

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

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30 **Concentrations and patterns of perfluorinated compounds in Georgia (USA) surface**  
31 **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 repellent 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.

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

85

## 86 **Introduction**

87           Perfluorinated compounds (PFCs) are a diverse group of chemicals that have unique  
88 properties due to their repulsion of both oil and water, and therefore have been used in many  
89 applications as surfactants for the surface protection of carpets, paper, food containers,  
90 upholstery, and fabric [1]. PFCs are used for many other applications including polymerization  
91 aids for fluoropolymer manufacturing and aqueous fire-fighting foam formulations. These fully  
92 fluorinated compounds have been manufactured for over 50 years and due to the strength of the  
93 carbon-fluorine bond, they are very stable and persistent in the environment. Consequently,  
94 PFCs have been detected in biotic (human and wildlife) and abiotic (water, sediment, air)  
95 samples worldwide [2-4] with some PFCs shown to bioaccumulate and biomagnify in coastal  
96 and Arctic food webs [5-6].

97           Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are the most  
98 commonly measured PFCs in environmental samples. While both of these compounds have  
99 direct uses, they are considered the terminal degradation products of other PFC precursors [7].  
100 In 2001, the 3M Company, one of the largest producers of PFCs, ceased production of PFOS and  
101 intermediates used in the production PFOS; other companies, although, are still producing PFOS  
102 and fluorotelomer alcohol based products [8]. In 2006, the major manufacturers of PFOA  
103 voluntarily agreed to reduce the production of this chemical and any precursors by 95% in 4  
104 years time [9]. Although these major reductions for PFOS and PFOA will decrease their  
105 presence in the environment in the future, the historical use of PFCs will be a cause for concern  
106 to wildlife and humans in the intermediate time frame due to their stability and persistence in the  
107 environment. Toxicity assessments of PFCs, with PFOS and PFOA gaining the most attention,  
108 indicate that they bind readily to blood plasma proteins [10] and can alter fatty acid metabolism  
109 [11] as well as adversely affect cellular membranes and intercellular communication [12-13].  
110 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](http://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

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

146 In this study, we assessed the concentrations of a series of PFCs in waters of Georgia.  
147 We investigated the distribution of these chemicals above and below the LAS in the Conasauga  
148 River near Dalton to understand the extent and fate of PFCs near the carpet industry. The second  
149 objective was to make a preliminary assessment of whether the Altamaha River, a river remote  
150 from the carpet industry, was a source of freshwater delivering PFCs to Georgia estuaries. In  
151 addition, a preliminary hazard assessment was undertaken to determine the potential risk to  
152 aquatic animals and predatory birds from exposure to PFOS in Georgia waters.

## 153 **Materials and Methods**

### 154 *Chemicals and standards*

155 The suite of native and mass labeled PFCs and their nomenclatures used in this study  
156 (Table 1) were obtained from Wellington Laboratories (Guelph, ON, Canada) with the exception  
157 of  $^{13}\text{C}_2$ -PFNA and  $^{18}\text{O}_2$ -PFOS, which were a gift from Dr. Sheryl Tittlermier (Health Canada,  
158 ON, Canada). Optima grade methanol and water were purchased from Caledon Laboratories  
159 Ltd. (Georgetown, ON, Canada).

### 160 *Sample collection*

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

163 location plus 3 blanks) within the Altamaha River (Figure 1B) in January 2005 (2 L). In the  
164 Conasauga River, one location (CR1: W-84°52'06", N34°42'32") was taken above, one at (CR2:  
165 W-84°55'05", N34°41'51"), and two were taken below (CR3: W-84°56'35", N34°40'50"; CR4:  
166 W-84°55'37", N34°40'00") the LAS (Figure 1A). Altamaha River samples were taken such that  
167 one location was in freshwater (AR1: W-81°32'51", N31°23'16") and two were taken in mixed  
168 salinity (AR2: W-81°26'22", N31°20'19; AR3: W-81°23'49", N31°20'13") (Table 1). Salinity  
169 measurements were taken with a Hydrolab Quanta (Hach Environmental, Loveland, CO). In  
170 addition, we collected water from ponds and streams within the city of Dalton, Georgia (4  
171 locations, n = 2 for each, plus 2 blanks) in January 2005 (2 L), but no GPS recordings were taken  
172 for these samples. These ponds are located approximately 7 km to northwest of the LAS and  
173 sampling locations on the Conasauga River. Water samples were collected by dipping a clean  
174 polypropylene sampling bottle just under the surface of the water (~0.25 m below surface), at  
175 one point in the middle of the river. Blanks consisted of Optima grade water, which were taken  
176 while sampling in the field by pouring the water into the collection bottles. All samples (surface  
177 water and blanks) were spiked with a recovery internal standard (RIS, see Table 1) and  
178 transported back to the laboratory on ice, where they were stored at 4°C until analysis. Samples  
179 were extracted within two weeks of collection.

#### 180 *Sample extraction, instrument analysis, and recovery standards*

181 The target perfluorinated analytes were extracted from water using Oasis HLB (20 mL, 1  
182 g, 60 µm) solid-phase extraction cartridges (Waters, Milford, MA) [23-24]. Before extraction,  
183 cartridges were preconditioned by elution with 5 mL of methanol and were kept wet at all times.  
184 Each water sample or field blank (spiked with 10 µL of 1 ng/µL solution of recovery internal  
185 standard; see Table 1) was filtered (1.0 µm glass fiber, Pall Corporation, East Hills, NY) and  
186 loaded onto the cartridge through the use of a peristaltic pump (flow rate 25 mL / min).  
187 Cartridges were wrapped in aluminum foil and shipped on ice to the Freshwater Institute for

188 analysis (Winnipeg, ON, Canada). Before the samples were extracted, the elution of PFCs off  
189 the HLB cartridge was optimized by spiking three cartridges with a 10 mL solution that was  
190 intentionally spiked with the RIS solution (10 uL of 1 ng/uL) and passed through the column and  
191 extracted using the following sequence: 5 mL of Optima grade water (fraction 1), 15 mL of  
192 Optima grade methanol (fraction 2) and 5 mL of methanol (fraction 3). The flow rate through  
193 the cartridge was 1 drop per second. PFCs were detectable in only fraction 2. Field samples  
194 were then processed by eluting first with 5 mL of Optima grade water and discarded, followed  
195 by 15 mL of Optima grade methanol, which was collected. Methanol extracts were then reduced  
196 in volume (500  $\mu$ L) and fortified with instrument performance internal standard (10 uL of 1  
197 ng/uL solution, see Table 1 for compounds).

198 An Agilent 1100 Series HPLC system (Agilent Technologies, Palo Alto, CA, USA)  
199 equipped with a vacuum degasser, binary pump, autosampler, and a Discovery C18 analytical  
200 column (5.0 cm  $\times$  2.1 mm i.d., 5  $\mu$ m particle size; Supelco, Oakville, ON, Canada) were used for  
201 all separations and analyses. The mobile phase system used consisted of water and methanol; a  
202 mobile phase flow rate of 300  $\mu$ L/min was utilized and sample injection volume was 3  $\mu$ L. The  
203 gradient employed started at 20% methanol, increasing to 95% in 9.5 minutes, and was held for 2  
204 minutes. Thereafter the mobile phase composition was returned to starting conditions in 5  
205 minutes. The column was allowed to equilibrate for 5 minutes between runs. PFC detection were  
206 performed with a Sciex API 2000 triple quadrupole mass spectrometer (MDS Sciex, Ontario,  
207 Canada) in the negative ion ES mode using multiple reaction monitoring. The optimized  
208 parameters were: ionspray voltage, -1200 V; curtain gas flow, 15.00 arbitrary units (a.u.); sheath  
209 gas flow, 30.00 a.u.; turbo gas flow, 35.00 a.u.; temperature 525°C; focusing potential, -360 V;  
210 collision assisted dissociation gas flow 8 a.u.. The collision cell was recently upgraded to  
211 improve instrument sensitivity (mSpec, Concorde, ON). The reactions monitored are given in  
212 Table 1. Italicized ion transitions were used in the quantitation while the other transitions were  
213 used for confirmation.

214 *Quality assurance/quality control*

215           The inherent problems associated with quantifying PFCs by LC/MS/MS in environmental  
216 samples, including high background signals of PFOA from injections of solvent (typically  
217 methanol and water), potential carryover between injections and lack of appropriate isotopically  
218 labeled internal standards has been well documented in the literature [4, 25]. Two types of  
219 blanks were employed in this study. Instrument blanks were injections of methanol run after  
220 every five samples and were used to monitor PFC contamination from the LC/MS/MS  
221 instrument. Extraction (or method) blanks consisted of Optima grade water, and were extracted  
222 along with each sample. Extraction blanks were used to monitor the potential for contamination  
223 to occur during extraction and work-up of the sample.

224           Ion signals of PFOA were consistently detected in all our blanks and the intensity of the  
225 signal was similar between the instrument and method blanks, suggesting that sample  
226 contamination during extraction and work-up was probably less important than from the  
227 instrument itself. The background signal of PFOA could be reduced appreciably (10x) by  
228 reducing the column equilibration time between sample injections. It appears that PFOA is  
229 continually leaching from the inner parts of the HPLC system and concentrating on the head of  
230 the analytical column. For all other PFCs, extraction blanks always had higher signals than  
231 instrument blanks, suggesting that contamination during extraction and work-up were more  
232 significant.

233           The average recoveries of  $^{13}\text{C}_2$ -PFDA,  $^{13}\text{C}_4$ -PFOA,  $^{13}\text{C}_5$ -PFNA and  $^{13}\text{C}_4$ -PFOS in the  
234 samples were  $48.6 \pm 10.1$ ,  $91.9 \pm 19.5$ ,  $80.7 \pm 12.9$ ,  $73.4 \pm 5.5$  %, respectively (mean  $\pm$  1 SE).  
235 PFC concentrations in samples were blank corrected by subtracting the signal from extraction  
236 blanks from the sample signals. Native PFCs in the samples were recovery corrected based on  
237 the recovery of the nearest labeled surrogate (see Table 1). Method detection limits (MDLs)  
238 were determined from known amounts of PFOS and PFOA spiked into the procedural blanks  
239 (n=6) that were previously analyzed and found to have non-detectable concentrations of PFCs

240 (i.e., response of PFCs were not above the response from the instrument blanks). Separate  
241 injections of the spiked extracts were then made. The ion signals obtained for PFCs were then  
242 adjusted to estimate concentrations that would give a signal-to-noise ratio of 5:1. In this manner,  
243 MDLs based on a 1L sample, of PFOA (2.8 ng/L), PFNA (0.6 ng/L), PFDA, PFUA, PFDoDa  
244 (0.1 ng/L) and PFOS (1.5 ng/L) were estimated.

## 245 **Results and Discussion**

### 246 *PFC concentrations and distribution*

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

260 The observation of elevated PFCs in the Conasauga River below the LAS in comparison  
261 to the upstream site indicates the LAS as a likely important point source of PFC contamination.  
262 A pattern of increasing concentration with distance below the LAS was found for PFNA, PFOS,  
263 PFDA, and PFOSA with the highest concentrations detected for all compounds at site CR3,  
264 before a decrease in concentration at the final site CR4. PFOA and PFUA were the exceptions to  
265 this pattern with a continual increase in concentration throughout the study range with distance

266 below the LAS. It is unclear why there is a drop for several of the PFCs, and for some a  
267 prominent decline (e.g., PFOS) at this last location, which is approximately 2.2 river km  
268 downstream from site CR3. PFOS appears to adsorb strongly to soil and sediment with  
269 distribution coefficients ( $K_d$ ) in soils between 9.7 L/kg (clay loam) and 35 L/kg (sandy loam)  
270 [26], with organic carbon to have shown to be the predominant factor in sorption [27]. Similar  
271  $K_{oc}$  values to PFOS have been reported for PFNA and PFDA [27], which may indicate sorption  
272 to sediments as a reason for their decrease at the last sampling site. The increase in concentration  
273 for PFOA throughout the sampling range would indicate little potential sorption to sediments for  
274 this compound, which has been suggested previously [28]. Due to PFOA's likely environmental  
275 fate predominantly remaining in the water compartment [29], a concern is increasing  
276 downstream concentrations of PFOA beyond the sampling frame carried out in this study.

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

#### 285 *Comparison of PFC concentrations to other areas*

286         Concentrations of PFOS and PFOA, and other PFCs, in the Conasauga River are among  
287 the highest ever recorded in surface waters, and much greater than those observed in freshwater  
288 environments outside of direct releases. The highest PFOS concentrations observed in this study  
289 (318 ng/L) are lower than PFOS concentrations found in a Canadian creek from an accidental  
290 fire-fighting foam release (190 – 2,210,000 ng/L) [31] and in groundwater at a fire-fighting air  
291 force base in Michigan, USA (lowest detected 8,000 ng/L) [32]. However, the elevated PFOS

292 concentrations in this study are greater than those found in the Tennessee River in Alabama  
293 below a manufacturing facility (highest detected 144 ng/L) [33] and in most freshwaters sampled  
294 in Korea (8 – 651 ng/L) [30]. The PFOS concentrations in the Conasauga River above the LAS,  
295 but not in the elevated levels below, are generally in the range of concentrations found in  
296 freshwaters of New York State and Michigan (range 2-5 ng/L, max 29 ng/L) [34], and would  
297 appear to be background levels. The highest concentration of PFOA (1150 ng/L) in the  
298 Conasauga River is higher than concentrations reported in the Tennessee River (max 598 ng/L)  
299 [33], in the range of the accidental fire-fighting foam release in Canada detected within the first 3  
300 days (mean 2859 ng/L, range 11 – 11300 ng/L) [31], but below the concentrations in  
301 groundwater at the fire-fighting air force base in Michigan (lowest detected 8000 ng/L) [32]. The  
302 PFOA concentrations in the Conasauga River are also generally higher than the majority of  
303 PFOA concentrations measured in rivers of Japan (0.1 – 456 ng/L) [35] and in the Great Lakes  
304 (15 -70 ng/L) [36]. The concentrations of the other PFCs, including PFDA, PFNA, PFUA, and  
305 PFOSA, in the Conasauga River may also be some of the highest reported. There is little  
306 information on the concentrations of these chemicals in waters, but the few data available  
307 suggest that the concentrations reported here are elevated [5, 18, 23, 30].

308 Concentrations of PFCs in the Altamaha River estuary are in similar range to those  
309 reported for estuarine and marine waters outside heavy industrialized areas [5, 24, 30]. Higher  
310 concentrations of PFOS (12.7- 24.4 ng/L) and PFOA (154.3 – 192.0 ng/L) have been measured  
311 in the heavily industrialized area of Tokyo Bay, Japan [23]. In the mid Atlantic Ocean that  
312 drains the Altamaha River, concentrations of PFOS (0.038 – 0.073 ng/L) and PFOA (0.10 – 0.15  
313 ng/L) were found at lower levels compared to the Altamaha River estuary [23], which may be a  
314 result of their decreased solubility and/or their possible transport via ocean currents, but may  
315 suggest that this river is a source of PFC contamination to the Georgia coast. These results would  
316 indicate a potential correlation with manufacturing and industrial activity and PFC inputs. Based  
317 on the available PFC concentration data, the Altamaha River appears to deliver PFCs to oceans

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

#### 325 *Potential sources*

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

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

350 To assess possible sources, the ratio of the concentrations of PFOS to PFOA was  
351 calculated in the waters of Georgia. In the Conasauga River, all locations showed a ratio less  
352 than 1.0, indicating PFOA was at higher concentrations than PFOS. PFOS to PFOA ratios of <  
353 1.0 were found in six different WWTP effluents from New York State and approximately half of  
354 the effluents in a limited survey of WWTPs in the United States, including one from the  
355 southeast [18, 37]. Ratios of PFOS to PFOA greater than 1.0 have been found in WWTP  
356 effluent from Columbus, Georgia, and Decatur, Alabama [42], which indicates that  
357 fluorochemical sources and the WWTP process used in each location must be taken into account  
358 when identifying potential PFC sources. The PFOS to PFOA ratios at all sites in the Altamaha  
359 River were near 1.0, suggesting that other possible sources besides WWTP effluent could be the  
360 cause of the PFC contamination in this river.

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

370 alcohols and sulfonamides have been detected in the troposphere above Georgia indicating that  
371 these compounds are used and likely heavily released in this region [16].

372 *Hazard assessment of PFOS exposure to aquatic species*

373 An evaluation of the ecological risk to aquatic animals from PFOS exposure was  
374 performed in this study as described by Rostkowski et al. [30]. Measured PFOS water  
375 concentrations in the Conasauga and Altamaha Rivers were compared with water-quality values  
376 (i.e., guidelines) that are protective of aquatic organisms (as determined in [44]). There are no  
377 current guidelines specifically derived for saltwater, but guideline values have been developed  
378 following the procedures outlined in the U.S. Environmental Protection Agency Great Lakes  
379 Initiative [45] and based on results from toxicity testing with freshwater organisms [44]. The  
380 hazard assessment was determined by comparing PFOS concentrations to these protective values  
381 (Figure 2A). None of the PFOS concentrations exceeded threshold values of toxicity but this  
382 comparison represents a conservative measure of risk to most aquatic organisms.

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

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

396 conservative, possibly by as much as 50 to 100 fold [30], depending on the true distribution of  
397 sensitivities among organisms as well as any differences in sensitivities between freshwater and  
398 saltwater organisms. Furthermore, the avian wildlife threshold value assumes that the targeted  
399 wildlife will stay in the area where the concentration of PFOS was determined, and would have  
400 eaten sufficient dietary prey in this area to result in a steady state diet. This potentially is true for  
401 some species, but it is unlikely that many large piscivorous birds would remain in only one area.  
402 To reduce the uncertainty of this avian wildlife hazard assessment, PFOS concentrations should  
403 be measured in the tissues of birds, such as the liver, blood, or eggs, which then could be  
404 compared to toxicity reference values (TRVs) calculated for birds [46].

405         The higher presence of PFOA as well as the elevated occurrence of several other PFCs at  
406 several sites (i.e., in the Conasauga River) would indicate that these compounds should be  
407 included in the hazard assessment. Currently, there are no water-quality values that are available  
408 for PFOA or any other PFC besides PFOS. A conservative estimate for the potential risk from  
409 exposure to all PFCs can be made assuming that the toxic potencies of all compounds are equal.  
410 Using this conservative approach, the sum of the mean concentration for each PFC indicated that  
411 all of the Conasauga River sites exceeded the avian wildlife value, some by more than 35 fold  
412 (Figure 2B). None of the Altamaha River sites exceeded the avian wildlife or chronic aquatic  
413 species guidelines. Sites CR3 and CR4 in the Conasauga River also exceeded the aquatic  
414 chronic water guideline; however, this hazard assessment for aquatic species and wildlife must  
415 be interpreted with extreme caution. First, the water guidelines we are using for comparison  
416 were developed from one chemical, PFOS, and as mentioned above are probably overly  
417 conservative (50 to 100 fold). Also, many perfluorinated chemicals bioaccumulate less into  
418 biota compared with PFOS, which will underestimate this hazard estimation for avian wildlife.  
419 Furthermore, there is little information on the toxic potency of other PFCs besides PFOS and  
420 PFOA, with several PFCs having been shown to be less toxic in comparison to PFOS [12-13].  
421 Given the decline in fish diversity, some of which are endangered and threatened, and a shift to

422 more benthic dwelling fishes in the Conasauga River [47], the potential historical and current  
423 elevated PFC concentrations is a cause of concern in this river, which may have potentially  
424 played a role, along with other factors (e.g., habitat degradation), in this change in the fish  
425 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)	$^{13}\text{C}_4$ – PFOA (417/ 372), (417/ 169)	$^{13}\text{C}_2$ – PFOA (415/ 370), (415/ 169)
PFOS (perfluorooctanesulfonate) (499/ 99), (499/ 80)	$^{13}\text{C}_4$ – PFOS (503/ 99), (503/ 80), (503/ 131)	$^{18}\text{O}_2$ – PFOS (503/ 103), (503/ 84)
PFNA (perfluorononoic acid) (463/ 419), (463/ 169)	$^{13}\text{C}_5$ – PFNA (468/ 423), (468/ 169)	$^{13}\text{C}_2$ - PFNA (465/ 420), (465/ 169)
PFDA (perfluorodecanoic acid) (513/ 269), (513/ 469)	$^{13}\text{C}_2$ – PFDA (515/ 269), (515/ 470)	$^{13}\text{C}_2$ - PFNA (465/ 420), (465/ 169)
PFUA (perfluoroundecanoic acid) (563/ 519), (563/ 169)	$^{13}\text{C}_2$ – PFDA (515/ 269), (515/ 470)	$^{13}\text{C}_2$ - PFDoA (615/ 570), (615/ 169)
PFDoA (perfluorododecanoic acid) (613/ 569), (613/ 169)	$^{13}\text{C}_2$ – PFDA (515/ 269), (515/ 470)	$^{13}\text{C}_2$ - 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)	$^{13}\text{C}_2$ – FTUCAs ( 6:2 (359/294)) , (dodecenoic acid; 10:2) (559/ 494))	$^{13}\text{C}_2$ – FTUCA (8:2; decenoic acid ) (459/ 394)

**Table 2.** Concentrations (ng/L; mean  $\pm$  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 <sup>a</sup>	PFNA <sup>a</sup>	PFOS <sup>a</sup>	PFDA <sup>a</sup>	PFUA <sup>a</sup>	PFOSA <sup>a</sup>	$\Sigma$ PFC <sup>b</sup>
CR1	5	< 0.001	32.4 $\pm$ 4.9 (21.5 - 46.7)	32.8 $\pm$ 11.8 (12.3 - 75.4)	6.0 $\pm$ 1.9 (2.3 - 12.8)	11.6 $\pm$ 4.1 (3.74 - 27.5)	2.5 <sup>c</sup>	74.9 $\pm$ 11.7 (10.7 - 102.4)	160.2
CR2	5	< 0.001	252.9 $\pm$ 14.2 (226.5 - 300.8)	201.6 $\pm$ 21.1 (136.2 - 247.8)	191.5 $\pm$ 14.5 (164.0 - 244.5)	72.4 $\pm$ 8.7 (47.4 - 97.1)	<0.1	161.7 $\pm$ 8.5 (146.7 - 187.4)	1000.9
CR3	5	< 0.001	480.1 $\pm$ 21.0 (448.3 - 559.4)	368.8 $\pm$ 31.9 (280.1 - 455.8)	318.3 $\pm$ 18.8 (262.2 - 367.9)	131.3 $\pm$ 8.5 (113.1 - 159.6)	58.0 $\pm$ 13.9 (28.7 - 94.2)	282.5 $\pm$ 32.7 (223.6 - 419.8)	1639.0
CR4	5	< 0.001	1150.0 $\pm$ 15.9 (1112.0 - 1284.7)	284.2 $\pm$ 34.9 (190.4 - 366.4)	1.0 $\pm$ 0.8 (0.2 - 3.1)	30.1 $\pm$ 1.9 (24.8 - 35.5)	99.2 $\pm$ 6.3 (81.9 - 117.2)	212.1 $\pm$ 17.8 (154.0 - 258.5)	1776.6
AR1	3	0.005	3.0 $\pm$ 0.1	0.5 <sup>c</sup>	2.6 $\pm$ 0.2	0.14 <sup>c</sup>	<0.1	—	6.32
AR2	3	0.07	3.1 $\pm$ 0.2	0.2 <sup>c</sup>	2.7 $\pm$ 0.1	<0.1	<0.1	—	5.99
AR3	3	0.10	3.1 $\pm$ 0.3	<0.6	2.6 $\pm$ 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

<sup>a</sup> PFOA = perfluorooctanoic acid; PFNA = perfluorononanoic acid; PFOS = perfluorooctane sulfonate; PFDA = perfluorodecanoic acid; PFUA = perfluoroundecanoic acid; PFOSA = perfluorooctane sulfonamide.

<sup>b</sup>  $\Sigma$ PFC = sum of the mean concentration for each PFC analyzed at that site

<sup>c</sup> Detected in one sample

Missing values indicate the analyte was not targeted

1 **Figure Legend**

2

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

6

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

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