Bulletin of Environmental Contamination and Toxicology (2021) 107:868–875
https://doi.org/10.1007/s00128-021-03365-7

Influence of Water Resource Recovery Facility Effluents on the Presence of Selected Trace Organic Contaminants (TOrCs) in the Reedy River, South Carolina

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Received: 22 February 2021 / Accepted: 23 August 2021 / Published online: 15 October 2021

Abstract

Wastewater reclamation facilities are known sources of emerging contaminants associated with human health and sanitation. This study evaluated the contribution of trace organic contaminants to a previously unmonitored river by water resource reclamation facilities. Six sampling events were conducted on the Reedy River in South Carolina. Sampling locations included sites upstream and downstream of two WRRFs located on the river to examine potential contributions under drought conditions where WRRF effluents comprise a large proportion of total stream flow. Five target analytes were monitored including atrazine, carbamazepine, 17β-estradiol, perfluorooctanoic acid, and sulfamethoxazole. On a mass basis, the WRRFs contributed additional loadings of carbamazepine ranging from 5.4 g/d to 7.2 g/d (mean: 6.3 ± 0.4 g/d), PFOA ranging from 8.6 to 31.9 g/d (mean: 20.0 ± 4.9), and sulfamethoxazole ranging from 49.4 g/d to 75.1 g/d (mean: 62.1 ± 4.8). 17β-estradiol was detected once and atrazine was not detected.

Keywords Atrazine · Carbamazepine · Sulfamethoxazole · PFOA · WRRF

Effluents from Water Resource Recovery Facilities (WRRF) are potential sources of complex mixtures of chemicals in receiving waters (Neale et al. 2017). Pharmaceuticals, personal care products, and other organic contaminants have been detected in surface waters receiving WRRF effluents for years (Bradley et al. 2017; Kolpin et al. 2002; Glassmeyer et al. 2017; Fernandez et al. 2014; Furlong et al. 2017). These contaminants are sometimes referred to as trace organic contaminants (TOrCs) due to their low concentrations and carbon-based molecular structures. The presence of TOrCs in both raw and treated wastewater and their removal effectiveness by different WRRF treatment methods are active topics of research (Grandclement et al. 2017) given that many TOrCs are not removed to non-detectable levels by conventional wastewater treatment methods. The potential ecological impacts of many TOrCs are not well known due to a lack of toxicity data for individual TOrCs as well as complex mixtures. This study describes the contributions of WRRFs to the export of five TOrCs into the Reedy River, located in South Carolina (USA).

The TOrCs targeted in this study included a herbicide (atrazine), a hormone (17β-estradiol), two pharmaceuticals (carbamazepine and sulfamethoxazole), and a perfluoroalkyl substance (perfluorooctanoic acid, PFOA). Atrazine is a widely used herbicide in urbanized and agricultural environments. It has a water solubility of 33 mg/L and a log K_{ow} of 2.61 (Shaner 2014), indicating a propensity for transport in the dissolved phase. Wilson and Boman (2011) reported atrazine in 87% of samples collected weekly from an urbanized watershed in southern Florida over a three-year period. Surface water contamination with atrazine may occur through stormwater runoff and groundwater infiltration directly into streams or through WRRFs that collect surface runoff water in addition to municipal waste streams.

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Studies have reported that atrazine may potentially act as an endocrine disruptor in aquatic organisms (de Souza et al. 2020).

Hormones and pharmaceuticals released into wastewater streams via excretion or improper disposal may enter surface waters through discharges of treated effluents (Batt et al. 2015). Carbamazepine is a commonly prescribed anticonvulsant with a water solubility of 17.7 mg/L and log K_{ow} of 2.45 (Abdel-Mottaleb and Wilson 2019). 17β-estradiol is a hormone that is excreted naturally from humans and other mammals. It is also a prescribed medication where hormone replacement therapy is needed. 17β-estradiol has a water solubility of approximately 12 mg/L and Log K_{ow} of 4.0 (de Mes et al. 2005). Sulfamethoxazole is a commonly prescribed antibiotic with a water solubility of 610 mg/L and Log K_{ow} of 0.89 (Abdel-Mottaleb 2019). These pharmaceuticals, as well as many others, have been commonly detected in WRRF effluents (Furlong et al. 2017, Bradley et al. 2017; Kolpin et al. 2002; Glassmeyer et al. 2017; Fernandez et al. 2014) and may negatively impact aquatic resources and human health (Ebele et al. 2017; Richmond et al. 2017). Furthermore, given the current state of knowledge, it is possible that laboratory studies may underestimate the environmental effects of pharmaceuticals in general (Ebele et al. 2017; Richmond et al. 2017).

PFOA is a legacy contaminant belonging to a class of "forever chemicals" called per- and polyfluoroalkyl substances (PFAS). These chemicals are very persistent and have been used for a variety of purposes including as fire retardants, non-stick coatings, textile material protectants, and manufacturing of many different consumer products. PFOA exists in its ionized acid form at environmental pHs, having a water solubility of 3300 mg/L (Abdel-Mottaleb and Wilson 2019). The health impacts of PFAS exposure are currently being investigated and potentially include cancer and developmental, immune, and thyroid effects in humans (USEPA 2019).

The Reedy River is a historically impaired yet under-characterized freshwater stream in the Piedmont region of South Carolina with great aesthetic, recreational, and consequently economic importance (City of Greenville 2020). The Greenville area became the textile center of the southern US between the early 1900s and 1970s, having up to 18 textile mills and 2 dye/finishing plants located close to the Reedy and within 4.8 km of downtown Greenville (Ferncreek Productions 2019). The textile-rich, pre-Clean Water Act (CWA) history of the Reedy River meant it regularly received direct wastewater discharges from a rapidly expanding industrial and municipal population (FORR 2019). Although CWA regulations gradually improved the Reedy River's water quality, the negative impacts of industrial discharges were still observed well into the 1980s when the color of the river would change daily as a reflection of industrial activity (FORR 2019). Previous studies have shown a loss of nearly all fish and macroinvertebrate life 55 km downstream of a 1996 Colonial Petroleum Pipeline rupture (Kubach et al. 2011), elevated levels of metals and polycyclic aromatic hydrocarbons (PAHs) in sediments within the Lake Conestee tributary impoundment (Otter et al. 2012; Schreiber et al. 2006), and elevated concentrations of primordial radionuclides in river sediments (Powell et al. 2007).

WRRF outfalls are usually located on higher-order, non-wadeable streams where effluents may be diluted to minimize impacts on aquatic resources (Bradley et al. 2016). The Reedy River is classified as a wadeable stream (<10 m wide and <1 m deep at baseflow) (Bradley et al. 2016). Bradley et al. 2016 indicated that the majority of previous monitoring for pharmaceuticals in streams associated with WRRFs was conducted on higher-order streams, and that more information was needed for wadeable streams. They conducted a limited sampling study on the Reedy River as well as 58 other small streams in the Piedmont region of South Carolina. Of the compounds analyzed in the current study, they semi-quantifiably detected carbamazepine and sulfamethoxazole at concentrations of <11 ng/L and <26 ng/L, respectively. They also detected atrazine at concentrations up to 19.4 ng/L. Notably, their sampling site on the Reedy River was located upstream of two WRRFs that discharge treated effluents directly into the Reedy River. Both facilities use a modified activated sludge process called Biological Phosphorus Removal (BPR) to reduce nutrient loadings into the Reedy. The most downstream WRRF (LR-WRRF) receives flow from a smaller municipal population and fewer hospitals, and consequently contributes less flow to the river relative to the upstream WRRF (MR-WRRF) (ReWa 2020). In addition to the one study focused on pharmaceuticals in the Reedy River, Hur et al. (2007) reported up to a 210% increase in dissolved organic matter due to WRRF discharges into the river. Other researchers reported a four-fold increase in bile estrogenic activity in bluegill fish (*Lepomis macrochirus*) (Truman and van den Hurk, 2009), which may have been induced by estrogenic TOrCs.

Given the limited monitoring on the Reedy River along with increasing knowledge of potential nontarget ecological effects associated with commonly reported TOrCs in WRRF effluents, the objectives of this study were to assess whether the selected TOrCs were present in the river upstream of the WRRFs as observed by Bradley et al. (2016), and to characterize the contribution of the downstream WRRFs to their presence in the Reedy. This is also the first study to report PFOA concentrations in the Reedy River.

Materials and Methods

This study was conducted on the Reedy River located in South Carolina. Originating north of Travelers Rest, SC, the river flows for approximately 105 km through Greenville and Laurens Counties until its confluence with the Saluda River at Lake Greenwood. The South Carolina Department of Health and Environmental Control (SCDHEC) officially classifies the Reedy watershed into two divisions (Upper Reedy, 0305010904; Lower Reedy, 0305010906), though it is generally considered one watershed and will be referred to as such for this study (2019). The watershed has a total area of 711.8 km^2 which includes 8.2 km^2 of lakes and 1132 km of streams. According to SCDHEC's Listing of Impaired Waters, multiple sites within the watershed are currently impaired due to exceedances of South Carolina Water Quality Standards for *Escherichia coli* and total nitrogen, as well as impaired macroinvertebrate communities (2018).

Six sites were identified based on practical accessibility and study goals (Fig. 1). Site 1 was located in the headwaters of the Reedy River, upstream of the city of Greenville and 21.4 km upstream of site 2. Sites 2 and 3 were respectively located 0.28 km upstream and 0.17 km downstream of the Mauldin Road WRRF in Mauldin, SC. Site 3 was 0.45 km downstream of Site 2 and 14.6 km upstream of Site 4. Site 4 was located 3.8 km upstream of the Lower Reedy WRRF and Site 5 was 0.3 km downstream of the same facility located in Simpsonville, SC. Site 6 was located in Hickory Tavern, SC and was the southernmost downstream location (33.7 km downstream of site 5). Two United States Geological Survey (USGS) monitoring stations (located in Greenville and Fork Shoals) were available from which to obtain flow data on sampling days (Fig. 1).

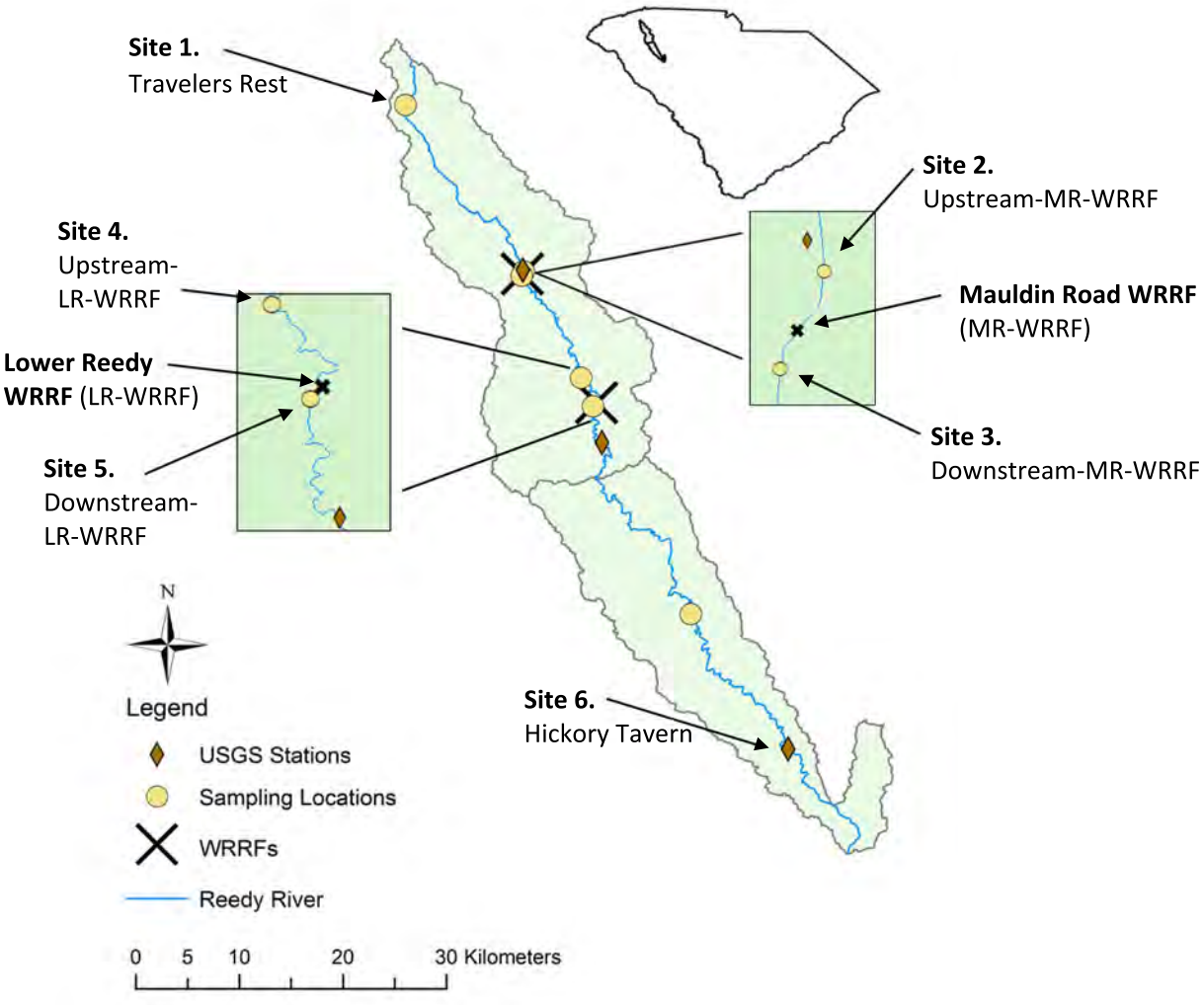

Fig. 1 The Reedy River watershed located in the Piedmont region of South Carolina, locations of water resource recovery facilities (WRRF), and sampling site locations

Six sampling events were conducted on the Reedy River between August and October of 2019. Sampling events progressed from the most downstream site to the uppermost upstream site on each sampling day. The shallow depth of the Reedy River allowed for wading and direct grab sampling of surface water via bottle submersion. Dissolved oxygen (DO), pH, electrical conductivity (EC), and turbidity measurements were taken *in situ* using portable equipment (Denver Instrument UP-25 pH Meter; YSI Inc. Model 50B DO Meter; Hanna HI 98,303; HF Scientific 20,000 MicroTPW Turbidimeter) that was calibrated (per manufacturer recommendations) before going into the field. Single samples were collected at each of the first five sites during each sampling event. At Site 1, the most upstream location, in addition to the sample for analysis, samples were also collected for use as matrix spikes (MS), matrix spike duplicates (MSD), and field duplicates (FD) for quality control analysis during each sampling event. Field blanks prepared from reagent grade water were also used to measure potential contamination during the sampling events. The field blanks were poured in the field and carried in the cooler with the samples throughout each event. All samples were collected in 1-L amber glass bottles, chilled to 4°C, and extracted within two days via solid phase extraction following methods based on those described by Vanderford and Snyder 2006.

A 500 mL aliquot of each sample from the first sampling event and a 400 mL aliquot of each sample from all subsequent sampling events was first filtered through a 1.5 µm glass microfiber filter (Whatman 934-AH 1827-090, Whatman Inc., Piscatway, NJ, USA). The filtered samples were adjusted to pH 3 ± 0.05 with 1 M HCl and spiked with a stable isotope-labelled standard (100 µL in the first event and 80 µL in all subsequent events of a 1 ppm solution which included all compounds) as a surrogate for evaluating extraction and analysis uniformity. The isotopically-labelled standards included ATZ-d_5, CBZ-d_{10}, and E2-d_5, $^{13}C_8$-PFOA and $^{13}C_6$-SMX. The deuterated standards were purchased from Cerilliant Co. (Round Rock, TX, USA) and the 13C standards were purchased from Cambridge Isotope Laboratories Inc. (Tewksury, MA, USA), respectively. The isotopically-labelled standards were dissolved in methanol to achieve a concentration of 1 µg mL^{-1} for each chemical. Oasis Hydrophilic-Lipophilic Balance (HLB) cartridges (6 cm^3, 200 mg, Waters, Milford, MA) were preconditioned with 5 mL methyl *tert*-butyl either (MTBE), 5 mL methanol (MeOH), and 5 mL reagent water. Samples were then passed through at a rate of 15 mL/min. The cartridges were then rinsed with 5 mL reagent water and dried under vacuum for 30 min. Cartridges were eluted with 5 mL methanol and 5 mL 10/90 (v/v) MeOH/MTBE. Eluents were then placed in a water bath at 50°C and evaporated with a gentle stream of nitrogen to less than 0.5 mL and brought up to 1 mL with MeOH prior to high-performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS) analysis.

Extracts were analyzed using a Waters Alliance 2695 HPLC (Waters Corp., Milford, MA) coupled to a Micro-Mass Quattro Ultima triple quadrupole mass spectrometer (Micromass UK Limited, Wythenshawe, England) equipped with a Z-spray electrospray ionization (ESI) interface under conditions described by United States Environmental Protection Agency (USEPA) Method 539 for 17β-estradiol (2010) and by Hwang et al. (2019) for all other analytes. Briefly, chromatographic separation for all compounds (except 17β-estradiol and PFOA) was achieved using a Phenomonex Luna C_{18} HPLC column (150 × 4.6 mm, 5 µm). PFOA was separated using an Agilent InfinityLab Poroshell 120 EC-C_{18} LC column (100 × 2.1, 2.7 µm) and 17β-estradiol was separated using an Agilent Eclipse XDB-C_{18} (2.1 × 100 mm, 3.5 µm) analytical column. Atrazine, carbamazepine, and sulfamethoxazole were analysed in multiple reaction monitoring (MRM) mode under ESI-positive conditions while 17β-estradiol and PFOA were analysed by MRM under ESI-negative conditions. All external calibration R^2 values were ≥ 0.99.

Analyte concentrations detected at each location were pooled and the nonparametric Kruskal-Wallis Test (One-Way ANOVA on Ranks) with the Tukey-Kramer HSD *post-hoc* test ($P = 0.05$) was used to identify differences in analyte concentration between sites using the statistical software program JMP (SAS, Cary NC). Load contributions from the two WRRF's was estimated on each sampling day using flow data collected at the USGS stations directly above the MR-WRRF (coordinates: 34.8001183, −82.3651213) and directly below the LR-WRRF (coordinates: 34.652778, −82.297778). Loadings of each TOrC at each site on each sampling date were calculated by multiplying the cumulative flow volume (L) on that day by the concentration (g/L) detected in the samples. Loadings at the upstream location were subtracted from loadings at the downstream location to measure the contribution of the WRRFs to the Reedy.

Mean recoveries (± standard deviation) from the MS and MSD samples (n = 6) were 128.5 ± 25.7% for atrazine, 72.8 ± 9.82% for carbamazepine, 77.1 ± 19.5% for 17β-estradiol, 99.1 ± 10.2% for PFOA, and 113.3 ± 11.5% for sulfamethoxazole. Mean relative percent differences (RPDs) for the MS and MSD were 12.8 ± 9.3% for atrazine, 10.0 ± 8.6% for carbamazepine, 21.4 ± 18.1 for 17β-estradiol, 9.4 ± 7.9% for PFOA, and 3.9 ± 1.7% for sulfamethoxazole. The RPDs for field duplicates collected at the Travelers Rest site was 3.12 ± 1.8% for PFOA, the only analyte detected there. The practical quantitation limit based on the lowest calibration standard (5 ng/mL) for all chemicals was 10 ng/L for the first sampling event and 12.5 ng/L for each subsequent sampling event. None of the analytes were detected in the field blanks.

Result and Discussion

Similar to findings in Hur et al. (2007), the MR-WRRF affected water quality more than the LR-WRRF. Mean pH at the upstream sites (Sites 1 and 2) was 6.29 ± 0.12 which increased to 6.78 ± 0.17 downstream of MR-WRRF (Site 3) and increased again to 6.89 ± 0.15 downstream of the LR-WRRF (Site 5). These nominal increases in pH are likely due to the addition of calcium hydroxide at both facilities to maintain National Pollutant Discharge Elimination System (NPDES) permit compliance of a pH 6.5 minimum.

DO concentrations were consistent at 7.37 ± 0.41 mg/L, 7.24 ± 0.29 mg/L, and 7.28 ± 0.34 mg/L upstream of the MR-WRRF, downstream of the MR-WRRF/upstream of the LR-WRRF, and downstream of the LR-WRRF sites respectively. EC increased from 83.0 ± 19.9 µS/cm to 288 ± 43.6 µS/cm downstream of the MR-WRRF (Site 3) and nominally decreased downstream of the LR-WRRF to 268 ± 47.7 µS/cm (Site 5).

Turbidity was slightly reduced immediately below the MR-WRRF (Site 3) possibly due to dilution from discharge of sand-filtered effluents. In this case mean turbidity nominally decreased from 3.70 ± 1.08 NTU to 2.48 ± 1.27 NTU. Turbidity increased to 6.24 ± 5.60 NTU downstream of the LR-WRRF (Sites 5 and 6), though this was clearly skewed by the tendency of the Hickory Tavern site (Site 6) to have higher turbidity measurements (maximum = 19.95 NTU).

At the uppermost site in Travelers Rest (Site 1), carbamazepine and PFOA were the only TOrCs detected during any sampling event (Fig. 2). All detectable concentrations of carbamazepine were less than the 12.5 ng/L practical quantitation limit of the method. PFOA concentrations ranged from 65 ng/L to 123 ng/L. Likewise, at the upstream-MR-WRRF site (Site 2), concentrations of carbamazepine were detectable but below the practical quantification limit (10/12.5 ng/L) in all of the samples and concentrations of PFOA ranged from 67 ng/L to 163 ng/L in all of the samples collected. This site is close to the one sampled previously by Bradley et al. (2016). In their study they detected carbamazepine and sulfamethoxazole at concentrations below their PQLs of 11 ng/L and 26 ng/L, respectively. Interestingly they did not sample below the WRRFs. Possible sources may have been leaching from on-site septic systems directly into the river or tributaries within the watershed as well as low water tables allowing for exfiltration of municipal wastewater and subsequent movement to the river through groundwater. Within this region, non-septic system wastewater is collected and conveyed via sewer lines to the MR-WRRF. The presence of PFOA was not unexpected due to the fact that PFAS compounds are ubiquitous in the environment due to their use in common consumer products and the history of textiles production in the region.

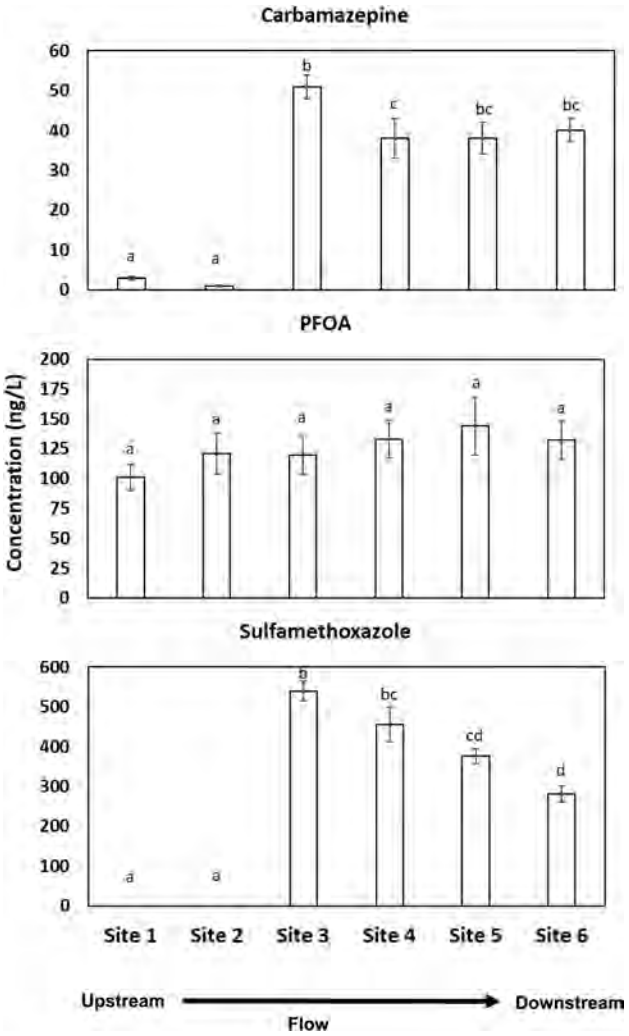

Fig. 2 Average concentrations (ng/L, n = 5) of carbamazepine, perfluorooctanoic acid (PFOA), and sulfamethoxazole at each of the six sampling locations over the length of the Reedy River. Sites: (1) Travelers Rest, (2) MR-WRRF-upstream, (3) MR-WRRF-downstream, (4) LR-WRRF-upstream, (5) LR-WRRF-downstream, and (6) Hickory Tavern. Different letters over the bars indicate significant differences in analyte concentrations between sites as determined by One-Way ANOVA on Ranks (Kruskal-Wallis Test) with Tukey-Kramer HSD post-hoc test ($P = 0.05$)

Concentrations of carbamazepine increased at the Mauldin Road WRRF (MR-WRRF-downstream) downstream site (Site 3), ranging from 43 ng/L to 62 ng/L; while concentrations of PFOA were similar ranging from 68 ng/L to 155 ng/L (Fig. 2). Sulfamethoxazole was also detected at this site during all sampling events, ranging from 438 ng/L to 598 ng/L, indicating a clear source to the Reedy.

Further downstream at the site upstream of the Lower Reedy WRRF (LR-WRRF-upstream, Site 4), concentrations of PFOA and sulfamethoxazole were similar to those at Site

3, ranging from 82 ng/L to 167 ng/L and 280–549 ng/L, respectively (Fig. 2). Concentrations of carbamazepine at this site were lower than at Site 3, ranging from 24 ng/L to 52 ng/L. Carbamazepine concentrations remained similar to the LR-WRRF-upstream concentrations at both the LR-WRRF-downstream (Site 5) and Hickory Tavern (Site 6) locations, ranging from 24 ng/L to 50 ng/L and 29–51 ng/L, respectively (Fig. 2). Likewise, PFOA concentrations were similar to the LR-WRRF-upstream (Site 4) concentrations at both downstream locations, ranging from 74 to 207 at the LW-WRRF-downstream site (Site 5) and 84–172 ng/L at the Hickory Tavern site (Site 6). The similarity of PFOA concentrations at all sampling stations may indicate historical contamination of groundwater that exchanges into the river resulting in a more continuous release. The Greenville area was the center of the textile industry in the southern US from the early 1900s until about the early 1970s, with 18 textile mills and 2 textile finishing plants within a short distance from the Reedy River (Ferncreek Creative 2019). Conversely, concentrations of sulfamethoxazole at the LR-WRRF-downstream site (376 ± 19 ng/L) (Site 5) were statistically similar to those at the upstream site (Site 4) (456 ± 43 ng/L) but were reduced (38% relative to Site 4) further downstream at the Hickory Tavern site (Site 6) (281 ± 20 ng/L) (Fig. 2).

17β-estradiol was only detected once downstream of the LR-WRRF (Site 5). The lack of additional detections may have been the result of the high rate of removal (up to 100.0%) in some biological wastewater treatment systems (Behera et al. 2011). Andersen et al. (2003) reported rapid biodegradation of the natural estrogens 17β-estradiol and estrone in the denitrifying and aerated nitrifying tanks of the activated sludge system in their WRRF. Monitoring of influents and effluents at both WRRFs as well as sediments in the river would yield greater insight into the presence and fate of 17β-estradiol.

Atrazine was not detected in any samples, which is in contrast to Bradley et al. (2016) who detected it close to Site 2 in the current study. Being a pesticide that is applied to the land and not flushed through municipal wastewater collection and treatment systems, the lack of detections may have been a result of it not being used within the watershed at the time or as a result of the drought as discussed below. Within the Piedmont region, atrazine is labelled for use in corn, grain sorghum, and sorghum-sudangrass hybrids (Clemson 2020) with applications typically occurring in the spring and summer. Corn is grown for grain in both Greenville and Laurens Counties, but on a relatively limited basis as compared to other counties (USDA 2017). It is also labelled for use in some types of turfgrass commonly found in golf courses and residential landscapes. Cumulative rainfall during the sampling period was only 12 mm based on the Greenville USGS Station (USGS 2019) which limited surface runoff and groundwater leaching. In all cases, extended sampling throughout additional seasons and sites would yield additional knowledge of the effect of temporal and spatial factors on the presence and concentrations of the contaminants.

On a mass basis, the WRRFs contributed significant amounts of carbamazepine, PFOA, and sulfamethoxazole. During the sampling period, additional loadings of carbamazepine ranged from 5.4 g/d to 7.2 g/d (mean: 6.3 ± 0.4 g/d), PFOA ranged from 8.6 g/d to 31.9 g/d (mean: 20.0 ± 4.9), and sulfamethoxazole loadings ranged from 49.4 g/d to 75.1 g/d (mean: 62.1 ± 4.8). To provide perspective, average loadings upstream of the WRRF's were 0.074 ± 0.024 g/d for carbamazepine and 7.6 ± 1.9 g/d for PFOA, and incalculable for sulfamethoxazole due to the lack of detectable concentrations. These results clearly indicate that the majority of carbamazepine and sulfamethoxazole importation into the Reedy is through the WRRF discharges. However, the WRRFs do not fully account for the carbamazepine given the detectable concentrations in the river upstream.

Contributors to the WRRF's loadings of TOrCs are diverse. In addition to the municipal wastes generated by the general public, pharmaceutical manufacturing and hospitals are major sources of these contaminants in wastewater (Grandclement et al. 2017). Combined, the two WRRFs received regulated wastewater flow from 55 industries (23 – MR-WRRF, 32 – LR-WRRF) and non-regulated flow from seven hospitals (6 – MR-WRRF, 1 – LR-WRRF). A large portion of the total flow/volume of the Reedy River is contributed by the WRRFs, especially during dry periods. For example, during this study the mean recorded flow on sampling days from the USGS Greenville Station (upstream of all WRRFs) was 0.65 ± 0.2 m^3/s, increasing to 2.04 ± 0.4 at the Fork Shoals Station (below the downstream WRRF) (Fig. 1). Throughout the year, flows from the MR-WRRF and the LR-WRRF averaged 0.72 m^3/s and 0.30 m^3/s, respectively (ReWa 2020). Over the sampling period, measured river flow at all three USGS stations decreased by approximately 50% due to the drought. As a result, the relative contributions of the MR-WRRF (and LR-WRRF) to the flow likely increased as previously observed by Hur et al. (2007).

Of the pharmaceuticals, carbamazepine appears to be more persistent than sulfamethoxazole as indicated by a lack of concentration reduction with downstream distance from WRRFs. Regarding potential ecotoxicity, maximum concentrations of carbamazepine ranged from 50 ng/L to 62 ng/L at the sampling sites downstream from the WRRFs. No impacts on aquatic resources would be expected given EC_{50} values of > 1,000,000 ng/L for bacteria, algae, macrophytes, and micro-invertebrates (Blaise et al. 2006). Sulfamethoxazole concentrations ranged from 280 ng/L to 598 ng/L. These concentrations are not likely to harm algal species (EC_{50}'s ranging from 27,000–13,400,000 ng/L, Blaise

et al. 2006, Bialk-Bielinska et al. 2011), macrophytes EC_{50} of 210,000 mg/L for *Lemna minor* L. (Bialk-Bielinska et al. 2011), micro-invertebrates (EC_{50} values of > 100,000 to 250,000,000 ng/L, Kim et al. 2007, Blaise et al. 2006) and fish (EC_{50} > 100,000,000 ng/L for Japanese Medaka (*O. litipes*) (Blaise et al. 2006).

PFOA was more uniformly distributed throughout the monitored section of the river, which is consistent with current consensus of the ubiquity of PFAS compounds in the environment (USEPA 2019) and might be expected given the prominence of the textiles industries in the region years ago. Concentrations ranged from 65 ng/L to 207 ng/L, which is similar to the range of PFOA concentrations (mean 43–46 ng/L, maximum 137–287 ng/L) detected in the Cape Fear River Basin in North Carolina (Nakayama et al. 2007; Sun et al. 2016). These concentrations are much lower than the reported EC_{50} values for invertebrates (181,000,000–672,000,000 ng/L) and fish (205,000,000 ng/L, Danio rerio), indicating low risks of toxicity.

In conclusion, the WRRFs contributed significant amounts of dissolved carbamazepine and sulfamethoxazole to the Reedy River during the monitored season. Their contributions of PFOA were less discernable due to the more cosmopolitan nature of this contaminant, and they contributed very little dissolved estradiol and presumably no dissolved atrazine at least during the monitored period. Given the plethora of potential TOrCs likely discharged into sanitary systems, much more work is needed to characterize potential inputs of these and other chemicals into the Reedy River system and to wholistically evaluate potential environmental risks.

Acknowledgements We graciously acknowledge the National Science Foundation. This project was conducted using standards and supplies left over from a project that was funded by NSF Grant No. CBET-1435522.

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