INFLUENCE OF WATER RESOURCE RECOVERY FACILITY EFFLUENT ON THE PRESENCE OF SELECTED ORGANIC CONTAMINANTS IN THE REEDY RIVER, SOUTH CAROLINA

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Abstract
Organic contaminants have been detected in surface waters globally and water resource reclamation facility (WRRF) effluents represent a potential source. Six sampling events were conducted on the Reedy River in the Piedmont region of South Carolina between August and October of 2019, during a period of moderate-to-severe drought. Sampling locations included sites upstream and downstream of two WRRFs located on the river to examine potential contributions under worst-case conditions where WRRF effluents make up a large proportion of total stream flow. For this exploratory organic contaminant characterization, six target analytes were selected including acetaminophen, atrazine, carbamazepine, 17β-estradiol, perfluorooctanoic acid (PFOA), and sulfamethoxazole. Of these, PFOA was detected most frequently followed by carbamazepine and sulfamethoxazole, respectively. Acetaminophen and 17β-estradiol were each detected once, and atrazine was never detected. Significant increases in carbamazepine and sulfamethoxazole were detected downstream of WRRF effluent influence, while PFOA was detected consistently at each site.

Introduction

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). Originating north of Travelers Rest, the river flows for approximately 105 km through Greenville and Laurens counties until its confluence with the Saluda River at Lake Greenwood. The state's environmental regulatory agency, 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. The watershed has a total area of 711.8 km^2 which includes 8.2 km^2 of lake and 1131.7 km of stream. According to SCDHEC's Listing of Impaired Waters, multiple sites in the watershed are currently impaired due to exceedances of South Carolina Water Quality Standards for the *E. coli*, macroinvertebrate, and total nitrogen parameters (2018).

The textile-rich, pre-Clean Water Act (CWA) history of the Reedy River meant it regularly received direct wastewater discharge from a rapidly expanding industrial and municipal population (FORR, 2019). Although the CWA gradually improved the Reedy River's water quality, the negative impact of industrial discharges was still observed well into the 1980s when the river would change color 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 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). Growth model predictions for regional urbanization effects through 2030 show potential for increased non-point source discharges and stormwater runoff resulting in increased inputs of nutrients and other contaminants (Privette et al. 2015).

Organic contaminants have been identified in surface water for years (Bradley et al. 2017; Kolpin et al. 2002; Glassmeyer et al. 2017), and their presence in both raw and treated wastewater and the removal effectiveness of WRRF treatment methods are continually being examined (Grandclement et al. 2017). With increasing knowledge of potential additive and synergistic effects due to complex mixtures of these chemicals in surface waters, their detection and characterization is important for assessing exposures within the Reedy River. Six organic contaminants (Table 1) were targeted in this study, including: an herbicide (atrazine), a hormone (17β-estradiol), three

pharmaceuticals (acetaminophen, carbamazepine, sulfamethoxazole), and a perfluoroalkyl substance (perfluorooctanoic acid (PFOA)).

Table 1 Names and attributes of target organic contaminants for characterization in the Reedy River. Values obtained from PubChem

Analyte	Group	Mol. Weight (g/mol)	CAS Number	Log K_{ow}	pK_a	Water Solubility (mg/L)
Acetaminophen	Pharmaceutical	151.16	103-90-2	0.46	9.38	14,000[1]
Atrazine	Herbicide	215.68	1912-24-9	2.61	1.60	33[1]
Carbamazepine	Pharmaceutical	236.27	298-46-4	2.45	13.9	18[1]
17β-Estradiol	Hormone	272.38	50-28-2	4.01	10.7	3.90[2]
Perfluorooctanoic acid (PFOA)	PFAS	414.07	335-67-1	4.81	1.30	3300[1]
Sulfamethoxazole	Pharmaceutical	253.28	723-46-6	0.89	1.6, 5.7	610[3]

[1]At 25°C, [2]At 27°C, [3]At 37°C

Atrazine is a widely used herbicide in urbanized and agricultural areas that has potential to enter streams through stormwater runoff and groundwater infiltration. Experimental studies have reported the potential of atrazine to act as an endocrine disruptor in aquatic organisms (de Souza et al. 2020). Hormones and pharmaceuticals released to wastewater streams via excretion or disposal may enter surface waters through treated effluent discharges (Batt et al. 2015). Acetaminophen (an analgesic), carbamazepine (an anticonvulsant), 17β-estradiol (a hormone), and sulfamethoxazole (an antibiotic) may negatively affect the aquatic environment and human health and 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 have been used for a variety of purposes including as fire retardants, non-stick coatings, textile protectants, and manufacturing of many different consumer products. The health impacts of PFAS exposure are currently being investigated, and broadly include cancer, developmental, immune, and thyroid effects in humans (USEPA 2019). A summary of chemical properties is shown in Table 1.

Two water resource reclamation facilities (WRRFs) discharge treated effluent directly into the Reedy River. WRRF effluents represent a potential source of complex mixes of chemicals in receiving waters (Neale et al. 2017). A previous study examining the influence of the WRRFs on the river reported up to a 210% increase in dissolved organic matter (DOM, Hur et al. 2007). Other researchers reported a four-fold increase in bile estrogenic activity in bluegill fish (*Lepomis macrochirus*) (Truman and van den Hurk, 2009). No studies have been published on the presence of herbicides, pharmaceuticals, or PFAS the river. To begin to compensate for this lack of data, this study aimed to provide an initial characterization of these contaminants in the Reedy River.

Materials and Methods

Six sampling events were conducted on the Reedy River between August and October of 2019. Six sites were identified based on practical accessibility and study goals (Fig. 1). Three USGS Monitoring Stations (located in Greenville, Fork Shoals, and Ware Shoals) were available from which to obtain flow data on sampling days (Fig. 1). 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 98303; HF Scientific 20000 MicroTPW Turbidimeter). Single field samples were collected at each of the first five sites. In addition to the sample for analysis, samples were also collected at the Travelers Rest location (uppermost site) for use as matrix spike (MS), matrix spike duplicate (MSD), and field duplicate (FD) samples 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.

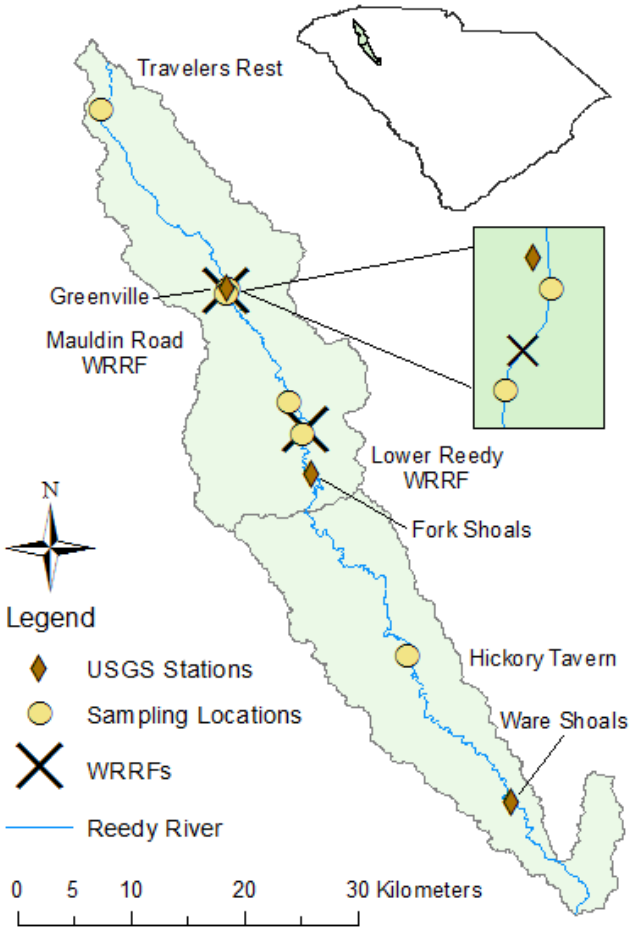

Fig. 1 The Reedy River watershed located in the Piedmont region of South Carolina. The six sampling points shown include Travelers Rest, locations upstream and downstream of the two water resource reclamation facilities (WRRFs) in Greenville and Simpsonville, and a location further downstream in Hickory Tavern. Figure generated in ArcMap 10.5.1

Samples were first filtered through 1.5 µm glass microfiber filters (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 (including all compounds) as a surrogate for evaluating extraction and analysis uniformity. 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 MicroMass 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 x 4.6 mm, 5 µm). PFOA was separated using an Agilent InfinityLab Poroshell 120 EC-C_{18} LC column (100 x 2.1, 2.7 µm) and 17β-estradiol was separated using an Agilent Eclipse XDB-C_{18} (2.1 x 100 mm, 3.5 µm) analytical column. Acetaminophen, 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.

All statistical analyses were performed using the statistical software program R. The nonparametric Kruskal-Wallis and Wilcoxon Rank Sum tests were chosen due to the non-normally distributed nature of environmental contaminants to examine differences in analyte concentration between sites. Simple linear regressions were used to correlate river flow at all three USGS Monitoring Stations with time, and river flow at the Fork Shoals Station with detected analyte concentrations at the LR-WRRF downstream sampling location. Analyte detections at concentrations below the lowest calibration standard (practical quantitation limits, PQL) were considered as positive detections for detection frequency calculations. However, when comparing concentrations between sites, these values (along with non-detects (NDs)) were replaced with values that were 20% of the PQL. In the rare event that an analyte was detected in the field blanks, analyte concentrations in samples that were less than 5x the concentration in the blank concentrations were removed for statistical analysis. Of all blanks (n=12), one carbamazepine, one PFOA, and one sulfamethoxazole blank detection resulted in removal of field sample concentration values.

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. Acetaminophen was not recovered in any of these samples. Mean MS and MSD relative percent differences (RPDs) 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. Mean Travelers Rest and FD RPD for PFOA was 3.12 ± 1.8%.

Results and Discussion

Similar to findings in Hur et al. (2007), the MR-WRRF appeared to impact water quality more than the LR-WRRF. Mean pH at the upstream sites was 6.29 ± 0.12 which increased to 6.78 ± 0.17 downstream of MR-WRRF and increased again to 6.89 ± 0.15 downstream of the LR-WRRF. 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, 7.24 ± 0.29, and 7.28 ± 0.34 mg/L at upstream, downstream of the MR-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 and nominally decreased downstream of the LR-WRRF to 268 ± 47.7 µS/cm. Turbidity was slightly improved immediately below the MR-WRRF possibly due to a dilution effect from discharge of sand-filtered effluents. In this case mean turbidity decreased to 2.48 ± 1.27 NTU from 3.70 ± 1.08 NTU. Turbidity then increased to 6.24 ± 5.60 NTU downstream of the LR-WRRF, though this was clearly skewed by the tendency of the Hickory Tavern site to have higher turbidity measurements (maximum = 19.95 NTU).

Over the sampled length of the river, PFOA was detected most frequently at 100%, followed by carbamazepine at 97.2% and sulfamethoxazole at 69.4% (Table1). Carbamazepine was detected at concentrations below the PQL at the Travelers Rest reference site and upstream of the uppermost WRRF. Possible sources may have been septic systems within the watershed as well as low water tables allowing for municipal wastewater exfiltration and subsequent movement to the river through groundwater. Within this region, non-septic system wastewater is collected and conveyed via underground sewer lines to the MR-WRRF. Sulfamethoxazole detections occurred almost exclusively downstream of the WRRFs except for one upstream detection that was removed due to detection in a blank for that sampling event. Both acetaminophen and 17β-estradiol were detected in only one sample (2.8%). Acetaminophen was detected upstream of the WRRFs and 17β-estradiol was detected downstream of the LR-WRRF. The lack of additional acetaminophen and 17β-estradiol detections may have been the result of the high rate of removal (up to 99.9% and 100.0%, respectively) in some biological wastewater treatment systems (Behera et al. 2011), though influent and effluent sampling and analysis of both WRRFs would yield greater insight. Atrazine was not detected in any samples. 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 or as a result of the drought. 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). 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.

Table 2 Detection frequencies, ranges, and median concentrations for all analytes overall (n = 6 sites), upstream of WRRF influence (n = 2 sites upstream of the MR-WRRF), and downstream of WRRF influence (n = 4 sites downstream of the MR-WRRF)

	Detection Frequency (%)	Range (ng/L)	Median (ng/L)
Overall			
Acetaminophen	2.8	<12.5 - 82	<12.5
Atrazine	0	<12.5	<12.5
Carbamazepine	97.2	<12.5 - 62	36
17β-Estradiol	2.8	<12.5 - 59	<12.5
PFOA	100	65 - 207	132
Sulfamethoxazole	69.4	<12.5 - 598	317
Upstream			
Acetaminophen	8.3	<12.5 - 82	<12.5
Atrazine	0	<12.5	<12.5
Carbamazepine	91.7	<12.5	<12.5
17β-Estradiol	0	<12.5	<12.5
PFOA	100	65 - 163	119.5
Sulfamethoxazole	0	<12.5	<12.5
Downstream			
Acetaminophen	0	<12.5	<12.5
Atrazine	0	<12.5	<12.5
Carbamazepine	100	24 - 62	42.5
17β-Estradiol	4.2	<12.5 - 59	<12.5
PFOA	100	68 - 207	148
Sulfamethoxazole	100	198 - 598	416

For contaminants detected in the river, Kruskal-Wallis tests revealed significant differences between sampling locations for carbamazepine ($\chi^2 = 24.3$, $p = 0.0002$) and sulfamethoxazole ($\chi^2 = 25.9$, $p = 0.00009$), but not PFOA ($\chi^2 = 4.15$, $p = 0.5$). Further analysis with the Wilcoxon Rank Sum tests indicated significant increases in carbamazepine ($W = 0$, $p = 0.007$) and sulfamethoxazole ($W = 0$, $p = 0.007$) downstream of MR-WRRF as compared to the sampling site immediately upstream (Fig. 2). The LR-WRRF effluent did not seem to contribute additional contaminants to the river (i.e. concentrations did not increase significantly), which may be associated with the fact that the LR-WRRF receives flow from a smaller municipal population and fewer hospitals; and consequently contributes less flow to the river relative to the MR-WRRF (ReWa 2019). Carbamazepine concentrations decreased following the initial spike downstream of the MR-WRRF but remained steady over the remaining sampled distance. Sulfamethoxazole concentrations progressively decreased with distance from the MR-WRRF. From downstream of the MR-WRRF to Hickory Tavern, carbamazepine concentrations decreased by 20% ($W = 31.5$, $p = 0.04$), while sulfamethoxazole concentrations decreased by 50% ($W = 25$, $p = 0.008$), which may reflect relatively higher rates of environmental degradation of sulfamethoxazole as compared to carbamazepine (Baena-Nogueras et al. 2017). Applying this scenario to the Reedy River is speculative and requires further study to better characterize fate processes. Though there were no statistically significant differences in concentrations of PFOA between sites, the consistent presence of the chemical over the sampled section of the river agrees with the current consensus of the environmental ubiquity of PFAS (USEPA 2019), and the range of detected concentrations corresponds with previously reported values in the Cape Fear River Basin in North Carolina (Nakayama et al. 2007; Sun et al. 2016).

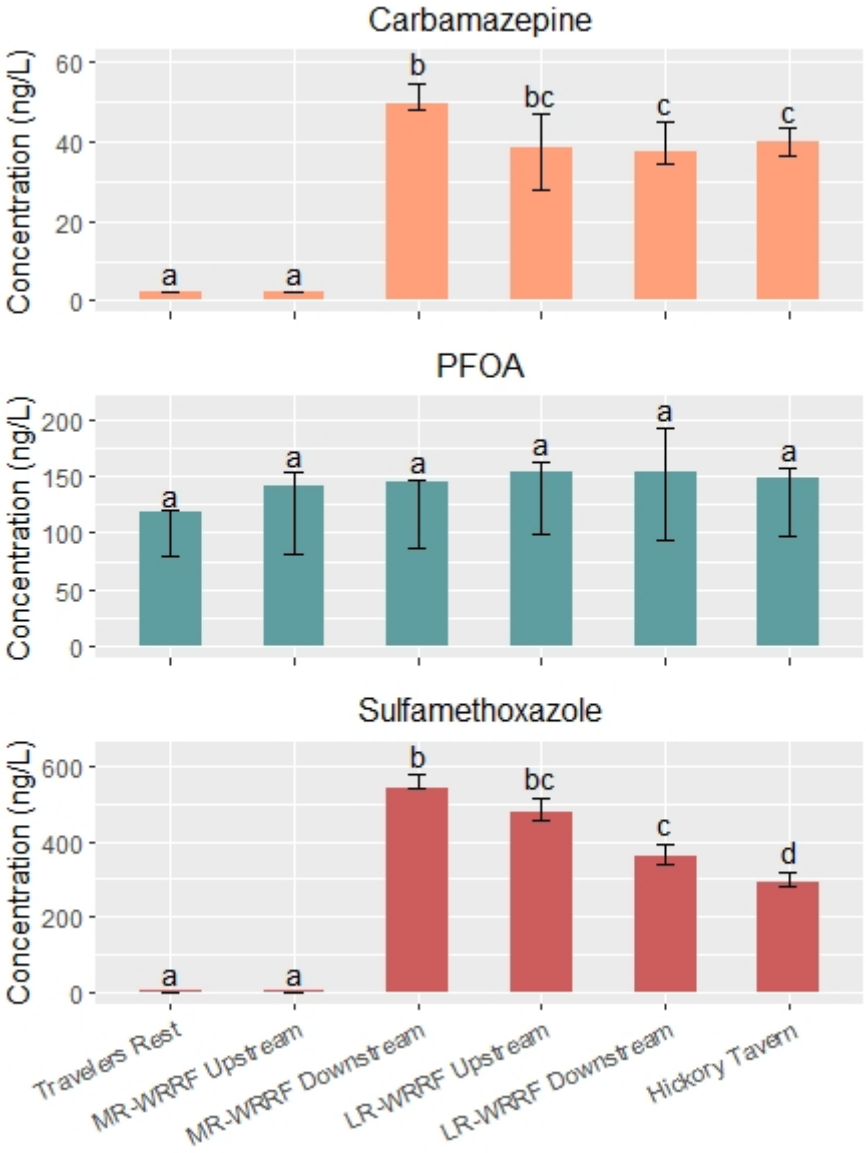

Fig. 2 Median and interquartile range concentrations (ng/L) of carbamazepine, perfluorooctanoic acid (PFOA), and sulfamethoxazole at each of the six sampling locations over the length of the Reedy River. Letters indicate significant differences in analyte concentrations between sites as determined by Wilcoxon Rank Sum analyses

Pharmaceutical manufacturing and hospitals, in addition to the general public, are major sources of these contaminants in wastewater (Grandclement et al. 2017). Combined, the WRRFs receive regulated wastewater flow from 55 industries (23 – MR-WRRF, 32 – LR-WRRF) and non-regulated flow from 7 hospitals (6 – MR-WRRF, 1 – LR-WRRF). The WRRF's contribute significant flow to the Reedy River, 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). In the previous year, flows from the MR-WRRF and the LR-WRRF averaged 0.71 and 0.29 m^3/s, respectively (ReWa 2019). Over the sampling period, measured river flow at all three USGS stations decreased by approximately 50% due to the drought ($R^2 = 0.86$, $p = 0.005$; $R^2 = 0.88$, $p = 0.003$; $R^2 = 0.75$, $p = 0.02$). As a result, the relative contributions of the MR-WRRF to the flow likely increased as previously observed by Hur et al. (2007). Regression analyses

comparing the LR-WRRF downstream analyte concentrations with the Fork Shoals USGS station measured flow showed a significant decrease in PFOA concentrations ($R^2 = 0.72$, $p = 0.04$) and a significant increase in carbamazepine concentrations ($R^2 = 0.78$, $p = 0.01$) associated with the decreasing river flows over the sampling period. As the WRRF effluents were not seen to be a significant source of PFOA, a dilution effect may explain this observation. As river flow decreased and the relative WRRF flow contributions increased, concentrations of carbamazepine also increased. Unexpectedly, sulfamethoxazole did not exhibit a significant relationship with river flow ($R^2 = 0.27$, $p = 0.73$) in this characterization, though expanded sampling and analyses using WRRF effluent flow data in addition to river flow data may clarify WRRF contribution and loading trends of all analytes.

The Reedy River in South Carolina has a long history of challenges and impairments and the expected continued rapid industrial, commercial, and human population growth in the region will place additional stress on the system. Organic contaminants may be disruptive to aquatic organism and human health, reproduction, and development, but extensive work has yet to be done to characterize organic contamination in the river. A diverse organic contaminant profile, in addition the chemicals identified in this exploratory study, is likely given continuing urbanization increasing runoff and two WRRFs discharging treated effluent into the river. This initial characterization has shown detectable levels of organic contaminants and justifies continued and expanded monitoring and examination.

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