Running head: Perfluorinated chemicals in Georgia (USA) surface waters

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Concentrations and patterns of perfluorinated compounds in Georgia (USA) surface waters near and distant to a major use source

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Abstract

Perfluorinated chemicals (PFCs) are widespread contaminants emanating from, among other things, the production/degradation of fluorinated chemicals used in surface repellant applications, such as carpet manufacturing. The goal of this work was to assess the concentrations of PFCs, including perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUA), perfluorooctane sulfonamide (PFOSA), fluorinated telomer carboxylic acids (FTCAs), and fluorinated telomer unsaturated carboxylic acids (FTUCAs) in surface waters of Georgia near (wastewater land application site (LAS) for Dalton, GA) and distant (Altamaha River and estuary, GA) to North America's largest carpet manufacturing site to understand the fate of PFCs in freshwater and estuaries of Georgia. Levels of PFCs were very high in the Conasauga River below the LAS (PFOA 252.9 – 1150.0 ng/L, PFOS 191.5 – 318.3 ng/L, PFNA 201.6 – 368.8 ng/L, PFDA 30.1 – 131/.3 ng/L, PFUA 58.0 – 99.2 ng/L, and PFOSA 161.7 – 282.5 ng/L) and in small streams and ponds in Dalton (PFOA 49.9 – 299.0 ng/L and PFOS 15.8 – 120.0 ng/L), and are among the highest ever measured at a non-spill or direct release location. PFCs in the Altamaha River were much lower (PFOA 3.0 – 3.1 ng/L and PFOS 2.6 – 2.7 ng/L), yet higher than reported in the Atlantic Ocean, suggesting this pathway as a potential source of PFC's to estuaries. No FTCAs or FTUCAs were detected in the water samples. The elevated concentrations of PFOS at two locations in the Conasauga River exceeded the threshold for effects predicted for predatory birds consuming aquatic organisms continuously exposed to these levels, suggesting further study in the Dalton region.

Keywords: *perfluorinated acids, perfluoroalkyl surfactants*, *carpet manufacturing, risk assessment*

Introduction

Perfluorinated compounds (PFCs) are a diverse group of chemicals that have unique properties due to their repulsion of both oil and water, and therefore have been used in many applications as surfactants for the surface protection of carpets, paper, food containers, upholstery, and fabric [1]. PFCs are used for many other applications including polymerization aids for fluoropolymer manufacturing and aqueous fire-fighting foam formulations. These fully fluorinated compounds have been manufactured for over 50 years and due to the strength of the carbon-fluorine bond, they are very stable and persistent in the environment. Consequently, PFCs have been detected in biotic (human and wildlife) and abiotic (water, sediment, air) samples worldwide [2-4] with some PFCs 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 PFCs in environmental samples. While both of these compounds have direct uses, they are considered the terminal degradation products of other PFC precursors [7]. In 2001, the 3M Company, one of the largest producers of PFCs, ceased production of PFOS and intermediates used in the production PFOS; other companies, although, are still producing PFOS and fluorotelomer alcohol based products [8]. In 2006, the major manufacturers of PFOA voluntarily agreed to reduce the production of this chemical and any precursors by 95% in 4 years time [9]. Although these major reductions for PFOS and PFOA will decrease their presence in the environment in the future, the historical use of PFCs will be a cause for concern to wildlife and humans in the intermediate time frame due to their stability and persistence in the environment. Toxicity assessments of PFCs, 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 [12-13]. However, a large amount of the above effects from PFC exposure, including decreases in fathead

111 minnow (*Pimephales promelas*) reproduction [14-15], occur at concentrations typically greater
112 than those reported in the environment.

113 The city of Dalton, Georgia (Figure 1) is known as the carpet capital of the world and
114 contains over 150 carpet plants and approximately 100 outlet stores, accounting for ~80% of the
115 carpets manufactured (www.northga.net/whitfield/indust.html). It has been suggested previously
116 that due to the high use of PFCs in the carpet industry, northwest Georgia may be a local source
117 for PFC exposure in the region [16]. However, there has been no attempt to determine the levels
118 of PFCs in the nearby Conasauga River (Figure 1), which has historically contained a high
119 diversity of fish species [17] and is one of five major rivers contributing to the Coosa River
120 watershed. Contamination by PFCs, both historic and current, may be significant in the
121 Conasauga River due to its close proximity to the extensive carpet industry in the area. One
122 potential route for contamination exists due to the land application of treated wastewater in
123 Dalton. After the local utility treats incoming wastewater from Dalton, it is pumped to a 9,200-
124 acre Land Application System (LAS) and sprayed to the landscape, which is bordered on one
125 side by the Conasauga River. Given that many PFCs are shown to resist biodegradation in the
126 waste-water treatment plant (WWTP) process, and can actually increase in concentration [18],
127 potential run-off of these chemicals into the river is a realistic concern. Thus, biomonitoring of
128 PFCs in the Conasauga River is particularly useful for understanding if concentrations are at
129 levels that may pose a risk to wildlife as well as the fate of these compounds in a lotic
130 environment, potentially from a point source.

131 Contaminants in estuaries are primarily derived from inland sources and transported via
132 rivers [19-20] where they may be trapped and impair the health of the estuarine ecosystem [19].
133 However, there is little information on the environmental behavior and distribution of organic
134 contaminants, specifically PFCs, as they move from a freshwater to saltwater system. Salinity
135 changes, for example, could potentially influence physical-chemical properties, such as water
136 solubility of organic contaminants [21], likely to include PFCs, which will in turn alter their

environmental distribution and dynamics. The Altamaha River (Figure 1) is the third largest U.S. watershed draining into the Atlantic Ocean, which can potentially be impacted by PFCs due to inland regional industries and/or other sources from industries that use PFCs along the river. Thus, it is critical to understand the extent of freshwater-derived PFCs to the Altamaha estuary ecosystem, which can have potential negative impacts on Southeastern U.S. marine and tidal biota that are commercially important. Examining riverine delivery of PFCs as a source to the Georgia coast is also important due to the reported bioaccumulation and biomagnification of these chemicals in the area [5, 22], and therefore may pose a risk to humans from consuming contaminated shellfish.

In this study, we assessed the concentrations of a series of PFCs in waters of Georgia. We investigated the distribution of these chemicals above and below the LAS in the Conasauga River near Dalton to understand the extent and fate of PFCs near the carpet industry. The second objective was to make a preliminary assessment of whether the Altamaha River, a river remote from the carpet industry, was a source of freshwater delivering PFCs to Georgia 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 waters.

Materials and Methods

Chemicals and standards

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

Sample collection

Water samples were collected from four locations (n = 5 for each location plus 3 blanks) within the Conasauga River (Figure 1A) in March 2006 (1 L) and three locations (n = 3 for each

location plus 3 blanks) within the Altamaha River (Figure 1B) in January 2005 (2 L). In the Conasauga River, one location (CR1: W-84°52′06″, N34°42′32″) was taken above, one at (CR2: W-84°55′05″, N34°41′51″), and two were taken below (CR3: W-84°56′35″, N34°40′50″; CR4: W-84°55′37″, N34°40′00″) the LAS (Figure 1A). Altamaha River samples were taken such that one location was in freshwater (AR1: W-81°32′51″, N31°23′16″) and two were taken in mixed salinity (AR2: W-81°26′22″, N31°20′19; AR3: W-81°23′49″, N31°20′13″) (Table 1). Salinity measurements were taken with a Hydrolab Quanta (Hach Environmental, Loveland, CO). In addition, we collected water from ponds and streams within the city of Dalton, Georgia (4 locations, n = 2 for each, plus 2 blanks) in January 2005 (2 L), but no GPS recordings were taken for these samples. These ponds are located approximately 7 km to 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 (~0.25 m below surface), at one point in the middle of the river. Blanks consisted of Optima grade water, 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 (RIS, see Table 1) and 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, instrument analysis, and recovery standards

The target perfluorinated analytes were extracted from water using Oasis HLB (20 mL, 1 g, 60 μm) solid-phase extraction cartridges (Waters, Milford, MA) [23-24]. Before extraction, cartridges were preconditioned by elution with 5 mL of methanol and were kept wet at all times. Each water sample or field blank (spiked with 10 μL of 1 ng/μL solution of recovery internal standard; see Table 1) was filtered (1.0 μm glass fiber, Pall Corporation, East Hills, NY) 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 for

analysis (Winnipeg, ON, Canada). Before the samples were extracted, the elution of PFCs off the HLB cartridge was optimized by spiking three cartridges with a 10 mL solution that was intentionally spiked with the RIS solution (10 uL of 1 ng/uL) 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 methanol (fraction 3). The flow rate through the cartridge was 1 drop per second. PFCs were detectable in only fraction 2. Field samples were then processed by eluting first with 5 mL of Optima grade water and discarded, followed by 15 mL of Optima grade methanol, which was collected. Methanol extracts were then reduced in volume (500 μL) and fortified with instrument performance internal standard (10 uL of 1 ng/uL solution, see Table 1 for compounds).

An Agilent 1100 Series HPLC system (Agilent Technologies, Palo Alto, CA, USA) equipped with a vacuum degasser, binary pump, autosampler, and a Discovery C18 analytical column (5.0 cm × 2.1 mm i.d., 5 μm particle size; Supelco, Oakville, ON, Canada) were used for all separations and analyses. The mobile phase system used consisted of water and methanol; a mobile phase flow rate of 300 μL/min was utilized and sample injection volume was 3 μL. The gradient employed started at 20% methanol, increasing to 95% in 9.5 minutes, and was held for 2 minutes. Thereafter the mobile phase composition was returned to starting conditions in 5 minutes. The column was allowed to equilibrate for 5 minutes between runs. PFC detection were performed with a Sciex API 2000 triple quadrupole mass spectrometer (MDS Sciex, Ontario, Canada) in the negative ion ES mode using multiple reaction monitoring. The optimized parameters were: ionspray voltage, –1200 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; collision assisted dissociation gas flow 8 a.u.. The collision cell was recently upgraded to improve instrument sensitivity (mSpec, Concorde, ON). The reactions monitored are given in Table 1. Italicized ion transitions were used in the quantitation while the other transitions were used for confirmation.

Quality assurance/quality control

The inherent problems associated with quantifying PFCs by LC/MS/MS 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 has been well documented in the literature [4, 25]. Two types of blanks were employed in this study. Instrument blanks were injections of methanol run after every five samples and were used to monitor PFC contamination from the LC/MS/MS 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 consistently detected 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 was probably less important than from the instrument itself. The background signal of PFOA could be reduced appreciably (10x) by reducing the column equilibration time between sample injections. It appears that PFOA is continually leaching from the inner parts of the HPLC system and concentrating on the head of the analytical column. For all other PFCs, extraction blanks always had higher signals than instrument blanks, suggesting that contamination during extraction and work-up were more significant.

The average recoveries of $^{13}C_2$-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, 73.4 ± 5.5 %, respectively (mean ± 1 SE). PFC concentrations in samples were blank corrected by subtracting the signal from extraction blanks from the sample signals. Native PFCs in the samples were recovery corrected based on the recovery of the nearest labeled surrogate (see Table 1). Method detection limits (MDLs) were determined from known amounts of PFOS and PFOA spiked into the procedural blanks (n=6) that were previously analyzed and found to have non-detectable concentrations of PFCs

(i.e., response of PFCs were not above the response from the instrument blanks). Separate injections of the spiked extracts were then made. The ion signals obtained for PFCs were then adjusted to estimate concentrations that would give a signal-to-noise ratio of 5:1. In this manner, MDLs based on a 1L sample, of PFOA (2.8 ng/L), PFNA (0.6 ng/L), PFDA, PFUA, PFDoDa (0.1 ng/L) and PFOS (1.5 ng/L) were estimated.

Results and Discussion

PFC concentrations and distribution

Concentrations of measured PFCs were highest in the Conasauga River, with PFOA occurring at the highest mean concentration followed by PFNA, PFOS, PFOSA, PFDA, and PFUA (Table 2). These elevated PFC concentrations were either from sample locations C3 or C4, which were downstream of the LAS. A similar PFC pattern, although at lower concentrations than the Conasauga River, was found in water sampled from streams and ponds around Dalton with PFOA 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 PFCs; however, mean concentrations of the two greatest PFCs detected (PFOA and PFOS) were consistent in this river despite changes in salinity. Some PFCs (e.g., PFNA and PFDA) were found in the freshwater and the lower mixed salinity location at low concentrations, but not in the higher mixed salinity location (Table 2). It should be noted that no FTCAs or FTUCAs were detected in any water sample collected in this study.

The observation of elevated PFCs in the Conasauga River below the LAS in comparison to the upstream site indicates the LAS as a likely important point source of PFC contamination. A pattern of increasing concentration with distance below 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. PFOA and PFUA were the exceptions to this pattern with a continual increase in concentration throughout the study range with distance

below the LAS. It is unclear why there is a drop for several of the PFCs, and for some a prominent decline (e.g., PFOS) at this last location, which is approximately 2.2 river km downstream from site CR3. PFOS appears to adsorb strongly to soil and sediment with distribution coefficients (K_d) in soils between 9.7 L/kg (clay loam) and 35 L/kg (sandy loam) [26], with organic carbon to have shown to be the predominant factor in sorption [27]. Similar K_{oc} values to PFOS have been reported for PFNA and PFDA [27], which may indicate sorption to sediments as a reason for their decrease at the last sampling site. The increase in concentration for PFOA throughout the sampling range would indicate little potential sorption to sediments for this compound, which has been suggested previously [28]. Due to PFOA's likely environmental fate predominantly remaining in the water compartment [29], a concern is increasing downstream concentrations of PFOA beyond the sampling frame carried out in this study.

The concentrations of the PFCs identified in the Altamaha River would suggest that riverine deliver is a likely pathway for these chemicals to estuaries. Of the two main PFCs identified (i.e., PFOS and PFOA), there was no significant difference in concentrations with salinity (ANOVA, $p > 0.05$). However, PFNA and PFDA were present in the freshwater and not in the higher mixed salinity (i.e., site AR3) suggesting that the Altamaha River is a likely source of PFCs to the estuary. Our findings must be interpreted with caution due to the low sample size and restricted sampling scheme employed, but are supported by the finding of a general increase in PFC concentrations measured in freshwater compared to marine waters in South Korea [30].

Comparison of PFC concentrations to other areas

Concentrations of PFOS and PFOA, and other PFCs, in the Conasauga River are among the highest ever recorded in surface waters, and much greater than those observed in freshwater environments outside of direct releases. The highest PFOS concentrations observed in this study (318 ng/L) are lower than PFOS concentrations found in a Canadian creek from an accidental fire-fighting foam release (190 – 2,210,000 ng/L) [31] and in groundwater at a fire-fighting air force base in Michigan, USA (lowest detected 8,000 ng/L) [32]. However, the elevated PFOS

concentrations in this study are greater than those found in the Tennessee River in Alabama below a manufacturing facility (highest detected 144 ng/L) [33] and in most freshwaters sampled in Korea (8 – 651 ng/L) [30]. The PFOS concentrations in the Conasauga River above the LAS, but not in the elevated levels below, are generally in the range of concentrations found in freshwaters of New York State and Michigan (range 2-5 ng/L, max 29 ng/L) [34], and would appear to be background levels. The highest concentration of PFOA (1150 ng/L) in the Conasauga River is higher than concentrations reported in the Tennessee River (max 598 ng/L) [33], in the range of the accidental fire-fighting foam release in Canada detected within the first 3 days (mean 2859 ng/L, range 11 – 11300 ng/L) [31], but below the concentrations in groundwater at the fire-fighting air force base in Michigan (lowest detected 8000 ng/L) [32]. The PFOA concentrations in the Conasauga River are also generally higher than the majority of PFOA concentrations measured in rivers of Japan (0.1 – 456 ng/L) [35] and in the Great Lakes (15 -70 ng/L) [36]. The concentrations of the other PFCs, including PFDA, PFNA, PFUA, and PFOSA, in the Conasauga River may also be some of the highest reported. There is little information on the concentrations of these chemicals in waters, but the few data available suggest that the concentrations reported here are elevated [5, 18, 23, 30].

Concentrations of PFCs in the Altamaha River estuary are in similar range to those reported for estuarine and marine waters outside heavy industrialized areas [5, 24, 30]. 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 [23]. 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 at lower levels compared to the Altamaha River estuary [23], which may be a result of their decreased solubility and/or their possible transport via ocean currents, but may suggest that this river is a source of PFC contamination to the Georgia coast. These results would indicate a potential correlation with manufacturing and industrial activity and PFC inputs. Based on the available PFC concentration data, the Altamaha River appears to deliver PFCs to oceans

on a similar level as those delivered to Sarasota Bay, FL and coastal southern Korea, but there appears to be greater PFC contamination in Charleston Harbor, western Korea, and Tokyo Bay in ascending order. The Altamaha River is relatively unindustrialized with no major port city, which may explain the lower PFC concentrations found here, although it should be noted that concentrations are not much lower than those in industrialized areas. Thus, a more detailed study of riverine delivery of PFCs and possibly other contaminants in the Altamaha River to the Georgia estuary needs to be explored.

Potential sources

Concentrations of PFCs in the Conasauga River were elevated below the LAS in comparison to the upstream site indicating that treated wastewater from this area is likely the source of the PFC contamination. Previous studies have indicated that PFOS, PFOA, PFNA, PFDA, and PFUA mass flows generally can, but not always, increase in WWTP effluent in comparison to the influent water, with no consistent reduction or enhancement in PFC levels with different treatment processes (i.e., activated sludge or trickling filter) [18, 37]. Treatment of the wastewater in Dalton is achieved by several different WWTPs through aeration basins and clarifiers with no tertiary treatment before the effluent from each is sent to the LAS (www.dutil.com/residential/ww_process.php). The fully fluorinated nature of PFOA and PFOS likely precludes their aerobic decomposition during the wastewater treatment process [38]; however, the biotransformation of the more highly substituted PFCs has been shown to occur. Specifically, there is evidence that 2-(*N*-ethyl-perfluorooctane-sulfonamido) ethanol (N-EtFOSE alcohol) and 2-(*N*-ethyl perfluorooctane sulfonamide) acetic acid (N-EtFOSAA) are biotransformed to PFOS and PFOSA during activated sludge treatment [39-40]. Telomer alcohols also have been shown to biotransform into perfluorocarboxylic acids during activated sludge treatment [41]. These precursor compounds may form an additional source of PFCs in the Dalton WWTP influent, outside of any direct use in nearby industries, leading to elevated levels of several PFCs in the WWTP effluent. Consequently, after spraying the effluent

containing PFCs onto the landscape in Dalton, these chemicals could possibly enter the Conasauga River from direct run-off, run-off into small tributaries that drain the Conasauga River, or underground leaching. In addition to any risks to wildlife, the city utilizes the Conasauga River as a source of drinking water after it undergoes treatment (www.dutil.com/residential/water_process.php), with the intake source unknown to us if it is above or below the LAS, which may potentially pose a risk to humans.

To assess possible sources, the ratio of the concentrations of PFOS to PFOA was calculated in the waters of Georgia. In the Conasauga River, all locations showed a ratio less than 1.0, indicating PFOA was at higher concentrations than PFOS. PFOS to PFOA ratios of < 1.0 were found in six different WWTP effluents from New York State and approximately half of the effluents in a limited survey of WWTPs in the United States, including one from the southeast [18, 37]. Ratios of PFOS to PFOA greater than 1.0 have been found in WWTP effluent from Columbus, Georgia, and Decatur, Alabama [42], which indicates that fluorochemical sources and the WWTP process used in each location must be taken into account when identifying potential PFC sources. The PFOS to PFOA ratios at all sites in the Altamaha River were near 1.0, suggesting that other possible sources besides WWTP effluent could be the cause of the PFC contamination in this river.

A pattern of decreasing PFCs with increasing chain length (from C8 to C12) was observed in the Conasauga River. The general even > odd carbon PFC pair pattern seen here in which PFOA > PFNA and PFDA > PFUA has been observed in a WWTP previously in New York State, where it was suggested that telomer alcohols was a possible source of the PFCs [18]. Telomer alcohols, manufactured as even carbon chains only, may biodegrade to form even and odd PFCs [4, 41]. There is growing evidence to suggest that telomer alcohols and sulfonamides are precursors to perfluorinated acids (i.e., PFOA and PFOS) [7], and they have been recently identified at significant amounts in various polymeric fluorinated materials used in the paper, textile, and carpet industry [43]. 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 heavily released in this region [16].

Hazard assessment of PFOS exposure to aquatic species

An evaluation of the ecological risk to aquatic animals from PFOS exposure was performed in this study as described by Rostkowski et al. [30]. 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 in [44]). There are no current guidelines specifically derived for saltwater, but guideline values have been developed following the procedures outlined in the U.S. Environmental Protection Agency Great Lakes Initiative [45] and based on results from toxicity testing with freshwater organisms [44]. The hazard assessment was determined by comparing PFOS concentrations to these protective values (Figure 2A). None of the PFOS concentrations exceeded threshold values of toxicity but this comparison represents a conservative measure of risk to most aquatic organisms.

Because PFOS can bioaccumulate in the food web [5-6], we also determined whether the PFOS concentrations observed in Georgia waters could adversely affect higher trophic level organisms, such as fish-eating birds [46]. The safe water concentration (i.e., avian wildlife value) that is protective of trophic level IV avian species that may potentially consume organisms at equilibrium with PFOS water concentrations has been determined to be 50 ng/L of PFOS [46]. Concentrations of PFOS at two locations (site CR2 and CR3) exceeded this protective value (Figure 2A), with concentrations well below this value at the remaining sites. However, due to the conservative nature of the risk analyses used to extrapolate from birds to safe water concentrations and the very localized nature of the PFOS concentrations in the Conasauga River from which we sampled, adverse effects at the population level would not be expected.

Due to limitations in available data, particularly for chronic effects in aquatic species, the use of uncertainty factors and a conservative acute to chronic ratio were required to derive the threshold levels for the protection of aquatic life. As a result, these values are probably overly

conservative, possibly by as much as 50 to 100 fold [30], 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 would have eaten 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 of birds, such as the liver, blood, or eggs, which then could be compared to toxicity reference values (TRVs) calculated for birds [46].

The higher presence of PFOA as well as the elevated occurrence of several other PFCs at several sites (i.e., in the Conasauga River) would indicate that these compounds should be included in the hazard assessment. Currently, there are no water-quality values that are available for PFOA or any other PFC besides PFOS. A conservative estimate for the potential risk from exposure to all PFCs can be made assuming that the toxic potencies of all compounds are equal. Using this conservative approach, the sum of the mean concentration for each PFC indicated that all of the Conasauga River sites exceeded the avian wildlife value, some by more than 35 fold (Figure 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 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 are probably overly conservative (50 to 100 fold). Also, many perfluorinated chemicals bioaccumulate less into biota compared with PFOS, which will underestimate this hazard estimation for avian wildlife. Furthermore, there is little information on the toxic potency of other PFCs besides PFOS and PFOA, with several PFCs having been shown to be less toxic in comparison to PFOS [12-13]. Given the decline in fish diversity, some of which are endangered and threatened, and a shift to

more benthic dwelling fishes in the Conasauga River [47], the potential historical and current elevated PFC concentrations is a cause of concern in this river, which may have potentially played a role, along with other factors (e.g., habitat degradation), in this change in the fish structure.

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Table 1. List of native and labeled perfluorinated chemicals (PFCs) used in this study (reactions monitored in parentheses).

Native PFC analyzed for	Recovery Internal Standard (RIS)	Labeled Instrument Performance Internal Standard (LIPIS)
PFOA (perfluorooctanoic acid) (413/ 369), (413/ 169)	$^{13}C_4$ – PFOA (417/ 372), (417/ 169)	$^{13}C_2$ – PFOA (415/ 370), (415/ 169)
PFOS (perfluorooctanesulfonate) (499/ 99), (499/ 80)	$^{13}C_4$ – PFOS (503/ 99), (503/ 80), (503/ 131)	$^{18}O_2$ – PFOS (503/ 103), (503/ 84)
PFNA (perfluorononoic acid) (463/ 419), (463/ 169)	$^{13}C_5$ – PFNA (468/ 423), (468/ 169)	$^{13}C_2$ - PFNA (465/ 420), (465/ 169)
PFDA (perfluorodecanoic acid) (513/ 269), (513/ 469)	$^{13}C_2$ – PFDA (515/ 269), (515/ 470)	$^{13}C_2$ - PFNA (465/ 420), (465/ 169)
PFUA (perfluoroundecanoic acid) (563/ 519), (563/ 169)	$^{13}C_2$ – PFDA (515/ 269), (515/ 470)	$^{13}C_2$ - PFDoA (615/ 570), (615/ 169)
PFDoA (perfluorododecanoic acid) (613/ 569), (613/ 169)	$^{13}C_2$ – PFDA (515/ 269), (515/ 470)	$^{13}C_2$ - PFDoA (615/ 570), (615/ 169)
FTUCAs (fluorotelomer unsaturated acids) octenoic acid ; 6:2 (357/293) dodecenoic acid; 10:2 (557/ 493) 8:2, decenoic acid (457/ 393)	$^{13}C_2$ – FTUCAs (6:2 (359/294)) , (dodecenoic acid; 10:2) (559/ 494))	$^{13}C_2$ – FTUCAs (8:2; decenoic acid) (459/ 394)

Table 2. Concentrations (ng/L; mean ± 1 SE and/or range) of perfluorinated compounds in the Conasauga River (CR), Altamaha River (AR), and streams and ponds of Dalton, GA (DP). See Figure 1 for map of sample locations.

Sample ID	N	Salinity	PFOA[a]	PFNA[a]	PFOS[a]	PFDA[a]	PFUA[a]	PFOSA[a]	∑PFC[b]
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[c]	74.9 ± 11.7 (10.7 - 102.4)	160.2
CR2	5	< 0.001	252.9 ± 14.2 (226.5 - 300.8)	201.6 ± 21.1 (136.2 - 247.8)	191.5 ± 14.5 (164.0 - 244.5)	72.4 ± 8.7 (47.4 - 97.1)	<0.1	161.7 ± 8.5 (146.7 – 187.4)	1000.9
CR3	5	< 0.001	480.1 ± 21.0 (448.3 - 559.4)	368.8 ± 31.9 (280.1 - 455.8)	318.3 ± 18.8 (262.2 - 367.9)	131.3 ± 8.5 (113.1 – 159.6)	58.0 ± 13.9 (28.7 - 94.2)	282.5 ± 32.7 (223.6 - 419.8)	1639.0
CR4	5	< 0.001	1150.0 ± 15.9 (1112.0 - 1284.7)	284.2 ± 34.9 (190.4 - 366.4)	1.0 ± 0.8 (0.2 – 3.1)	30.1 ± 1.9 (24.8 - 35.5)	99.2 ± 6.3 (81.9 - 117.2)	212.1 ± 17.8 (154.0 - 258.5)	1776.6
AR1	3	0.005	3.0 ± 0.1	0.5[c]	2.6 ± 0.2	0.14[c]	<0.1	_	6.32
AR2	3	0.07	3.1 ± 0.2	0.2[c]	2.7 ± 0.1	<0.1	<0.1	_	5.99
AR3	3	0.10	3.1 ± 0.3	<0.6	2.6 ± 0.1	<0.1	<0.1	_	5.75
DP1	2	< 0.001	238.0 - 224.0	11.1 - 12.2	81.6 - 86.3	5.2 - 5.6	0.1 – 0.3	_	332.2
DP2	2	< 0.001	293.0 - 299.0	40.6 - 41.0	119.0 – 120.0	17.8 - 19.7	0.3 – 0.9	_	475.7
DP3	2	< 0.001	103.0 - 113.0	4.8 – 6.3	53.3 - 61.7	1.8 - 2.3	0.1 – 0.5	_	173.4
DP4	2	< 0.001	49.9 - 53.7	2.1 – 2.5	15.8 - 25.2	0.1 – 1.0	<0.1	_	75.1

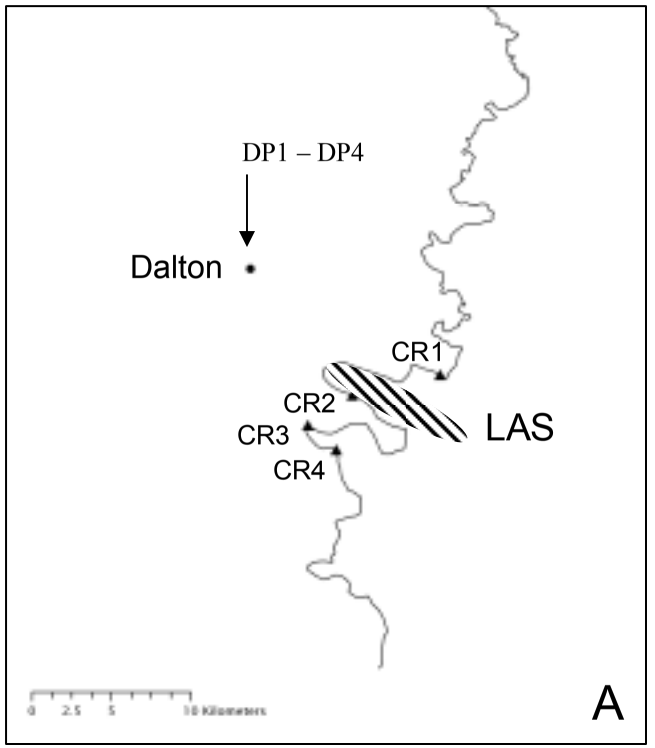
[a] PFOA = perfluorooctanoic acid; PFNA = perfluorononanoic acid; PFOS = perfluorooctane sulfonate; PFDA = perfluorodecanoic acid; PFUA = perfluoroundecanoic acid; PFOSA = perfluorooctane sulfonamide.
[b] ∑PFC = sum of the mean concentration for each PFC analyzed at that site
[c] Detected in one sample
Missing values indicate the analyte was not targeted

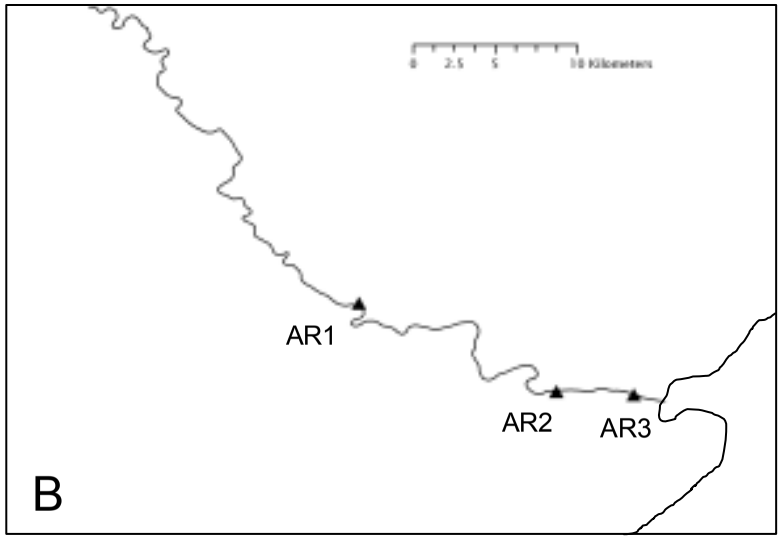
Figure Legend

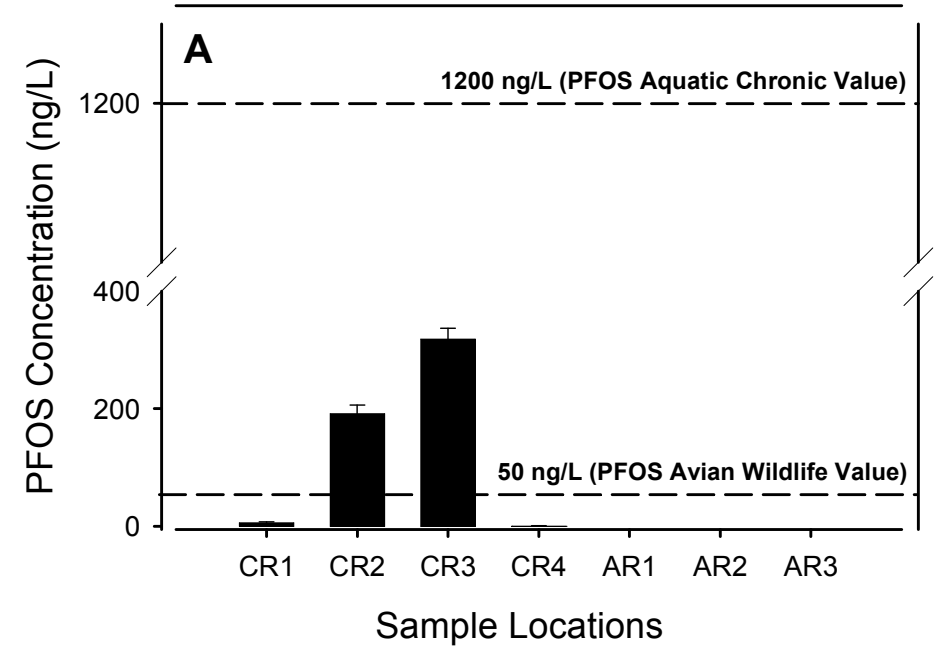
Figure 1. Map of Georgia with sampling locations (triangles) on the Conasauga River (A) and Altamaha River (B). The approximate location of the Land Application System (LAS), which sprays treated wastewater nearby the Conasauga River, is noted by the shaded area.

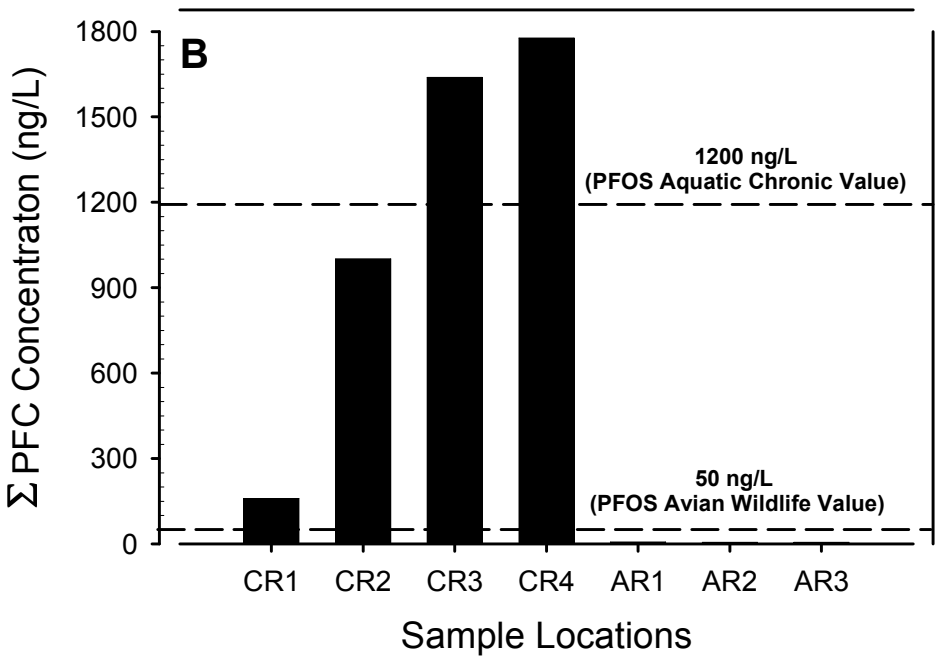
Figure 2. Comparison of perfluorooctane sulfonate (PFOS) concentrations (A) and ∑PFC concentrations (B) measured in Georgia waters (Conasauga (CR1-CR4) and Altamaha (AR1-AR3) Rivers) to PFOS values protective of aquatic and avian life. See text for details on the derivation of the PFOS quality criteria.


Dalton
A
Conasauga River
Atlanta
Savannah
Altamaha River
B


DP1 – DP4
Dalton
CR1
CR2
CR3
CR4
LAS
A


AR1
AR2
AR3
B


A
1200 ng/L (PFOS Aquatic Chronic Value)
50 ng/L (PFOS Avian Wildlife Value)
PFOS Concentration (ng/L)
1200
400
200
0
CR1
CR2
CR3
CR4
AR1
AR2
AR3
Sample Locations


B
1200 ng/L
(PFOS Aquatic Chronic Value)
50 ng/L
(PFOS Avian Wildlife Value)
ΣPFC Concentraton (ng/L)
1800
1500
1200
900
600
300
0
CR1
CR2
CR3
CR4
AR1
AR2
AR3
Sample Locations