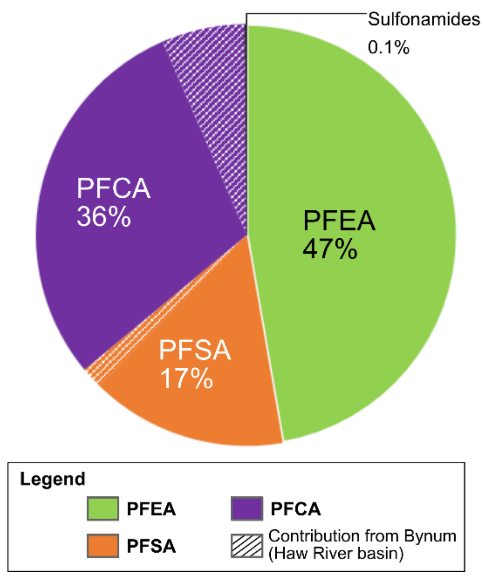


Figure S7 Average PFAS composition in the Cape Fear River at the Kings Bluff sampling station from September 2018 to February 2021. The shaded areas correspond to the contribution of the Haw River basin at Bynum

Table S8 Drinking water standards for selected PFAS and corresponding maximum concentrations (ng/L) measured at Bynum and Kings Bluff.

				Maximum Contaminant Levels (ng/L)		
	Maximum Conc. at Bynum	**Maximum Conc. at Kings Bluff**	**EPA Health Advisory**	**New Jersey**	**Michigan**	**Massachusetts**
PFOA	32.1	12.1	70	14	8	
PFOS	58.3	21.4	70	13	16	
Sum of PFOA & PFOS	90.4	30.0	70			
Sum of PFOS, PFOA,PFHxS, PFHpA, PFNA, PFDA	216.1	65.4				20