



Spatial distribution and mass transport of Perfluoroalkyl Substances (PFAS) in surface water: A statewide evaluation of PFAS occurrence and fate in Alabama



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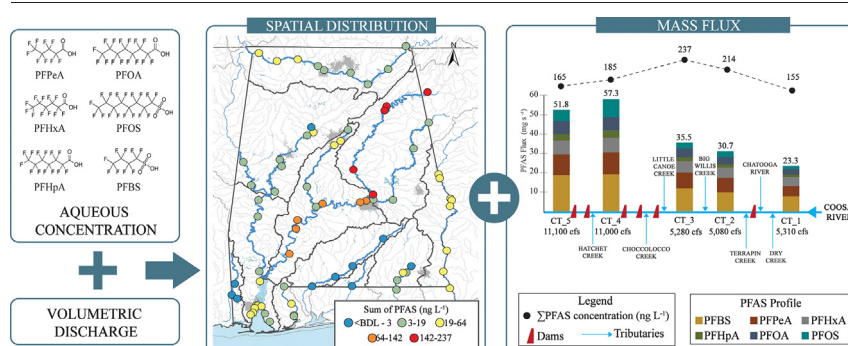
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HIGHLIGHTS

- This study evaluated the distribution and mass transport of 17 PFAS in Alabama.
- PFAS were detected in 88% of surface water samples, reaching up to 237 ng L⁻¹.
- Short-chain PFAS accounted for the majority of the contamination in the samples.
- Increases in mass fluxes were observed as rivers moved through Alabama.
- Mass flux is a simple approach to understand mass transport trends in large rivers.

GRAPHICAL ABSTRACT



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ABSTRACT

Per- and polyfluoroalkyl substances (PFAS) have been previously detected near suspected sources in Alabama, but the overall extent of contamination across the state is unknown. This study evaluated the spatial distribution of 17 PFAS within the ten major river basins in Alabama and provided insights into their transport and fate through a mass flux analysis. Six PFAS were identified in 65 out of the 74 riverine samples, with mean Σ_6 PFAS levels of 35.2 ng L⁻¹. The highest Σ_6 PFAS concentration of 237 ng L⁻¹ was detected in the Coosa River, a transboundary river that receives discharges from multiple sources in Alabama and Georgia. PFAS distribution was not observed to be uniform across the state: while the Coosa, Alabama, and Chattahoochee rivers presented relatively high mean Σ_6 PFAS concentrations of 191, 100 and 28.8 ng L⁻¹, respectively, PFAS were not detected in the Conecuh, Escatawpa, and Yellow rivers. Remaining river systems presented mean Σ_6 PFAS concentrations between 7.94 and 24.7 ng L⁻¹. Although the short-chain perfluoropentanoic acid (PFPeA) was the most detected analyte (88%), perfluorobutanesulfonic acid (PFBS) was the substance with the highest individual concentration of 79.4 ng L⁻¹. Consistent increases in the mass fluxes of PFAS were observed as the rivers flowed through Alabama, reaching up to 63.3 mg s⁻¹, indicating the presence of numerous sources across the state. Most of the mass inputs would not have been captured if only aqueous concentrations were evaluated, since concentration is usually heavily impacted by environmental conditions. Results of this study demonstrate that mass flux is a simple and powerful complementary approach that can be used to broadly understand trends in the transport and fate of PFAS in large river systems.

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1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are the focus of thousands of studies due to their adverse health effects in humans and wildlife. PFAS encompass a large group of anthropogenic organic substances widely used in industrial applications and consumer products, including in the coating of cookware and food packaging, stain- and water-repellent products and fabrics, as well as in the formulation of aqueous film forming foam (AFFF) fire extinguishers, ski wax, and much more (Johns and Stead, 2000; KEMI, 2015; Pan et al., 2018). In the late 1990s, 3M reported to the United States Environmental Protection Agency (US EPA) evidence that certain PFAS could bioaccumulate in humans (3M, 1998) and agreed to end the production of perfluorooctanesulfonic acid (PFOS) and its related salts by 2002 (3M, 2000). Since then, several studies have reported that certain PFAS might have negative health impacts in humans, including carcinogenic (Steenland and Winquist, 2021) and endocrine disrupting (Gong et al., 2019) effects, increased blood cholesterol levels (Seo et al., 2018), and obesity (Braun, 2017). In wildlife, PFAS can bioaccumulate and biomagnify through food chains (Xu et al., 2014), inhibit growth (McCarthy et al., 2017), and act as endocrine disruptors (Pedersen et al., 2016). Thus, the presence of PFAS in aquatic environments is of great concern.

Due to their stability and heterogeneity, the remediation of PFAS-contaminated waste is challenging (Ross et al., 2018), and PFAS are often discharged into the environment without proper treatment. Sources include municipal wastewater treatment plants (WWTPs), industrial facilities, landfills, airports, military bases, and firefighting training facilities, among others (Hu et al., 2016). As a result, PFAS have been identified on every continent, from remote Antarctica (Casal et al., 2017) to populous areas of Asia (Pan et al., 2017; Zushi et al., 2011) and Europe (Gobelius et al., 2018; Munoz et al., 2015). In the US, Alabama is a particular hotspot for PFAS. Previous studies, conducted in 2002 and 2017, identified an area of increased PFAS concentration in the Tennessee River downstream of several chemical facilities, including a 3M plant (Hansen et al., 2002; Newton et al., 2017). The 2017 study also identified nine previously unknown PFAS and two other novel substances that were structurally similar to existing PFAS (Newton et al., 2017). Even more troublesome, the Decatur WWTP distributed over 34,000 metric tons of biosolids contaminated with PFAS to local farmers between 1995 and 2008 (Lindstrom et al., 2011). Lindstrom et al. (2011) found PFAS levels up to 31,906 ng L⁻¹ in surface water near fields that received the contaminated biosolids. In response, the Alabama Department of Environmental Management (ADEM) announced a consent order with 3M, stating that the company must remediate contaminated sites in the Decatur area, as well as “monitor, test, and research impacts of exposure” (ADEM, 2020). Similarly, high levels of PFAS were also identified in the Coosa River (Lasier et al., 2011) – the main drinking water source for several cities in Alabama. The City of Gadsden, AL is currently litigating against more than 30 textile companies located in Georgia, arguing that these companies are responsible for the high levels of PFAS in the Coosa River. Recently, ADEM conducted a survey in 290 public water systems (PWS) for 18 PFAS (ADEM, 2021). According to their report, PFAS were found in 57 PWS, with ΣPFAS reaching up to 384 ng L⁻¹, indicating the presence of PFAS in their corresponding source waters, as these substances are not likely to be removed through conventional treatment processes (Crone et al., 2019).

While previous studies have greatly enhanced the understanding on PFAS sources and their overall distribution, much remains unknown regarding their transport and fate in the environment. This is partially related to the fact that most studies express PFAS contamination in terms of concentration, which is not sufficient to track contamination in large river systems. This is because aqueous concentrations are affected by a variety of environmental factors, such as precipitation and stormwater runoff. Thus, considering aqueous concentration alone can lead to erroneous conclusions regarding the amount and transport of contaminant mass through interconnected river systems. Moreover, identification of sources can be difficult, as variable environmental conditions may mask potential PFAS inputs. Mass

flux analysis is a simple complimentary approach that combines volumetric discharge and aqueous concentration. Most studies have used the concept of mass flux to estimate yearly mass discharge of tributaries into lakes or bays, using an annual average flow rate. For instance, Ma et al. (2018) calculated the fluxes of tributaries discharging into Taihu Lake and used them to determine sources, while Zhao et al. (2020) calculated the mass discharge of tributaries into the Bohai Sea. Results from those studies enhanced the understanding of the fate of PFAS in the environment, but not so much about their transport behavior. On the other hand, Nakayama et al. (2010) performed a mass flux analysis to track the mass transport of PFAS in the Upper Mississippi River Basin, by calculating the mass flux for sampling points using a 72-h average volumetric flow rate.

The ultimate fate of PFAS in the environment remains unclear. Studies have shown that some PFAS can be removed from water by partitioning to sediments and suspended particulates, volatilization, and sequestration by biota and wildlife (Casal et al., 2017; Liu et al., 2019; Munoz et al., 2019), depending on their chemical properties. Regardless of the environmental compartment, most terminal (stable) PFAS will persist virtually unchanged (Guelfo and Adamson, 2018), hence their nickname “forever chemicals”. Thus, this study aims to determine the spatial distribution of seventeen PFAS in surface water in Alabama and identify trends in their transport behavior through a mass flux analysis. Results of the mass flux analysis were also used to identify locations within the state serving as potential PFAS source areas. This is the first study to use mass flux analysis to systematically track PFAS contamination in multiple river systems at a state level in the US and demonstrates that mass flux analysis is a broadly applicable, reasonably simple approach for capturing large-scale trends in the transport of PFAS through interconnected surface water systems.

2. Methods

2.1. Chemicals and reagents

Target analytes include six perfluorocarboxylic acids (PFBA, PFPeA, PFHxA, PFHpA, PFOA, and PFNA), six perfluorosulfonic acids (PFBS, PFPeS, PFHxS, PFHpS, PFOS, and PFNS), and five perfluoroethers (HFPO-DA, NaDONA, PF4OPeA, PF5OHxA, and 3,6-OPFHpA). For the above analytes, eleven are considered short-chain PFAS (PFBA, PFPeA, PFHxA, PFHpA, PFBS, PFPeS, and all the perfluoroethers). Analytical grade PFAS standards were purchased from Wellington Laboratories (Ontario, Canada). The molecular weight, chemical structure, nomenclature, and CAS of analytes are listed in Table S1. High purity LC-MS grade solvents (water, methanol, and acetonitrile) were purchased from VWR international (Suwanee, GA), and mobile phase modifiers (ammonium formate) were purchased from Agilent Technologies (Wilmington, DE).

2.2. Field sampling

Given the geographic scale of this project, individual major river systems were not extensively sampled. Instead, sample locations were strategically determined to capture inlets and outlets of each river basin, confluence of rivers, changes in land use (agricultural vs. urban vs. forested), zones of hydrographical and geographical relevance, and inputs from industrial and municipal wastewater (see S2 for more details). Based on these criteria, 74 sampling locations were selected from fourteen river systems across ten river basins, namely the Alabama (AC-1,6), Black Warrior (BT-1,6), Cahaba (AC-7,10), Chattahoochee (CH-1,8), Choctawhatchee (CW-1,5), Conecuh (CO-1,4), Coosa (CT-1,5), Escatawpa (ES-1,2), Perdido (FP-2,5), Tallapoosa (CT-6,9), Tennessee (TN-1,9), Tombigbee (BT-7,8 and TM-1,3), and Yellow rivers (FP-1), and Mobile River and Tributaries (TM-4,12).

Samples were collected between June 27th and August 30th, 2020, during seven sampling events, with each trip covering at least one river basin. A complete list of geographical coordinates and time/date of sampling is available in Table S2. Samples were collected from bridges, public access areas, and boat ramps. A sampling device consisting of a 1-gallon high-density polyethylene (HDPE) storage bottle attached to a 100 ft. rope and

5 lb. weight was developed (Fig. S2). At each location, the sampling device was used to collect 2 L of surface water, which was transferred to a labeled HDPE storage bottle. One sample was collected in each location, as previous studies conducted by the authors suggest little to no variation in replicates (Mulabagal et al., 2018). Water parameters such as temperature, pH, and conductivity were measured in-situ using a Hanna HI98130 combo tester (Hanna Instruments, Inc.). To avoid cross-contamination between samples, the sampling device was thoroughly rinsed with deionized water (DI water) before and after each sampling collection. In between excursions, the sampler was rinsed with methanol and DI water in the laboratory. For quality control, a field blank was collected at each sampling excursion by transferring 2 L of DI water from the sampler to a labeled HDPE storage bottle. Samples and field blanks were transferred to the laboratory in coolers (-4°C).

2.3. Quantitative analysis

Surface water samples (2 L) were filtered under vacuum through $0.7\ \mu\text{m}$ GE Whatman glass microfiber filters (GE, Boston, MA, USA) to remove suspended particulates and large debris. Filtration was conducted within 48 h of samples arriving at the laboratory, and samples were either immediately processed or stored at -20°C . Samples were processed through solid phase extraction (SPE) following a previously published method (Mulabagal et al., 2018), with slight modifications. Briefly, 500 mL were loaded into Oasis WAX cartridges (6 cc, 150 mg; Waters Corporation, Milford, MA, US) pre-conditioned with 0.1% ammonium hydroxide in methanol (4 mL), methanol (4 mL), and LC grade water (4 mL). After loading, the cartridges were washed with a 25 mM ammonium acetate buffer (pH 4.0) in LC grade water (4 mL) and dried under vacuum. Target analytes were then extracted from SPE cartridges with methanol (1.5 mL) followed by 0.1% ammonium hydroxide in methanol (1.5 mL). Final extracts were filtered through $0.2\ \mu\text{m}$ Agilent glass fiber nylon syringe filters. Samples were spiked with a mass-labeled internal standard (MPFOS) before analysis. While MPFOS was spiked after extraction, previous recovery experiments for target PFAS have indicated that SPE performance was within acceptable limits (Table S4). Further, quantitation using an electrospray ion source requires an internal standard-based approach to minimize variation of ionization during analysis of the target analytes and ideally, multiple isotopically-labeled standards would be employed. Although MPFOS was used to quantify all 17 target analytes in this study, detection response of MPFOS in calibration solutions and analytical samples was similar over several sample batches, indicating a consistent internal standard performance. A series of calibration levels spiked with MPFOS were analyzed by measuring the peak response ratio for the target analytes and MPFOS. PFAS calibration curves were tested for linearity, accuracy, and precision, presenting $r^2 > 0.994$ and accuracy ranging from 83% to 113% (Table S4). Target analytes were then quantified using an Agilent ultra-high performance liquid chromatography, triple quadrupole mass spectrometer (UHPLC-MS/MS), composed of a 1290 Infinity II high-speed pump (Model G7120) coupled to a triple quadrupole mass spectrometer (Model G6460) and Jet-Stream Electrospray Ionization source. Water samples were analyzed in multiple reaction monitoring (MRM) mode. Each sample was analyzed five times, with two method blanks (acetonitrile: water 80:20) in between each sample. A 7-point calibration was also run for each batch. Additional information is provided in S3.

2.4. Data analysis

Statistical analyses were conducted using R v.4.0.2 (R Foundation for Statistical Computing). Concentrations below detection limits were treated as zero for summary statistics. Possible correlations among the concentration of the different detected PFAS were evaluated through the Spearman correlation method. LC-MS/MS data was processed using Agilent Mass Hunter software version B.07.1. Spatial analyses were conducted using ArcMap v 10.7.1 (Esri - Environmental Systems Research Institute). Information related to spatial analyses and data sources is presented in S4. Mass flux of PFAS ($\Phi_{\Sigma\text{PFAS}}$) was calculated by multiplying the sum of

PFAS concentration (ΣPFAS) at a given location by the 48-h average volumetric flow rate (\bar{Q}), as shown in Eq. (1). Volumetric flow rate data were acquired from the United States Geological Survey (USGS), when stations were located near sampling points, or from the National Water Model (NWM) supported by the US National Oceanic and Atmospheric Administration (US-NOAA), within 48 h of sampling (S6). Mass fluxes were estimated based on point concentration at one location across the entire cross-section of a given river. An important assumption in this approach is that PFAS originating from upstream sources are well-mixed in both the vertical and transverse (perpendicular to river flow) directions at any given sampling location. This assumption is reasonably valid for vertical mixing but may be less valid in the transverse direction for sampling locations in close proximity to PFAS sources (Fischer et al., 1979; Lane et al., 2008; Pouchoulin et al., 2020; Wu and Wu, 2019). Determining the longitudinal extent of a transverse mixing zone for PFAS introduced into natural surface water channels requires information on channel geometry, transverse water velocity and PFAS concentration distributions, and other location-specific conditions in the vicinity of each sample location, which was well outside the scope of this study. Thus, this study assumes that uncertainties associated with potentially incomplete transverse mixing at some sampling locations in close proximity to PFAS source areas do not invalidate the overall trends in PFAS mass transport for interconnected river systems within a large geographic area.

$$\Phi_{\Sigma\text{PFAS}} \left[\text{mg s}^{-1} \right] = \Sigma\text{PFAS} * \bar{Q} \quad (1)$$

3. Results and discussion

3.1. PFAS profile in Alabama

Of the seventeen target analytes, only six were detected, including three short-chain and one long-chain perfluorocarboxylic acids (PFCAs): PFPeA, PFHxA, PFHpA, and PFOA, and one short-chain and one-long chain perfluorosulfonic acids (PFSAs), PFBS and PFOS. The perfluoroethers were not found in any of the samples. Despite the relatively low number of detected analytes, at least one PFAS was found in 88% ($n = 65$) of all surface water samples. The short-chain PFPeA was the most detected substance, found in 88% of all samples in a range of 2.11 to $54.9\ \text{ng L}^{-1}$. PFPeA was also found to be among the highest detected PFAS in several previous studies, including in two urban watersheds in Nevada, US (Bai and Son, 2021) and in the Asan Lake area in South Korea (Lee et al., 2020). PFOA and PFHxA were detected in 74 and 58% of samples, respectively, with concentrations ranging between 0.24 and 30.2 and 0.88 – $39.1\ \text{ng L}^{-1}$, respectively. PFOS and PFHpA were detected at lower frequencies (22 and 19%, respectively) with a concentration range of 7.39 – 30.7 and 5.26 – $13.1\ \text{ng L}^{-1}$, respectively. Although PFBS was only quantified in 15% of samples, it was the substance with the highest individual concentration of $79.4\ \text{ng L}^{-1}$.

Despite the fact that the PFAS profile varied substantially among the river basins in Alabama (Table 1), a significant ($p < 0.05$) correlation in their concentration was observed among all analytes. Spearman coefficients ranged from 0.59 for PFOS and PFPeA to 0.90 for PFHpA and PFBS (see Table S6 for correlation matrix). The high correlation between PFHpA and PFBS might be linked to their use in the carpet industry, since PFHpA is a breakdown product of stain- and grease-repellent coatings for carpets (Wang et al., 2015), and PFBS is used as a PFOS alternative in the production of stain-repellent fabric protectors (DEPA, 2015). This hypothesis is further supported by the fact that both substances were mostly detected in the Coosa and Alabama Rivers, which are suspected to receive discharges from carpet manufacturers in Georgia. PFPeA and PFHxA also presented a high correlation (0.85), which could be related to the fact that both analytes are the degradation products of several precursors, including the fluorotelomers 6:2 FTOH (Liu et al., 2010) and 6:2 FTSA (Wang et al., 2011).

In terms of PFAS families, PFCAs were quantified much more frequently (88%) than PFSAs (22%). This pattern has been widely observed, as PFSAs

Table 1

Range (min-max) and average (in parenthesis) of different PFAS for each of the analyzed rivers. Overall detection frequencies (D.F.) are also displayed. Concentrations are expressed in ng L⁻¹.

River Basin	PFBS	PFPeA	PFHxA	PFHpA	PFOA	PFOS	ΣPFAS
Alabama	28.2–33.3 (30.1)	20.8–23.5 (21.9)	13.2–15.3 (14.1)	7.55–8.18 (7.78)	14.0–15.3 (14.6)	10.7–13.0 (11.7)	96.4–108 (100)
Black Warrior	n.d.	2.11–23.1 (8.66)	n.d.-11.5 (1.93)	n.d.	0.243–6.14 (1.99)	n.d.	2.35–40.76 (12.6)
Cahaba	n.d.	8.50–15.0 (10.9)	n.d.-7.31 (2.79)	n.d.	n.d.-7.11 (3.85)	n.d.	8.50–29.4 (17.6)
Chattahoochee	n.d.	8.40–17.5 (12.30)	3.56–10.8 (6.51)	n.d.-6.22 (2.11)	4.33–10.2 (7.91)	n.d.	21.4–43.5 (28.8)
Choctawhatchee	n.d.	n.d.-15.7 (7.42)	n.d.-15.0 (3.00)	n.d.	n.d.-14.0 (2.80)	n.d.-19.1 (3.82)	n.d.-63.8 (17.0)
Conecuh	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Coosa	52.8–79.4 (63.9)	33.8–54.9 (42.1)	22.5–39.3 (30.4)	8.83–13.1 (11.1)	18.3–30.2 (23.7)	11.0–29.6 (19.9)	155–237 (191)
Escatawpa	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Mobile Bay	n.d.	4.39–14.7 (11.4)	n.d.-6.50 (4.17)	n.d.	2.68–7.53 (5.73)	n.d.-30.7 (3.41)	8.48–56.7 (24.7)
Perdido	n.d.	4.16–13.9 (10.4)	n.d.-6.07 (3.68)	n.d.	2.59–9.01 (6.46)	n.d.	6.75–29.0 (20.5)
Tallahpoosa	n.d.	5.56–8.55 (6.95)	n.d.	n.d.	n.d.-5.78 (2.80)	n.d.	5.56–14.0 (9.76)
Tennessee	n.d.	5.26–8.78 (7.38)	0.882–7.02 (4.54)	n.d.	3.02–10.70 (5.58)	n.d.-9.51 (2.89)	9.17–35.6 (20.4)
Tombigbee	n.d.	5.78–9.05 (7.75)	n.d.	n.d.	n.d.-0.554 (0.191)	n.d.	6.33–9.05 (7.94)
Yellow	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
D.F. (%)	14.9	87.8	58.1	18.9	74.3	21.6	87.8

n.d. = not detected.

are more likely to be removed from water by partitioning to sediments and suspended particulate matter than PFCAs (Ahrens et al., 2010; Higgins and Luthy, 2006). Moreover, short-chain (PFBS, PFPeA, PFHxA, and PFHpA) and long-chain PFAS (PFOS and PFOA) were detected at similar frequencies (88 and 74%). However, their contributions to the overall concentration differed: concentrations of short-chain PFAS were, on average, three times higher than long-chains. This is further evidenced when computing the concentration ratio of long-chain PFAS to their shorter-chain replacements: PFPeA/PFOA and PFBS/PFOS averaged 2.58 ± 2.87 and 2.98 ± 0.78 , respectively. This is likely a reflection of the restrictions in the production of many long-chain PFAS and their subsequent replacement by shorter-chain PFAS. For example, after PFOS production was phased-out in the US in 2002, PFBS has been used as its alternative in several products, including 3M's Scotchgard®, a stain-repellent fabric protector (DEPA, 2015; Wang et al., 2013). The prevalence of short-chain PFAS was also observed in previous studies. For instance, Gao et al. (2020) observed PFBA and PFBS to be the most detected analytes in the Xi River (China), while Bai and Son (2021) found PFHxA and PFPeA to be predominant in their study in Nevada (US). The dominance of short-chain PFAS is to be expected since they are generally more easily transported, more stable, and presently used in higher amounts when compared to their long-chain homologues (Blum et al., 2015). Although short-chain PFAS are widespread, fluorochemical manufacturers have suggested that short-chain PFAS are less likely to bioaccumulate in humans and wildlife. However, the potential toxicity effects of short-chain PFAS should not be neglected. For instance, the US EPA recently released a toxicity assessment for PFBS, linking several adverse health effects, especially to the thyroid, to PFBS exposure (USEPA, 2021).

3.2. Spatial distribution of PFAS in Alabama

Results from this study confirmed the ubiquity of PFAS in sampled river systems in Alabama. Σ₆PFAS levels ranged from below detection limits to 237 ng L⁻¹ (Fig. 1), while mean and median Σ₆PFAS were equal to 35.2 and 17.8 ng L⁻¹, respectively. The highest Σ₆PFAS concentration of 237 ng L⁻¹ was found in the Coosa River (CT-3), with PFBS and PFPeA as the predominant analytes. The Coosa River was previously sampled for PFAS at a similar location to CT-1, the first sampling location in Fig. 1. In that study, Lasier et al. (2011) detected ΣPFAS concentration of 564 ng L⁻¹ and PFOS and PFBS as major analytes, compared to the 155 ng L⁻¹ found in this study. The authors linked the contamination to carpet manufacturers in Dalton, GA that have their effluents treated by a municipal wastewater treatment plant. Carpet and textile industries are known to be potential sources of PFAS, due to the use of PFAS as stain-, fire-, and water-repellents in fabrics (Zheng and Salamova, 2020; Zhu et al., 2021). The fact that PFBS, used as a PFOS-alternative in the formulation of these

products (DEPA, 2015), was found at high concentrations in the Coosa River further supports the hypothesis that carpet industries in Georgia are a major source of PFAS in the Coosa River. The Alabama and Chattahoochee rivers also presented relatively high mean Σ₆PFAS concentrations of 100 and 28.8 ng L⁻¹, respectively. Aqueous concentrations were fairly uniform across the course of both the Alabama and Chattahoochee, with slight increases after the cities of Montgomery and Columbus, respectively. The highest Σ₆PFAS concentration of 40.8 ng L⁻¹ in the Black Warrior River basin was detected in Locust Fork (BT-1), a tributary that receives inputs from the Birmingham area, including a WWTP and a large landfill. PFAS profile in Locust Fork included PFPeA, PFHxA, and PFOA, the same observed in the Cahaba River, which flows through the eastern side of Birmingham.

Concentration of Σ₆PFAS in the Tennessee River averaged 20.4 ± 10.2 ng L⁻¹, ranging from 9.17 ng L⁻¹ at the first sampling point (TN-1) to 35.6 ng L⁻¹ after the Wheeler Lake Dam (TN-7). PFAS levels in the Tennessee River were previously studied by Hansen et al. (2002) and Newton et al. (2017), in which they reported ΣPFAS up to 731 and 750 ng L⁻¹, respectively, directly downstream from fluorochemical plants in Decatur, AL. In this study, low levels of PFAS (Σ₆PFAS = 15.9 ng L⁻¹) were detected downstream from Decatur (TN-6). This difference is likely related to the fact that sample TN-6 was collected on the northern side of a wide (3 km) section of the Tennessee River, opposite from the Decatur industries and discharges from these industries were most likely not completely mixed across the entire river width. One of the assumptions of this study is that the sampled rivers are well-mixed systems and variation in concentration at any cross-section is negligible. However, this assumption is not true in reservoirs such as Wheeler Lake, where some of the Tennessee River samples were collected. Even for well-mixed systems, PFAS concentrations have been observed to exponentially decrease as distance from sources increases. For instance, Chen et al. (2018) observed the concentration of certain PFAS to decrease by an average of 75% within 5 km from a fluorochemical manufacturing park in Fuxin, China, which further supports our hypothesis. Although PFOA was detected in all samples in the Tennessee River, PFOS was only observed in TN-7,9, after the Wheeler Lake Dam. This raises questions regarding the role of dams in the transport of PFAS. It is possible that certain PFAS will accumulate more easily behind dams due to the increase in water residence time. In fact, Nakayama et al. (2010) noticed an increase in the concentration of PFOA in samples collected on the Mississippi River immediately downstream from a dam, relating it to possible increased vertical mixing and resuspension of previously deposited material. More research is needed to understand the effects of dams on the transport of PFAS.

Selected tributaries to Mobile Bay were also sampled. The Σ₆PFAS levels in these tributaries were very similar, between 24.2 and 28.0 ng L⁻¹ (TM-5,7). The eastern side of the bay is mainly composed of residential and

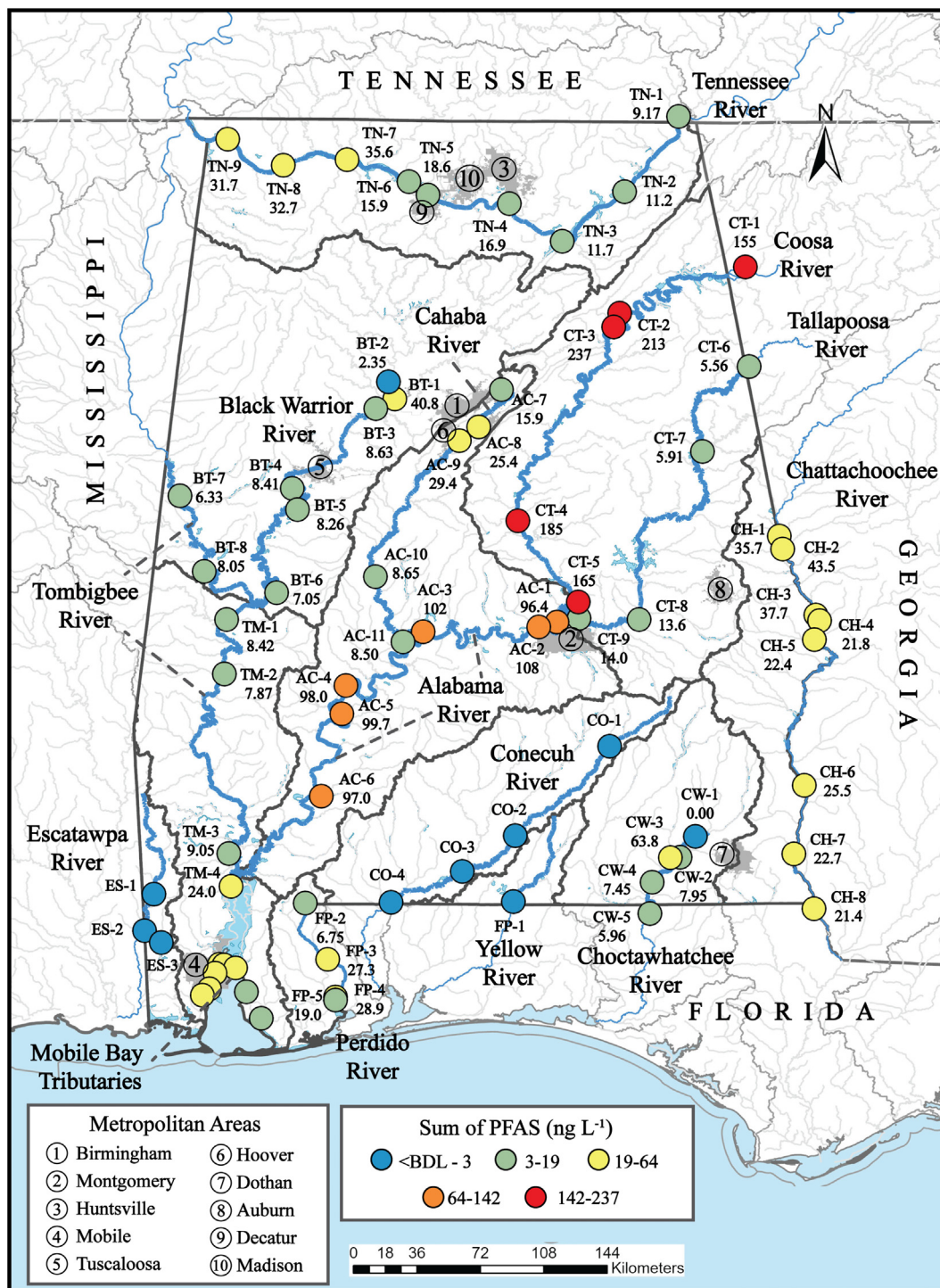


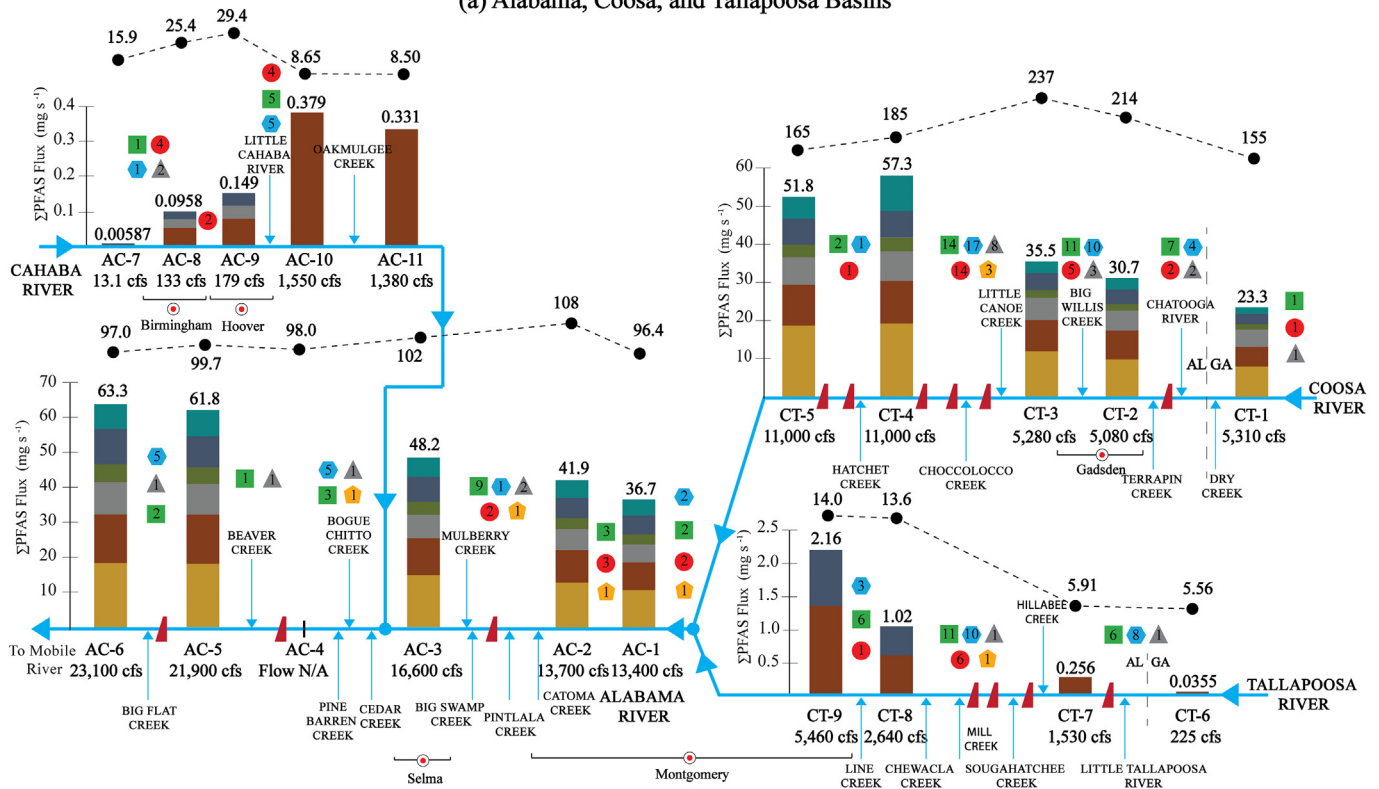
Fig. 1. Spatial Distribution of PFAS in Alabama. Σ_6 PFAS concentrations (in ng L⁻¹) are displayed for sampling locations, ranging from below detection limits (<BDL) to 237 ng L⁻¹. The 10 largest metropolitan areas are indicated for reference. WGS84 projection. (1.5-column fitting figure; print in color).

forested areas and sampled tributaries presented low Σ_6 PFAS levels, ranging between 8.48 and 10.1 ng L⁻¹. The western side, where the city of Mobile is located, is much more industrialized. As expected, Σ_6 PFAS levels were much higher in those tributaries, ranging from 22.2 to 56.7 ng L⁻¹. Although PFOA was detected in all tributaries, PFOS was only found in one sample (TM-10, PFOS concentration of 30.7 ng L⁻¹), in the Deer River, downstream of several chemical industries. The fact that PFOS was identified does not necessarily mean that those facilities are discharging PFOS into the river, since PFAS precursors like several sulfonamides can breakdown into PFOS (Benskin et al., 2012; Gilljam et al., 2016). However,

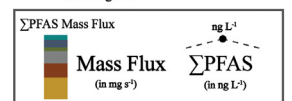
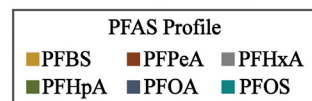
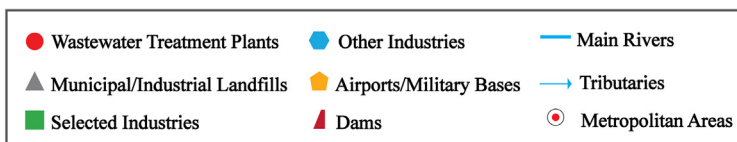
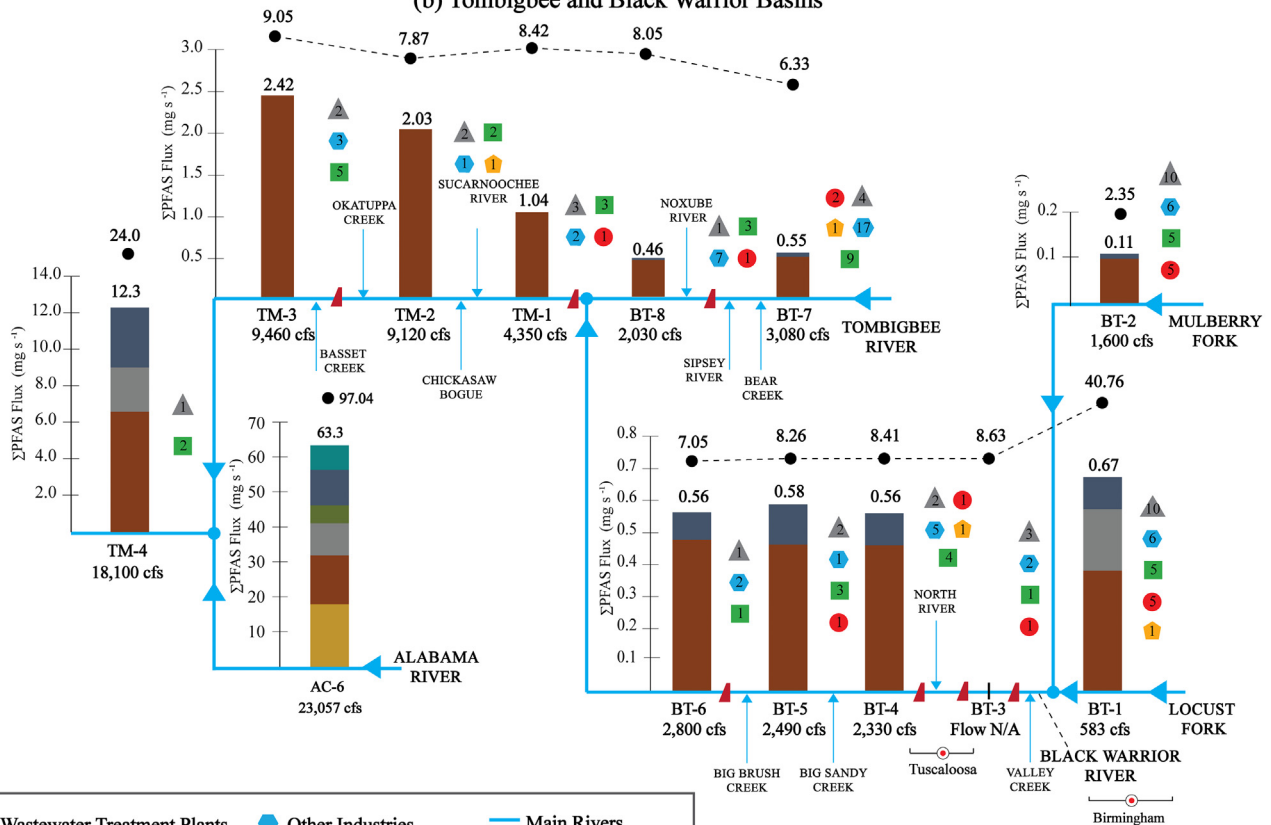
the detection of PFOS is a potential concern as it can pose a risk to wildlife in the bay, as PFOS was observed to cause developmental effects in several fish species (Wang et al., 2011) and to cause cellular damage to oysters (Aquilina-Beck et al., 2020). The Conecuh, Escatawpa, and Yellow Rivers did not present any measurable amounts of the 17 target PFAS.

PFAS has been identified on every continent around the globe, with concentrations ranging from pg L⁻¹ (Brumovsky et al., 2016) to mg L⁻¹ (Moody et al., 2002), and given the geographic scale of this project, comparisons to other large-scale studies are more appropriate. For instance, Gobelius et al. (2018) conducted a nationwide survey of 26 PFAS in

(a) Alabama, Coosa, and Tallapoosa Basins



(b) Tombigbee and Black Warrior Basins



Sweden, with Σ PFAS concentrations reaching up to 13,000 ng L⁻¹, but a median Σ PFAS of 3.9 ng L⁻¹ in the 289 surface water samples. While mean concentration of PFOS (24 ng L⁻¹) and PFHxA (13 ng L⁻¹) in Swedish surface waters were considerably higher than in Alabama (3.31 ng L⁻¹ for PFOS and 5.74 ng L⁻¹ for PFHxA), mean concentrations of PFOA were similar (6.2 ng L⁻¹ versus 6.14 ng L⁻¹ in this study). Similarly, Munoz et al. (2015) conducted a survey of 22 PFAS in France and detected at least one PFAS in 89% of the 333 samples, with Σ PFAS reaching up to 725 ng L⁻¹ and a mean and median of 28 and 7.9 ng L⁻¹, respectively. The authors detected the highest mean individual concentrations of PFOS (5.14 ng L⁻¹), PFHxS (4.72 ng L⁻¹), PFHxA (3.56 ng L⁻¹), and PFOA (2.54 ng L⁻¹), compared to 3.31, <BDL, 5.74, and 6.14 ng L⁻¹ found in this study. However, concentrations of PFPeA (1.66 ng L⁻¹) and PFBS (1.27 ng L⁻¹) in French waterbodies were considerably lower than in Alabama (11.6 and 6.74 ng L⁻¹ for PFPeA and PFBS, respectively). Pan et al. (2018) conducted a worldwide survey of 24 PFAS in surface water, including some of the emerging ethers targeted in this study. Mean concentrations of PFOA, PFHxA, PFOS, and PFBS of 8.19, 4.74, 4.39, and 5.65 ng L⁻¹, respectively, found in that study are comparable to what was observed in Alabama (6.14, 5.74, 3.31, and 6.76 ng L⁻¹, respectively). However, the authors detected PFHxS and HFPO-DA at high frequencies, which were not detected above detection limits in any of the samples from Alabama.

3.3. Mass flux of PFAS in Alabama

One of the main goals of this study was to conduct a mass flux analysis to broadly identify trends in the transport of PFAS in Alabama. Mass fluxes were calculated by multiplying the Σ PFAS concentration by the 48-h average discharge rate at each sampling location, and results are displayed in Figs. 2 and 3. These figures show that transboundary rivers, either flowing into Alabama or at the border with its neighboring states, are an important vector of PFAS contamination into the state. For instance, the first sampling point on the Coosa River, CT-1, indicates a mass flux of PFAS (Φ_{Σ PFAS) of 23.3 mg s⁻¹ from Georgia into Alabama, while Φ_{Σ PFAS in CT-2 (30.7 mg s⁻¹) also reflects possible inputs through tributaries from Georgia, including the Chattooga River. Moreover, sources in neighboring states are also contributing to the PFAS contamination in the Chattahoochee and Perdido Rivers, transboundary rivers located at the border with Georgia and Florida, respectively. Other rivers, such as the Tallapoosa and Tombigbee, generally presented lower background fluxes of 0.0350 and 0.550 mg s⁻¹, representing inputs from Georgia and Mississippi, respectively. The issue of the movement of PFAS mass through transboundary rivers is not confined to Alabama or the US and exemplifies the need for inter-state and international strategies to mitigate PFAS contamination.

In addition to the background flux from neighboring states, consistent increases in the mass fluxes of PFAS were generally observed as the rivers flowed through Alabama. Considerable increases were observed in the Coosa and Alabama Rivers, in which the mass flux increased by 2.2 and 1.7 folds, respectively, as the rivers progressed through the basins. Sources in the Upper Coosa River were most likely related to inputs from carpet industries and WWTPs, expanding to other industries, WWTPs, landfills, and military bases as the river moved through the basin. In the Alabama River, WWTPs, landfills, and the Maxwell Air Force Base are potential sources in the upper section of the river, while various paper industries seem to be the major contributors of PFAS in the lower section. Previous studies have suggested that facilities that produce paper products could be major sources of PFAS in the environment (Clara et al., 2008; Langberg et al., 2020). Langberg et al. (2020) also noticed that paper fibers from paper mills can be a major vector for the transport and exposure of PFAS. It is also worth noting that the major mass inputs from these potential sources

would not have been captured if only aqueous concentrations were considered. For instance, Σ PFAS concentrations across the Alabama River are fairly constant, with a variation of only 0.642 ng L⁻¹ between the first and last sampling point. A similar trend was also observed in the Chattahoochee River, where the Φ_{Σ PFAS more than doubled between samples CH-4 and 8 while the aqueous concentration was fairly constant. Such differences exemplify the usefulness of the mass flux analysis in tracking PFAS contamination in large river systems.

Similarly, a consistent increase in the Φ_{Σ PFAS was observed in the Tallapoosa River, reaching up to 2.16 mg s⁻¹ before it merged with the Coosa River. Interestingly, PFOA was only identified after sample location CT.7, after potential inputs from the Auburn area discharged through the Chewacla and Saugahatchee creeks, local inputs from a large sewage pond in Tallassee, and inputs from a large landfill. Landfills are a major source of PFAS to the environment due to the disposal of many PFAS-containing products and waste (Lang et al., 2017). Alabama has 173 operating landfills, with many of them located in poor rural areas and accepting toxic waste from all states in the US (Milman, 2019). Further, low Φ_{Σ PFAS of 0.55 and 0.46 mg s⁻¹ were detected in the first two sampling points in the Tombigbee River, prior to discharges from the Black Warrior River. A consistent increase in the Φ_{Σ PFAS was observed between samples TM-1,3, reaching 2.42 mg s⁻¹. Although the Tombigbee River watershed is primarily rural, samples TM-1 and 2 were sampled immediately downstream from paper industries, and TM-3 from a chemical facility, which could have contributed to the increase in mass.

The Claybank Creek, located in the Choctawhatchee River watershed, was sampled to assess the accuracy of the mass flux. A mass flux of 0.198 mg s⁻¹ was calculated for sample CW-3 in Claybank Creek (Fig. 3b), downstream from the Fort Rucker military base and the City of Enterprise WWTP. High concentrations of PFAS, primarily in groundwater, have been found near military installations in the US due to the use of AFFF (Barzen-Hanson et al., 2017; Moody and Field, 1999). The next sample, CW-4, captured the fluxes of both CW-2 and CW-3. CW-4 presented a Φ_{Σ PFAS of 0.179 mg s⁻¹, lower than what would have been estimated by simply adding fluxes from the upstream samples. This difference, however, is explained by flow inputs from tributaries between those points. For instance, CW-2 and CW-3 presented flow rates of 496 and 109 cfs, while the flow rate in CW-4 was 850 cfs. This indicates that the inflow from tributaries of about 245 cfs contained little to no PFAS.

Finally, most of the state drains into Mobile Bay, especially through the Alabama and Tombigbee Rivers. A mass flux of 63.3 mg s⁻¹, the highest in the state, was detected in the last sampling point in the Alabama River, right upstream of the confluence with the Tombigbee River. After the merge, the Mobile River is formed, captured by the sample TM-4, in which a flux of 12.3 mg s⁻¹ was detected. The Φ_{Σ PFAS in TM-4 is substantially lower than the fluxes in the upstream rivers. A possible explanation for this decrease could be the high-water exchange in the region, as the area is dominated by wetlands. The Mobile River is further divided into several tributaries before reaching Mobile Bay. The Σ PFAS levels in these tributaries were very similar, between 24.2 and 28.0 ng L⁻¹ (TM-5,7).

4. Conclusions

The results of this study raise important considerations for the possible implications of PFAS to humans and wildlife in Alabama. PFAS were found to be ubiquitous in the majority of rivers and tributaries sampled, being detected in 88% of surface water samples, even in less industrialized areas, with Σ PFAS levels reaching up to 237 ng L⁻¹. PFAS can pose a risk to wildlife, especially in rivers where PFAS were found at higher concentrations. This could also indirectly affect humans that consume PFAS-contaminated

Fig. 2. Schematic diagram of Σ PFAS mass flux (vertical bars, expressed in mg s⁻¹) and aqueous concentration (black circles, expressed in ng L⁻¹) for the (a) Alabama, Coosa, and Tallapoosa and (b) Tombigbee and Black Warrior River Basins. The fluxes of individual PFAS are also displayed for each sampling point. Main metropolitan areas, dams, and likely sources are also displayed. Selected industries (green squares) include sectors that have been previously related to PFAS use, such as paper, automotive, plastics/packaging, chemical, flooring/tile, and textile/carpets. Respective number on icons represent the number of potential sources within the catchment associated with that category. Distances between sampling points are not to scale. (2-column fitting figure; print in color).

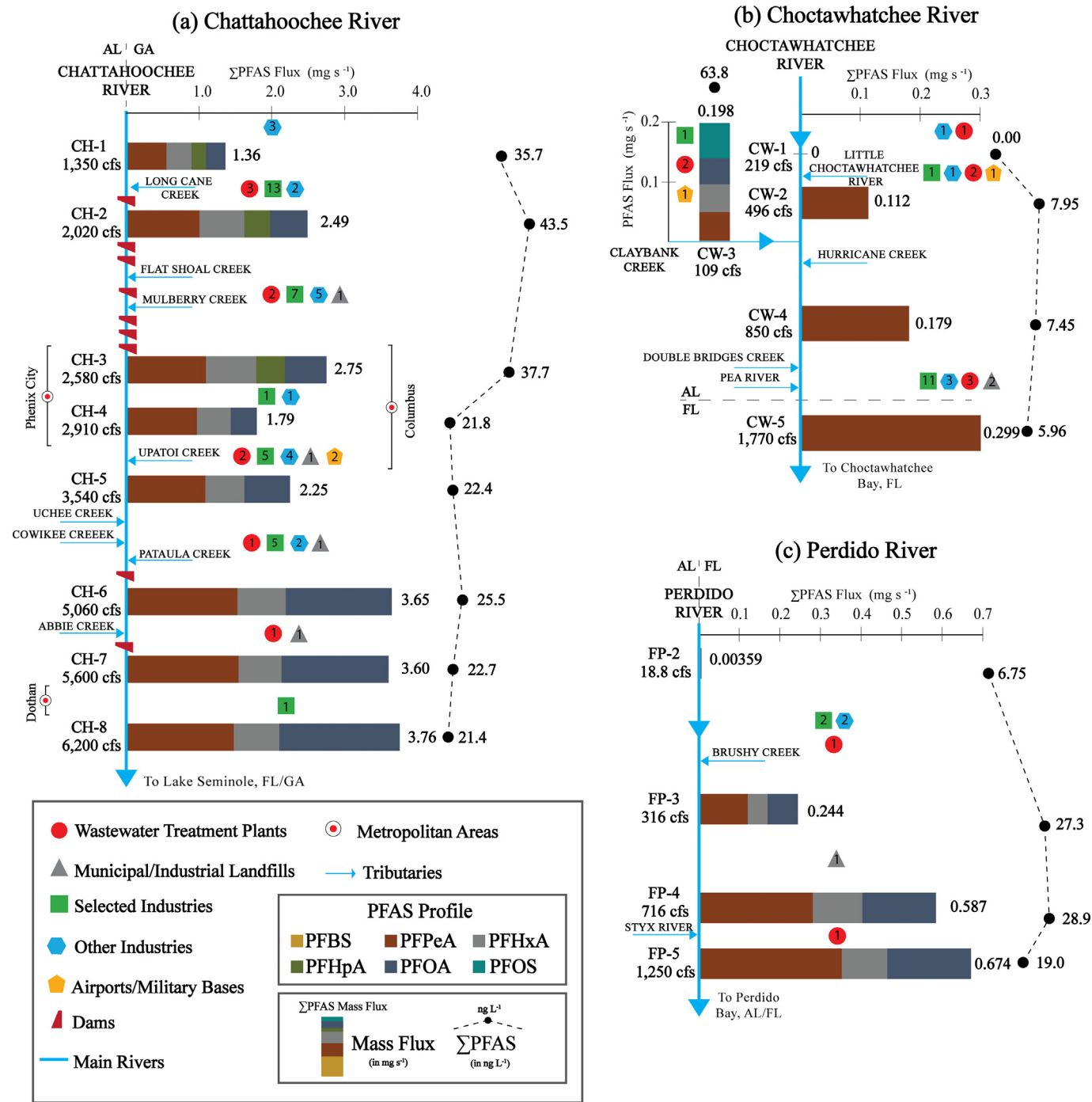


Fig. 3. Schematic diagram of Σ_6 PFAS mass flux (vertical bars, expressed in mg s^{-1}) and aqueous concentration (black circles, expressed in ng L^{-1}) for the (a) Chattahoochee, (b) Choctawhatchee, and (c) Perdido River Basins. The fluxes of individual PFAS are also displayed for each sampling point. Main metropolitan areas, dams, and likely sources are also displayed. Selected industries (green squares) include sectors that have been previously related to PFAS use, such as paper, automotive, plastics/packaging, chemical, flooring/tile, and textile/carpets. Respective number on icons represent the number of potential sources within the catchment associated with that category. Distances between sampling points are not to scale. (1.5-column fitting figure; print in color).

wildlife, as some PFAS are known or suspected to bioaccumulate and biomagnify through food webs (Xu et al., 2014). Since these samples were taken from riverine water, the results of this work are not directly applicable to human exposure through drinking water. However, many of the sampled rivers are used as drinking water sources, and several studies have considered the inability of conventional water treatment facilities to remove PFAS from water (Crone et al., 2019).

This study also exemplifies the usefulness of the mass flux analysis in tracking PFAS contamination in interconnected river systems flowing

through large geographical areas. Although background fluxes from neighboring states are an important vector of PFAS into the state, consistent increases in the mass fluxes were generally observed as the rivers flowed through Alabama. These increases suggest the existence of a considerable number of local sources within catchments and river basins. As demonstrated, mass inputs from these sources would not have been captured if only aqueous concentrations were observed. Results from the mass flux analysis also provide empirical evidence of the long-range transport of PFAS, especially short-chain analytes, in interconnected river systems.

Finally, most of the PFAS contamination in Alabama is ultimately being discharged into bays and other coastal areas, which poses a risk for those ecosystems.

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CRediT authorship contribution statement

Roger L. Viticoski: Conceptualization, Investigation, Methodology, Writing – original draft. **Danyang Wang:** Methodology, Formal analysis, Writing – review & editing. **Meredith A. Feltman:** Methodology, Formal analysis, Writing – review & editing. **Vanisree Mulabagal:** Formal analysis, Investigation, Supervision, Writing – review & editing. **Stephanie R. Rogers:** Methodology, Writing – review & editing. **David M. Blersch:** Methodology, Writing – review & editing. **Joel S. Hayworth:** Funding acquisition, Project administration, Methodology, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

More details on target analytes, sampling determination and collection, quantitative analysis, data analysis, basin-level distribution of PFAS, and mass flux analysis are provided in the supplementary information. Supplementary data to this article can be found online at doi: <https://doi.org/10.1016/j.scitotenv.2022.155524>.

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