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CONCENTRATIONS AND PATTERNS OF PERFLUOROALKYL ACIDS IN GEORGIA, USA SURFACE WATERS NEAR AND DISTANT TO A MAJOR USE SOURCE

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Abstract—Perfluoroalkyl acids (PFAAs) are widespread contaminants emanating from, among other sources, the production/degradation of fluorinated chemicals used in surface repellant applications, such as carpet manufacturing. The goal of the present study was to assess the concentrations of PFAAs, including perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUA), and perfluorooctane sulfonamide (PFOSA), in surface waters both near a wastewater land application system (LAS) in Dalton (GA, USA), home to North America's largest carpet manufacturing site, and distant to this location (Altamaha River, GA, USA) to understand the fate of PFAAs in freshwater. Levels of PFAAs were high in the Conasauga River (GA, USA) downstream of the LAS (PFOA, 253–1,150 ng/L; PFOS, 192–318 ng/L; PFNA, 202–369 ng/L; PFDA, 30.1–113 ng/L; PFUA, 58.0–99.2 ng/L; PFOSA, 162–283 ng/L) and in streams and ponds in Dalton (PFOA, 49.9–299 ng/L; PFOS, 15.8–120 ng/L), and were among the highest measured at a nonspill or direct-release location. Perfluoroalkyl acids in the Altamaha River were much lower (PFOA, 3.0–3.1 ng/L; PFOS, 2.6–2.7 ng/L), but were a source of PFAAs to Georgia's estuaries. A preliminary hazard assessment indicated that concentrations of PFOS at two sites in the Conasauga River exceeded the threshold effect predicted for birds consuming aquatic organisms that are exposed continuously to the PFOS levels at these sites. Assuming that toxicity for all PFAAs quantified is equal to that of PFOS, the sum total PFAAs at two sites within the Conasauga River exceeded PFOS thresholds for aquatic and avian species, warranting additional research.

Keywords—Perfluorinated surfactants Perfluorooctane sulfonamide Carpet manufacturing Risk assessment

INTRODUCTION

Perfluoroalkyl acids (PFAAs) are a diverse group of chemicals that have unique properties resulting from their repulsion of both oil and water and, therefore, are used in many applications for surface protection of carpets, paper, food containers, upholstery, and fabric [1]. Perfluoroalkyl acids also are used for many other applications, including polymerization aids for fluoropolymer manufacturing and aqueous formulations of firefighting foam. These fully fluorinated compounds have been manufactured for more than 50 years, and because of the strength of the carbon–fluorine bond, these compounds are very stable and persistent in the environment. Consequently, PFAAs have been detected in biotic samples (human and wildlife) and abiotic samples (water, sediment, and air) worldwide [2–4], with some PFAAs shown to bioaccumulate and biomagnify in coastal and Arctic food webs [5,6].

Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are the most commonly measured PFAAs in environmental samples. Both compounds have direct uses, but they also are the terminal degradation products of higher-molecular-weight PFAAs [7]. In 2001, the 3M Company (St. Paul, MN, USA), one of the largest producers of PFAAs, ceased production of PFOS and intermediates used in the production of PFOS; other companies, however, still manufacture fluorotelomer alcohol–based products [8]. In 2006, the major manufacturers of PFOA voluntarily agreed to reduce by 95% the production of this chemical and any precursors by 2010 [9]. Although these major reductions for PFOS and PFOA will minimize their future presence in the environment, the historical use of PFAAs will be a cause for concern regarding wildlife and humans during the intermediate time frame because of their stability and persistence in the environment. Toxicity assessments of PFAAs, with PFOS and PFOA gaining the most attention, indicate that they bind readily to blood plasma proteins [10] and can alter fatty acid metabolism [11] as well as adversely affect cellular membranes and intercellular communication [12–15]. A high incidence of the above-mentioned effects from PFAA exposure, however, including decreases in fathead minnow (*Pimephales promelas*) reproduction [16,17], occur at concentrations typically greater than those reported in the environment.

The city of Dalton (GA, USA) (Fig. 1A) is known as the carpet capital of the world and accounts for approximately 90% of the carpets manufactured worldwide (http://www.daltoncvb.com/carpetindustry.html). It has been suggested that because of the high use of PFAAs in the carpet industry, northwestern Georgia may be a regional source of PFAAs [18]. To our knowledge, however, no attempt has been made to determine the levels of PFAAs in the nearby Conasauga River (GA, USA) (Fig. 1), which historically has contained a high diversity of fish species (D.M. Walters, University of Georgia, Athens, GA, USA, unpublished data) and is one of five major rivers contributing to the Coosa River watershed (USA). Contamination by PFAAs, both historic and current, may be significant in the Conasauga River because of its close proximity to the extensive carpet industry. One potential route for contamination exists as a result of the method

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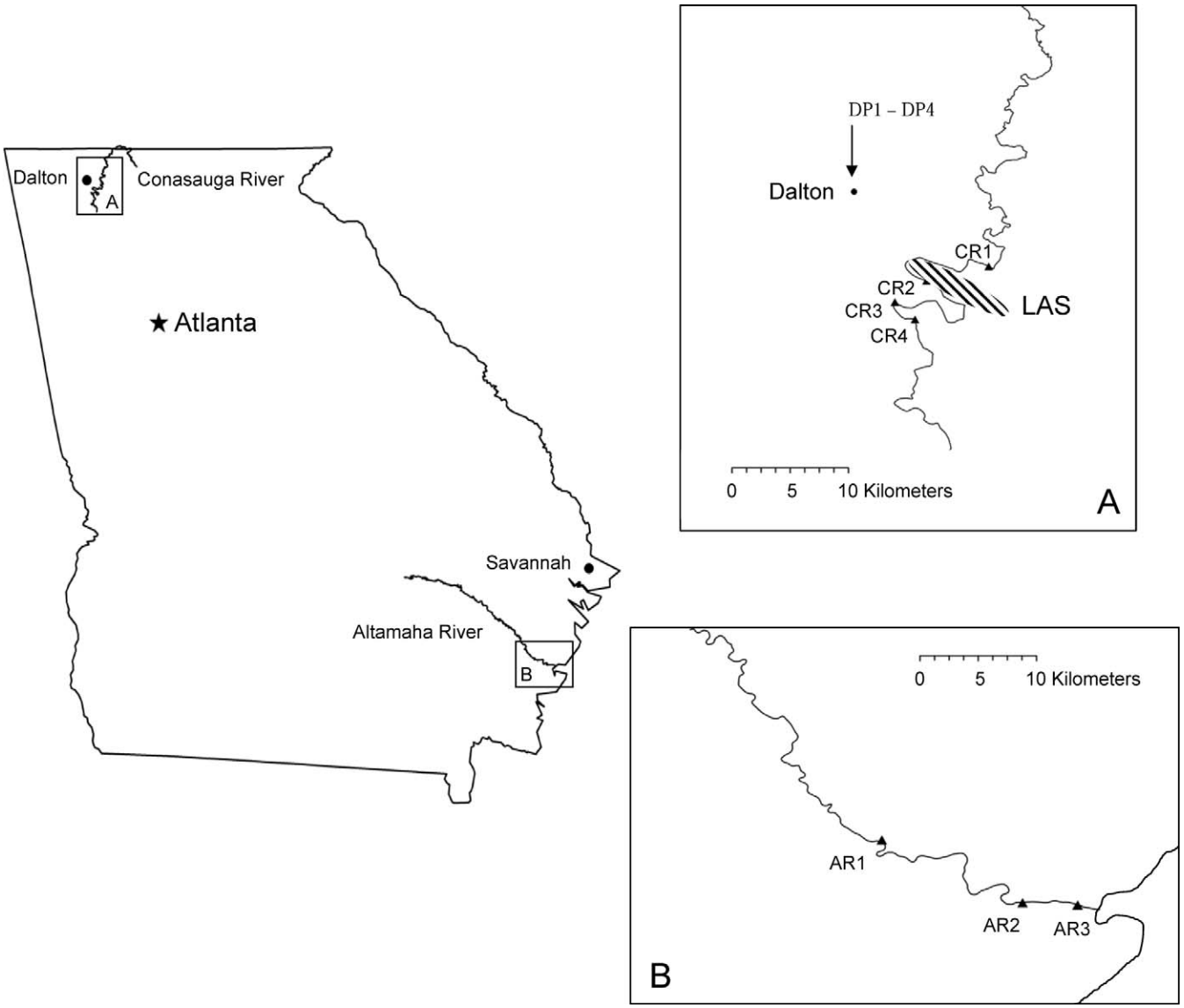

Fig. 1. Map of Georgia (USA), with sampling locations (triangles) on the Conasauga River (**A**) and Altamaha River (**B**). The approximate location of the land application system (LAS), which sprays treated wastewater nearby the Conasauga River, is noted by the shaded area. AR = Altamaha River; CR = Conasauga River; DP = Dalton.

used to treat wastewater, which in Dalton is approximately 87% industrial. After the local utility treats incoming wastewater from Dalton, the treated wastewater is pumped to a 9,200-acre land application system (LAS) and sprayed to the landscape, which is bordered on two sides by the Conasauga River. Given that many PFAAs resist biodegradation in the wastewater treatment plant (WWTP) process and actually can increase in concentration [19], potential runoff or leaching of these chemicals into the river is a realistic concern. Thus, biomonitoring of PFAAs in the Conasauga River is particularly useful for understanding if concentrations are at levels that may pose a risk to wildlife and for understanding the fate of these compounds in a lotic environment.

Contaminants in estuaries are derived primarily from inland sources and are transported via rivers [20,21], where they may be trapped and impair the health of the estuarine ecosystem [20]. Little information, however, is available regarding the environmental behavior and distribution of organic contaminants, specifically PFAAs, as they move from a freshwater to a saltwater system. Changes in salinity, for example, could potentially influence physicochemical properties, such as water solubility of organic contaminants [22], likely including PFAAs, which in turn will alter the environmental distribution and dynamics of such contaminants. The Altamaha River (GA, USA) (Fig. 1) is the third-largest U.S. watershed draining into the Atlantic Ocean, which can potentially be impacted by PFAAs resulting from inland regional industries and/or other sources from industries that use PFAAs along the river. Thus, it is critical to understand the extent of freshwater-derived PFAAs to the Altamaha estuary ecosystem, which can have potential negative impacts on commercially important, southeastern U.S. marine and tidal biota. Examining riverine delivery of PFAAs as a source to the Georgia coast also is important because of the reported bioaccumulation and biomagnification of these chemicals in the area [5,23] and, therefore, may pose a risk to humans from consuming contaminated shellfish.

In the present study, we assessed the concentrations of a series of PFAAs in waters of Georgia. We investigated the distribution of these chemicals upstream and downstream of the LAS in the Conasauga River near Dalton to understand the extent and fate of PFAAs near the carpet industry. The second objective was to

Table 1. List of native and labeled perfluoroalkyl acids (PFAAs) used in the present study

Native PFAA analyzed (name, acronym, chemical formula)	Recovery internal standard	Labeled instrument performance internal standard
Perfluorooctanoic acid, PFOA, $CF_3(CF_2)_6CO_2H$ (413/369, 413/169)[a]	$^{13}C_4$-PFOA (417/372, 417/169)	$^{13}C_2$-PFOA (415/370, 415/169)
Perfluorooctane sulfonate, PFOS, $CF_3(CF_2)_7SO_3H$ (499/99, 499/80)	$^{13}C_4$-PFOS (503/99, 503/80, 503/131)	$^{18}O_2$-PFOS (503/103, 503/84)
Perfluorononoic acid, PFNA, $CF_3(CF_2)_7CO_2H$ (463/419, 463/169)	$^{13}C_5$-PFNA (468/423, 468/169)	$^{13}C_2$-PFNA (465/420, 465/169)
Perfluorodecanoic acid, PFDA, $CF_3(CF_2)_8CO_2H$ (513/269, 513/469)	$^{13}C_2$-PFDA (515/269, 515/470)	$^{13}C_2$-PFNA (465/420, 465/169)
Perfluoroundecanoic acid, PFUA, $CF_3(CF_2)_9CO_2H$ (563/519, 563/169)	$^{13}C_2$-PFDA (515/269, 515/470)	$^{13}C_2$-PFDoA (615/570, 615/169)
Perfluorododecanoic acid, PFDoA, $CF_3(CF_2)_{10}CO_2H$ (613/569, 613/169)	$^{13}C_2$-PFDA (515/269, 515/470)	$^{13}C_2$-PFDoA (615/570, 615/169)

[a] Reactions monitored are given in parentheses.

make a preliminary assessment of whether the Altamaha River, a river that is remote from the carpet industry, is potentially delivering PFAAs to Georgia's estuaries. In addition, a preliminary hazard assessment was undertaken to determine the potential risk to aquatic animals and predatory birds from exposure to PFOS in Georgia's waters.

MATERIALS AND METHODS

Chemicals and standards

The suite of native and mass-labeled PFAAs and their nomenclatures used in the present study (Table 1) were obtained from Wellington Laboratories (Guelph, ON, Canada) with the exception of $^{13}C_2$-perfluorononanoic acid (PFNA) and $^{18}O_2$-PFOS, which were a gift from Sheryl Tittlermier (Health Canada, Ottawa, ON). Optima-grade methanol and water were purchased from Caledon Laboratories (Georgetown, ON, Canada).

Sample collection

Water samples were collected on the same day from four locations ($n = 5$ for each location, plus three field blanks) within the Conasauga River (Fig. 1A) in March 2006 (1 L/sample) and from three locations on the same day ($n = 3$ for each location, plus three field blanks) within the Altamaha River (Fig. 1B) in January 2005 (2 L/sample). In the Conasauga River, one location (CR1: 34°42′32″N, 84°52′06″W) was taken upstream, one at the LAS (CR2: 34°41′51″N, 84°55′05″W), and two downstream (CR3: 34°40′50″N, 84°56′35″W; CR4: 34°40′00″N, 84°55′37″W) of the LAS (Fig. 1A). Altamaha River samples were taken such that one location was in freshwater (AR1: 31°23′16″N, 81°32′51″W) and two were in mixed salinity (AR2: 31°20′19″N, 81°26′22″W; AR3: 31°20′13″N, 81°23′49″W) (Table 2). Salinity measurements were taken with a Hydrolab Quanta (Hach Environmental, Loveland, CO, USA). In addition, we collected water from ponds and streams within the city of Dalton (four locations, $n = 2$ for each, plus two field blanks) in January 2005 (2 L/sample), but no GPS recordings were taken for these samples. These ponds are located approximately 7 km northwest of the LAS and sampling locations on the Conasauga River. Water samples were collected by dipping a clean polypropylene sampling bottle just under the surface of the water (depth, ~0.25 m) at one point in the middle of the river. Field blanks consisted of Optima-grade water (Caledon Laboratories), which were taken while sampling in the field by pouring the water into the collection bottles. All samples (surface water and blanks) were spiked with a recovery internal standard (see Table 1) and then transported back to the laboratory on ice, where they were stored at 4°C until analysis. Samples were extracted within two weeks of collection.

Sample extraction, instrumental analysis, and recovery standards

The target perfluorinated analytes were extracted from water using Oasis hydrophilic-lipophilic-balance (20 ml, 1 g, 60 μm) solid-phase extraction cartridges (Waters, Milford, MA, USA) [24,25]. Before extraction, cartridges were preconditioned by elution with 5 ml of Optima-grade methanol and were kept wet at all times. Each water sample or field blank (spiked with 10 μl of a 1 ng/μl solution of recovery internal standard) (see Table 1) was filtered (1.0-μm glass fiber; Pall Corporation, East Hills, NY, USA) and loaded onto the cartridge through the use of a peristaltic pump (flow rate, 25 ml/min). Cartridges were wrapped in aluminum foil and shipped on ice to the Freshwater Institute (Winnipeg, ON, Canada) for analysis.

Before the samples were extracted, the elution of PFAAs from the hydrophilic-lipophilic-balance cartridge was optimized by spiking three cartridges with a 10-ml solution that had been spiked with the recovery internal standard solution (10 μl of a 1 ng/μl solution) and passed through the column and extracted using the following sequence: 5 ml of Optima-grade water (fraction 1), 15 ml of Optima-grade methanol (fraction 2), and 5 ml of Optima-grade methanol (fraction 3). The flow rate through the cartridge was one drop per second. Perfluoroalkyl acids were detectable in only fraction 2. Field samples then were extracted following this method. Methanol extracts then were reduced in volume (500 μl) by a gentle stream of nitrogen and fortified with the instrument performance internal standard (10 μl of a 1 ng/μl solution) (see Table 1 for compounds).

An Agilent 1100 Series high-performance liquid chromatography system (Agilent Technologies, Palo Alto, CA, USA) equipped with a vacuum degasser, binary pump, autosampler, and a Discovery C18 analytical column (length, 5.0 cm; inner diameter, 2.1 mm; particle size, 5 μm; Supelco, Oakville, ON, Canada) were used for all separations and analyses. The mobile-phase system consisted of water and methanol. A mobile-phase flow rate of 300 μl/min was used, and the sample injection volume was 3 μl. The gradient employed started at 20% methanol, increased to 95% in 9.5 min, and was held for 2 min. Thereafter, the mobile-phase composition was returned to starting conditions in 5 min. The column was allowed to equilibrate for 5 min between runs. Perfluoroalkyl acid detection was performed with a Sciex API 2000 triple-quadrupole mass spectrometer (MDS Sciex, Concord, ON, Canada) in the negative-ion electrospray mode using multiple-reaction monitoring. The optimized parameters were as follows: Ionspray voltage, −1,200 V; curtain gas flow, 15.00 arbitrary units (a.u.); sheath gas flow, 30.00 a.u.; turbo gas flow, 35.00 a.u.; temperature 525°C; focusing potential, −360 V; and collision-

Table 2. Concentrations of perfluoroalkyl acids in the Conasauga River (CR), Altamaha River (AR), and streams and ponds of Dalton (DP; all GA, USA)[a]

Sample ID	*n*	Salinity (ppt)	Concentration (mg/L)						
			PFOA	PFNA	PFOS	PFDA	PFUA	PFOSA	ΣPFAA
CR1	5	<0.001	32.4 ± 4.9 (21.5–46.7)	32.8 ± 11.8 (12.3–75.4)	6.0 ± 1.9 (2.3–12.8)	11.6 ± 4.1 (3.74–27.5)	2.5[b]	74.9 ± 11.7 (10.7–102)	160
CR2	5	<0.001	253 ± 14.2 (226–301)	201.6 ± 21.1 (136–248)	192 ± 14.5 (164–245)	72.4 ± 8.7 (47.4–97.1)	<0.1	162 ± 8.5 (147–187)	1,000
CR3	5	<0.001	480 ± 21.0 (448–559)	369 ± 31.9 (280–456)	318 ± 18.8 (262–368)	131 ± 8.5 (113–160)	58.0 ± 13.9 (28.7–94.2)	282.5 ± 32.7 (224–420)	1,640
CR4	5	<0.001	1,150 ± 15.9 (1,110–1,280)	284 ± 34.9 (190–366)	1.0 ± 0.8 (0.2–3.1)	30.1 ± 1.9 (24.8–35.5)	99.2 ± 6.3 (81.9–117)	212 ± 17.8 (154–259)	1,770
AR1	3	0.005	3.0 ± 0.1 (2.9–3.3)	0.6[b]	2.6 ± 0.2 (2.3–2.9)	0.14[c]	<0.1	—	6.32
AR2	3	0.07	3.1 ± 0.2 (2.6–3.3)	<0.6	2.7 ± 0.1 (2.6–2.8)	<0.1	<0.1	—	5.99
AR3	3	0.10	3.1 ± 0.3 (2.6–3.7)	<0.6	2.6 ± 0.1 (2.5–2.8)	<0.1	<0.1	—	5.75
DP1	2	<0.001	238–224	11.1–12.2	81.6–86.3	5.2–5.6	0.1–0.3	—	332
DP2	2	<0.001	293–299	40.6–41.0	119–120	17.8–19.7	0.3–0.9	—	476
DP3	2	<0.001	103–113	4.8–6.3	53.3–61.7	1.8–2.3	0.1–0.5	—	173
DP4	2	<0.001	49.9–53.7	2.1–2.5	15.8–25.2	0.1–1.0	<0.1	—	75.1

[a] See Figure 1 for map of sample locations. Values are presented as the mean ± standard error and/or the range. PFOA = perfluorooctanoic acid; PFNA = perfluorononanoic acid; PFOS = perfluorooctane sulfonate; PFDA = perfluorodecanoic acid; PFUA = perfluoroundecanoic acid; PFOSA = perfluorooctane sulfonamide; ΣPFAA = sum of the mean concentration for each perfluoroalkyl acid (PFAA) analyzed at that site; — = analyte was not targeted for analysis.
[b] Detected in one sample.

assisted dissociation gas flow, 8 a.u. The reactions monitored are provided in Table 1.

Quality assurance/quality control

The inherent problems associated with quantifying PFAAs by liquid chromatography–tandem mass spectrometry in environmental samples, including high background signals of PFOA from injections of solvent (typically, methanol and water), potential carryover between injections, and lack of appropriate isotopically labeled internal standards, have been well documented in the literature [4,26]. Two types of blanks were employed in the present study. Instrument blanks were injections of methanol run after every five samples and were used to monitor PFAA contamination from the liquid chromatography–tandem mass spectrometry instrument. Extraction (or method) blanks consisted of Optima-grade water and were extracted along with each sample. Extraction blanks were used to monitor the potential for contamination to occur during extraction and work-up of the sample.

Ion signals of PFOA were detected consistently in all our blanks, and the intensity of the signal was similar between the instrument and method blanks, suggesting that sample contamination during extraction and work-up probably was less important than contamination from the instrument itself. The background signal of PFOA could be reduced appreciably (10-fold) by reducing the column equilibration time between sample injections. It appeared that PFOA was leaching continually from the inner parts of the high-performance liquid chromatography system and is concentrating on the head of the analytical column. For all other PFAAs, extraction blanks always had higher signals than instrument blanks, suggesting that contamination during extraction and work-up was more significant.

The recoveries (mean ± standard error, $n = 6$) of $^{13}C_2$-perfluorodecanoic acid (PFDA), $^{13}C_4$-PFOA, $^{13}C_5$-PFNA, and $^{13}C_4$-PFOS in the samples were 48.6% ± 10.1%, 91.9% ± 19.5%, 80.7% ± 12.9%, and 73.4% ± 5.5 %, respectively. Perfluoroalkyl acid concentrations in samples were blank corrected by subtracting the signal from extraction blanks from the sample signals. Native PFAAs in the samples were recovery corrected based on the recovery of the labeled surrogate with the nearest retention time (Table 1). Method detection limits were determined from known amounts of PFOS and PFOA spiked into the procedural blanks ($n = 6$) that were analyzed previously and found to have nondetectable concentrations of PFAAs (i.e., response of PFAAs was not greater than response from the instrument blanks). Separate injections of the spiked extracts then were made, and the ion signals obtained for each PFAAs were adjusted to estimate concentrations that would give a signal to noise ratio of 5:1. In this manner, method detection limits based on a 1-L sample of PFOA (2.8 ng/L), PFNA (0.6 ng/L), PFDA (0.1 ng/L), perfluoroundecanoic acid (PFUA; 0.1 ng/L), perfluorododecanoic acid (0.1 ng/L), and PFOS (1.5 ng/L) were estimated.

Concentrations of PFAAs in the Altamaha River samples were evaluated against salinity to determine any correlations (linear regression, $\alpha = 0.05$) using Systat® software (Ver 8.0; Systat Software, Inc., Chicago, IL, USA). Because no correlations were found, differences in concentrations for each PFAA and salinity were analyzed using an analysis of variance with Tukey's post hoc test ($\alpha = 0.05$).

RESULTS AND DISCUSSION

Concentrations and distribution of PFAAs

Concentrations of measured PFAAs were highest in the Conasauga River, with PFOA occurring at the highest mean concentration, followed by PFNA, PFOS, perfluorooctane sulfonamide (PFOSA), PFDA, and PFUA (Table 2). These elevated PFAA concentrations were from sample locations CR3 or CR4, which were downstream of the LAS. A similar PFAA pattern, although at lower concentrations than found in the Conasauga River, was found in water sampled from streams and ponds around Dalton, with PFOA being detected at the

highest concentration, followed by PFOS, PFNA, PFDA, and PFUA (Table 2); PFOSA was not analyzed in these samples. Altamaha River samples showed the lowest concentrations of PFAAs; however, mean concentrations of the two greatest PFAAs detected (PFOA and PFOS) were consistent in this river despite changes in salinity. Some PFAAs (e.g., PFNA and PFDA) were found in the freshwater and the lower mixed-salinity location at low concentrations but were not found in the higher mixed-salinity location (Table 2).

The observation of elevated PFAAs in the Conasauga River downstream of the LAS in comparison to the upstream site suggests the LAS as being a likely important point source of PFAA contamination. A pattern of increasing concentration with distance downstream of the LAS was found for PFNA, PFOS, PFDA, and PFOSA, with the highest concentrations detected for all compounds at site CR3, before a decrease in concentration at the final site, CR4. Perfluorooctanoic acid and PFUA were the exceptions to this pattern, with a continual increase in concentration throughout the study range with distance downstream of the LAS. This general trend of increasing concentration with increasing downstream distance from the LAS may suggest that considerable flow from contaminated groundwater originating at the LAS is impacting these downstream locations. It is unclear why a decline occurs for several of the PFAAs, particularly PFOS, at the last sampling location, which is approximately 2.2 river km downstream from site CR3. Perfluorooctane sulfonate appears to adsorb strongly to soil and sediment, having distribution coefficients in soils of between 9.7 L/kg (clay loam) and 35 L/kg (sandy loam) [27] and with organic carbon shown to be the predominant factor in sorption [28]. Another study found similar organic carbon partition coefficients for PFNA and PFDA in comparison to those for PFOS [28], which may indicate sorption to sediments, particularly organic carbon, as the reason for the decrease of some PFAAs (e.g., PFOS, PFNA, and PFDA) at the last sampling site. The increase in PFOA concentration throughout the sampling range would indicate little potential sorption to sediments for this compound, as suggested previously [29,30]. Therefore, one concern is elevated downstream concentrations of PFOA in the water column beyond the sampling frame carried out in the present study.

The PFAA concentrations identified in the different salinities of the Altamaha River suggest that riverine delivery is a source for these chemicals to Georgia's estuaries. An initial goal of the present study was to analyze how concentration dynamics of PFAAs responded as they enter a saltwater gradient. Our study design, however, restricted us from drawing any conclusions because of the low sample size and limited sampling scheme employed, but some general observations should be noted. In the present study, of the two main PFAAs identified (i.e., PFOS and PFOA), no significant difference in concentration was found with salinity (analysis of variance, $p > 0.05$). Both PFNA and PFDA, however, were present in freshwater but not in the higher mixed-salinity location (i.e., AR3), suggesting again that the Altamaha River is a likely source of PFAAs to the estuary. Other evidence also supports the idea that freshwater delivery of PFAAs is an important source to coastal environments based on concentration data only; for example, higher concentrations of PFAAs have been measured in freshwater compared to marine waters in South Korea [31].

Comparison of PFAA concentrations to those in other areas

Concentrations of PFOS, PFOA, and other PFAAs in the Conasauga River are among the highest ever recorded in surface waters, and they are much greater than those observed in freshwater environments outside of direct releases. The highest PFOS concentrations observed in the present study (318.3 ng/L) are lower than the PFOS concentrations found in a Canadian creek after an accidental release of firefighting foam (190–2,210,000 ng/L) [32] and in groundwater at a firefighting U.S. Air Force base in Michigan (USA; lowest detected concentration, 8,000 ng/L) [33]. The elevated PFOS concentrations in the present study, however, are greater than those found in the Tennessee River in Alabama (USA) downstream of a manufacturing facility (highest detected concentration, 144 ng/L) [34] and in the majority of freshwaters sampled in Korea (8–651 ng/L) [31]. The PFOS concentrations in the Conasauga River upstream of the LAS, but not the elevated levels downstream, generally are comparable to concentrations found in freshwaters of New York (USA) and Michigan (range, 2–5 ng/L; maximum, 29 ng/L) [35] and would appear to be background levels. The highest concentration of PFOA (1,150.0 ng/L) in the Conasauga River was higher than concentrations reported in the Tennessee River (maximum, 598 ng/L) [34], being in the range of the accidental release of firefighting foam in Canada detected within the first 3 d (mean, 2,859 ng/L; range, 11–11,300 ng/L) [32] but less than the concentrations in groundwater at the firefighting U.S. Air Force base in Michigan (lowest detected concentration, 8,000 ng/L) [33]. The PFOA concentrations in the Conasauga River also generally were higher than the majority of PFOA concentrations measured in rivers of Japan (0.1–456 ng/L) [36] and in the Great Lakes (15–70 ng/L) [37]. The concentrations of the other PFAAs, including PFDA, PFNA, PFUA, and PFOSA, in the Conasauga River also may be some of the highest reported. Little information is available regarding the concentrations of these longer perfluorocarboxylates in water, but the few data that are available suggest the concentrations reported in the study are elevated [5,19,24,31].

Concentrations of PFAAs in the Altamaha River estuary are in a range similar to those reported for estuarine and marine waters outside heavy industrialized areas [5,25,31]. Higher concentrations of PFOS (12.7–24.4 ng/L) and PFOA (154.3–192.0 ng/L) have been measured in the heavily industrialized area of Tokyo Bay (Japan) [24]. In the mid–Atlantic Ocean that drains the Altamaha River, concentrations of PFOS (0.038–0.073 ng/L) and PFOA (0.10–0.15 ng/L) were found to be lower than those in the Altamaha River estuary [24], which may be a result of dilution, their decreased solubility, and/or their possible transport via ocean currents. These results indicate a potential correlation with manufacturing and industrial activity and PFAA inputs. Based on the available PFAA concentration data only, the Altamaha River appears to deliver PFAAs to oceans at a level similar to those delivered into Sarasota Bay (FL, USA) and coastal southern Korea, but there appears to be greater PFAA contamination in Charleston Harbor (SC, USA), western Korea, and Tokyo Bay (in ascending order). The Altamaha River is relatively unindustrialized, with no major port city, which may explain the lower PFAA concentrations found there, although it should be noted that concentrations were not much lower than those in industrialized areas. Thus, a more detailed study of riverine delivery (spe-

cifically, loadings calculated based on flow) of PFAAs and, possibly, other contaminants in the Altamaha River to the Georgia estuary needs to be explored.

Potential sources of PFAAs

Concentrations of PFAAs in the Conasauga River were elevated downstream of the LAS in comparison to those of the upstream site, indicating that treated wastewater from this area likely is the source of the PFAA contamination. Previous studies have indicated that PFOS, PFOA, PFNA, PFDA, and PFUA mass flows generally, but not always, can increase in WWTP effluent in comparison to influent, with no consistent reduction or enhancement in PFAA levels being observed with different treatment processes (i.e., activated sludge or trickling filter) [19,38]. Treatment of wastewater in Dalton is achieved by three different WWTPs using activated sludge through aeration basins, clarifiers, and chlorination before the effluent from each is sent to the LAS (http://www.dutil.com/residential/ww_process.php). Because of the fully fluorinated nature of PFOA and PFOS, this likely precludes any aerobic decomposition of these compounds during the wastewater treatment process [39] in Dalton. In addition, precursor compounds to PFOA, such as telomer alcohols, may biotransform to PFOA during the wastewater treatment process [40], contributing to elevated concentrations of this compound downstream of the LAS. Consequently, after spraying the effluent containing PFAAs onto the landscape in Dalton, these chemicals could possibly enter the Conasauga River from direct runoff, from runoff into small tributaries that drain the Conasauga River, or from underground leaching. In addition to any risks to wildlife in the region, public health concerns exist regarding possible PFAA-contaminated drinking water. Samples of drinking water collected in the Dalton region during the summer of 2006 found levels of PFOA ranging from 4.1 to 9.7 ng/L in private wells (detected in two of three samples) and from 4.1 to 6.9 ng/L in tap water from the public water system ($n = 4$). Levels of PFOS were only found in one (6.1 ng/L) of the three private wells and ranged from 3.8 to 10.0 ng/L in the public water supply (S. Gilchrist, United Steel Workers, Pittsburgh, PA, USA, unpublished data). Current health-based values regarding human consumption of drinking water for PFOA (0.5 μg/L) and PFOS (0.3 μg/L) have been developed by the state of Minnesota (USA; http://www.health.state.mn.us/news/pressrel/pfc030107.html). The highest levels found for PFOA and PFOS in Dalton drinking water in this limited survey are more than an order of magnitude below these drinking water standards.

To assess possible sources, the ratio of the concentrations of PFOS to those of PFOA was calculated in the waters of Georgia. In the Conasauga River, all locations showed a ratio of less than 1.0, indicating that PFOA was at higher concentrations than PFOS. Ratios of PFOS to PFOA of less than 1.0 were found in six different WWTP effluents from New York and in approximately half of the effluents in a limited survey of WWTPs in the United States, including one from the southeastern United States [19,38]. Ratios of PFOS to PFOA of greater than 1.0, however, have been found in WWTP effluent from Columbus (GA, USA) and Decatur (AL, USA) [41], which indicates that fluorochemical sources and the WWTP process used in each location must be taken into account when identifying potential sources of PFAAs. The PFOS to PFOA ratios at all sites in the Altamaha River were near 1.0, suggesting that other sources besides WWTP effluent could be the cause of the PFAA contamination in this river.

A pattern of decreasing PFAAs with increasing chain length (from C8 to C12) was observed in the Conasauga River during the present study. This observation of a general even carbon > odd carbon PFAA pair pattern, where PFOA concentrations > PFNA concentrations and PFDA concentrations > PFUA concentrations, was documented at a WWTP previously in New York [19]. Those authors hypothesized that telomer alcohol biodegradation was a possible source of the PFAAs, because although manufactured as even carbon chains only, telomer alcohols may biodegrade to form even and odd PFAAs, with the even chain being greater in concentration than the odd chain [4,42]. Growing evidence suggests that telomer alcohols and sulfonamides are important precursors to other PFAAs (i.e., PFOA and PFOS) [7] and likely contribute to the measurement of PFAAs in this region. For example, significant amounts of telomer alcohols and sulfonamides have been measured in various polymeric fluorinated materials used in the paper, textile, and carpet industries as well as in a commercial surface protection product [43,44]. Furthermore, high concentrations of fluorinated telomer alcohols and sulfonamides have been detected in the troposphere above Georgia, indicating that these compounds are used and likely are heavily released in this region [18].

Hazard assessment of PFOS exposure to aquatic species

An evaluation of the ecological risk to aquatic animals from PFOS exposure was performed in the present study as described by Rostkowski et al. [31]. Measured PFOS water concentrations in the Conasauga and Altamaha rivers were compared with water-quality values (i.e., guidelines) that are protective of aquatic organisms (as determined by Beach et al. [45]). No current guidelines have been derived specifically for saltwater, but guidelines have been developed following the procedures outlined in the U.S. Environmental Protection Agency Great Lakes Initiative [46] and based on results from toxicity testing with freshwater organisms [45]. The hazard assessment was determined by comparing PFOS concentrations to these protective values (Fig. 2A). None of the PFOS concentrations exceeded threshold values of toxicity. This comparison represents a conservative measure of risk to most aquatic organisms, however, because the most sensitive species were used in the determination.

Because PFOS can bioaccumulate in the food web [5,6], we also determined whether the PFOS concentrations observed in Georgia's waters could adversely affect higher-trophic-level organisms, such as fish-eating birds [47]. The safe water concentration (i.e., avian wildlife value) that is protective of trophic-level-4 avian species that may potentially consume organisms at steady state with PFOS water concentrations has been determined to be 50 ng/L of PFOS [47]. Concentrations of PFOS at two locations (CR2 and CR3) exceeded this protective value (Fig. 2A), with concentrations well below this value being found at the remaining sites. Because of the conservative nature of the risk analyses used to extrapolate from birds to safe water concentrations, however, and the very localized nature of the elevated PFOS concentrations in the Conasauga River from which we sampled, adverse effects at the population level have not necessarily occurred.

As a result of limitations in available data, particularly regarding chronic effects in aquatic species, the use of uncertainty factors and a conservative acute to chronic ratio were required

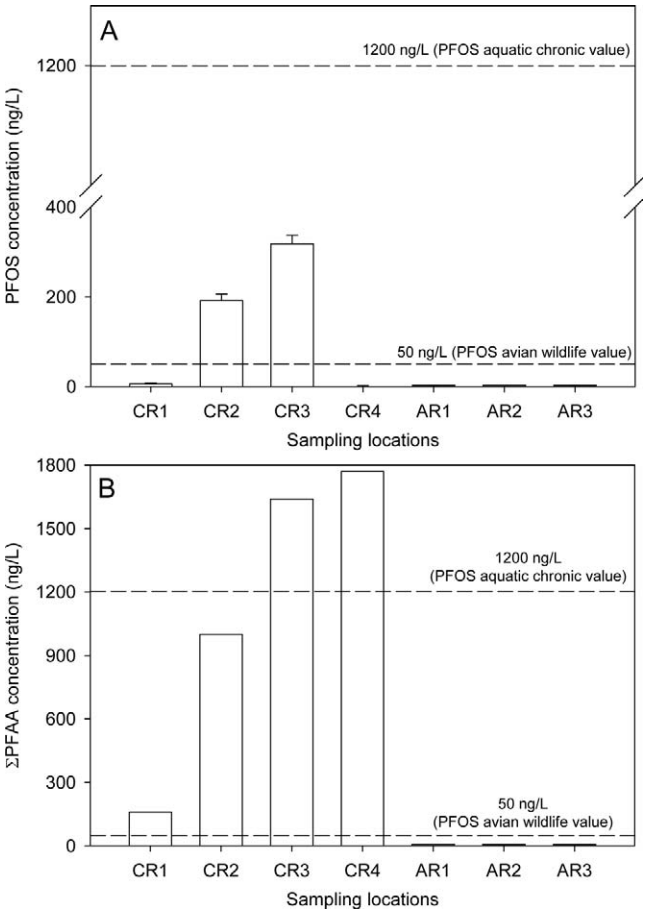

Fig. 2. Comparison of perfluorooctane sulfonate (PFOS) concentrations (mean ± standard error) (**A**) and sum of the perfluoroalkyl acid (ΣPFAA) concentrations (**B**) as measured in Georgia (USA) waters (Conasauga [sites CR1–CR4] and Altamaha [sites AR1–AR3] rivers) to PFOS values protective of aquatic and avian life. See text for details regarding derivation of the PFOS quality criteria.

to derive the threshold levels for the protection of aquatic life. Therefore, these values probably are overly conservative, possibly by as much as 50- to 100-fold [31], depending on the true distribution of sensitivities among organisms as well as any differences in sensitivities between freshwater and saltwater organisms. Furthermore, the avian wildlife threshold value assumes that the targeted wildlife will stay in the area where the concentration of PFOS was determined and eat sufficient dietary prey in this area to result in a steady-state diet. This potentially is true for some species, but it is unlikely that many large piscivorous birds would remain in only one area. To reduce the uncertainty of this avian wildlife hazard assessment, PFOS concentrations should be measured in the tissues, such as the liver, blood, or eggs, which then could be compared to toxicity reference values calculated for birds [47].

The greater presence of PFOA, as well as the elevated occurrence of several other PFAAs at several sites (i.e., in the Conasauga River), would indicate that these compounds should be included in the hazard assessment. Currently, no water-quality values are available for PFOA or any other PFAA besides PFOS. A preliminary estimate for the potential risk from exposure to all PFAAs can be made by assuming that the toxicity and accumulation of all compounds are similar to those of PFOS. This preliminary approach can be seen as a median between a significant underestimation or overestimation of potential hazards based on the toxicity and bioaccumulation data of PFAAs. In this preliminary approach, the sum of the mean concentration for each PFAA indicated that all the Conasauga River sites exceeded the avian wildlife value, some by more than 35-fold (Fig. 2B). None of the Altamaha River sites exceeded the avian wildlife or chronic aquatic species guidelines. Sites CR3 and CR4 in the Conasauga River also exceeded the aquatic chronic water guideline; however, this preliminary hazard assessment for aquatic species and wildlife must be interpreted with extreme caution. First, the water guidelines we are using for comparison were developed from one chemical, PFOS, and as mentioned above, they probably are overly conservative (by 50- to 100-fold). Also, some perfluorinated chemicals can bioaccumulate more (e.g., perfluorododecanoic acid, although not detected here) or less into biota compared with PFOS [48], which will result in uncertainty concerning this hazard estimation for avian wildlife. In addition, little information exists regarding the toxic potency of other PFAAs besides PFOS and PFOA, although some data indicate that some PFAAs are less (e.g., PFOSA) or more (e.g., PFDA) toxic in comparison to PFOS [12–15], thus providing further uncertainty in interpreting this preliminary hazard assessment.

The potential historical and current elevated PFAA concentrations in the Conasauga River are a cause for concern. The LAS has been in operation since the mid-1980s, with approximately half the 9,200 acres being irrigated daily with the treated wastewater (up to 33 million gallons daily permitted) on a rotating basis. In 2001, the local utility entered into a consent decree with the U.S. Environmental Protection Agency and the Georgia Environmental Protection Division because of numerous violations of the Clean Water Act (http://www.epa.gov/region4/ead/attachments/2001_accomplishments_report.pdf), suggesting that past PFAA contamination may have been higher from the operation of the LAS. This cannot be confirmed, however, because the present study is, to our knowledge, the first published report of PFAAs in the Conasauga River or any other surface water in the Dalton region. Given the decline in the diversity of fish, some of which are endangered and threatened, and a shift to more benthic dwelling fishes in the Conasauga River [49], the potential role of PFAA contamination along with other factors (e.g., habitat degradation) may have contributed to this change in the fish structure in this river.

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