



## Pharmaceuticals, herbicides, and disinfectants in agricultural water sources

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### ARTICLE INFO

#### Keywords:

Pharmaceuticals  
PPCPs  
Herbicides  
Atrazine  
Climate change  
LC/MS  
LC-MS/MS  
Reclaimed water  
Waste water

### ABSTRACT

Agricultural water withdrawals account for the largest proportion of global freshwater use. Increasing municipal water demands and droughts are straining agricultural water supplies. Therefore, alternative solutions to agricultural water crises are urgently needed, including the use of nontraditional water sources such as advanced treated wastewater or reclaimed water, brackish water, return flows, and effluent from produce processing facilities. However, it is critical to ensure that such usage does not compromise soil, crop, and public health. Here, we characterized five different nontraditional water types ( $n = 357$  samples) for the presence of pharmaceuticals, herbicides, and disinfectants using ultra-high-pressure liquid chromatography tandem mass spectrometry based method (UPLC-MS/MS). We then evaluated whether the levels of these contaminants were influenced by season. The highest level of herbicides (atrazine) was detected in untreated pond water (median concentration 135.9 ng/L). Reclaimed water had the highest levels of antibiotics and stimulants including azithromycin (215 ng/L), sulfamethoxazole (232.1 ng/L), and caffeine (89.4 ng/L). Produce processing plant water also tended to have high levels of atrazine (102.7 ng/L) and ciprofloxacin (80.1 ng/L). In addition, we observed seasonal variability across water types, with the highest atrazine concentrations observed during summer months, while the highest median azithromycin concentrations were observed in reclaimed water during the winter season. Further studies are needed to evaluate if economically feasible on-farm water treatment technologies can effectively remove such contaminants from nontraditional irrigation water sources.

### 1. Introduction

Agriculture accounts for 41% of freshwater withdrawals in the United States, a measure of water quantity diverted from surface and ground water sources (Wiebe and Gollehon, 2006). Agricultural share of consumptive use, measured by the total amount of water not returned to the immediate water environment, is considerably higher,

accounting for 80% of national estimate (Wiebe and Gollehon, 2006). The most recent USGS report suggests that freshwater withdrawal for agricultural purposes has increased by 2% between 2010 and 2015 (Dieter et al., 2018). The growth in human populations combined with continued outward expansion of urban areas into agricultural land has placed agricultural water demands on a direct collision course with municipal water demands (Satterthwaite et al., 2010). This problem is

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<https://doi.org/10.1016/j.envres.2019.04.011>

Received 1 August 2018; Received in revised form 9 April 2019; Accepted 12 April 2019

Available online 17 April 2019

0013-9351/ © 2019 Published by Elsevier Inc.

exacerbated by ongoing droughts that are projected to increase in future decades in response to changing climate (IPCC, 2014a; Wuebbles et al., 2017; Ebi and Bowen, 2016). Thus, there is a pressing need to identify additional sources of water for agricultural use, including nontraditional irrigation water sources such as advanced treated municipal wastewater (also referred to as reclaimed or recycled water), return flows, and brackish waters (Dery et al., 2018). However, these nontraditional sources of water need to be characterized for both microbial as well as chemical hazards to ensure that their use does not compromise soil, crop, or public health (USEPA, 2012; Sapkota, 2019). The results reported here focus exclusively on chemical hazards. An evaluation of potential microbial hazards is addressed in a companion publication within this special issue (Zhu et al., 2019).

Pharmaceuticals and personal care products (PPCPs) are ubiquitous in the environment, often discharged through municipal wastewater treatment plants (WWTPs) (Michael-Kordatou et al., 2015) as they are not designed to remove these contaminants from the wastewater (Verlicchi et al., 2012). Pharmaceutical compounds from consumers reach WWTPs via excretion, bathing, and disposal of unwanted drugs down the drain (Daughton and Ruhoy, 2008). Numerous prior studies have characterized the concentration profiles of PPCPs in municipal wastewater and surface water (Hedgespeth et al., 2012; Kolpin et al., 2002; Ebele et al., 2017; Heidler and Halden, 2008; Young et al., 2008). In addition to PPCPs, surface water is also contaminated with runoff from agricultural fields that may contain pesticides and herbicide residues (Stamatis et al., 2013), particularly in areas characterized by intensive agricultural practices (Konstantinou et al., 2006). Others have demonstrated seasonal patterns of PPCP concentrations, with higher values observed during spring and summer and lower concentrations detected over winter months (Stamatis et al., 2013). However, there is a paucity of studies that provides a comprehensive overview of different classes of contaminants (antibiotics, stimulants, and herbicides) across a number of water types that could be used for agricultural purposes, including reclaimed water, brackish water, as well as water from produce processing plants.

This study reports on levels of selected pharmaceuticals, disinfectants, stimulants, and herbicides in field water samples collected from wastewater reclamation facilities, non-tidal freshwater creeks, ponds, brackish river water, and a produce processing plants. This research was conducted as part of CONSERVE: A Center of Excellence at the Nexus of Sustainable Water Reuse, Food and Health, established in 2016 through funding from the United States Department of Agriculture, National Institute of Food and Agriculture (USDA-NIFA). CONSERVE aims to facilitate the adoption of transformative on-farm solutions that enable the safe use of nontraditional water on food crops and effectively reduce the nation's water challenges that are exacerbated by climate change. As part of this objective, the CONSERVE team has been characterizing several nontraditional water sources in the Mid-Atlantic and southwest US for bacterial, viral, and protozoal pathogens, and as reported in this study, chemical contaminants, prior to evaluating on-farm treatment technologies for their removal.

## 2. Material and methods

### 2.1. Chemical standards

The specific chemicals included in the analyses were chosen following a dialogue between the study team and the CONSERVE advisory board, which consists of stakeholders and experts in water reuse. This process helped to align the laboratory capacity with the broader community interest in specific chemicals included in the study. All chemical standards used in this study (alachlor, (ALA)alachlor-d13, atrazine (ATR), atrazine-d5, azithromycin dihydrate (AZI), erythromycin (ERY), linezolid (LIN), linezolid-d3, caffeine (CAF), caffeine-d9, caffeine-13C3, ciprofloxacin (CIP), oxacillin sodium salt (OXA), oxolinic acid (OXO), oxolinic acid-d5, penicillin G (PEN), penicillin G-d7 potassium salt,

pipemidic acid (PIP), sulfamethoxazole (SUL), sulfamethoxazole-d4, triclocarban (TCC), triclocarban-13C6, tetracycline (TET), tetracycline-d6, triflurin (TRI) and vancomycin monohydrochloride (VAN)) were purchased from Toronto Research Chemicals (TRC, Ontario, Canada). All standard stock solutions were stored at  $-20^{\circ}\text{C}$ .

### 2.2. Sample collection

The sampling sites consisted of 2 untreated freshwater ponds, 3 wastewater reclamation sites, 2 untreated tidal brackish rivers, 2 untreated non-tidal fresh water creeks, and 1 produce processing plant (wash water) from two Mid-Atlantic States - Maryland and Delaware. A total of 357 samples collected over a 2 year period were included in this study, of which 130 were from untreated non-tidal freshwater creeks, 68 were from untreated pond water, 66 were from untreated tidal brackish river, 80 were from wastewater reclamation sites, and 13 samples were from a produce processing plant. All samples were collected into sterile 250 mL polypropylene Nalgene wide mouthed environmental sampling bottles (Thermo Fisher Scientific, Waltham, MA) that had been pretreated with hydrochloric acid, transported to the laboratory at  $4^{\circ}\text{C}$ , and stored in the freezer at  $-80^{\circ}\text{C}$  until the analysis was carried out.

### 2.3. Sample preparation

Frozen samples were allowed to thaw overnight at room temperature. Two hundred mL aliquots of thawed samples were extracted as previously described (Sapkota et al., 2007). In brief, the samples were spiked with 10  $\mu\text{L}$  of 10  $\mu\text{g}/\text{mL}$  internal standards mix (alachlor-d13, atrazine-d5, caffeine-13C3, linezolid-d3, oxolinic acid-d5, penicillin G-d7, tetracycline-d6, and triclocarban-13C6). After thorough mixing, samples were extracted using Oasis HLB (500 mg) cartridges (Waters Corp; Milford MA) that were conditioned with 5 mL of methanol, followed by 5 mL of HPLC grade water. After loading the samples, the cartridges were eluted with 5 mL of a 50:50 methanol/acetone mix followed by 3 mL of methanol with 0.1% formic acid. The extracts were dried under gentle nitrogen flow at  $45^{\circ}\text{C}$ . Finally, the samples were reconstituted with 1 mL of 90:10 water:methanol mix and transferred to 1.5 mL autosampler vials for LC-MS/MS analysis.

### 2.4. LC-MS/MS analysis

The extracted samples were analyzed using an Agilent 1290 Infinity II HPLC coupled with an Agilent 6470 QQQ triple-quad mass spectrometer (MS/MS). An autosampler was used to inject 5  $\mu\text{L}$  of sample onto the UPLC system, and chromatographic separation was achieved using an Agilent C18 Zorbax Eclipse Plus  $3.0 \times 50$  mm, 1.8  $\mu\text{m}$  column. Gradient mobile phase was used with 0.8 mL/min flowrate, and consisted of 99% A (95:5 water:acetonitrile with 0.1% formic acid) at 0 min, ramping up to 90% B (95:5 acetonitrile:water with 0.1% formic acid) at 7.5 min with the total run time of 12 min. Analytes were introduced into the mass spectrometer using electrospray ionization probe operated on dynamic MRM mode, which allowed polarity switching between negative and positive ionization mode. A 7-point calibration curve ranging from 0 to 200 ng/mL was used to quantify the analytes. After every 10 sample injections, a blank and spiked standard were injected for QA/QC purposes.

### 2.5. Statistical analyses

Prior to statistical analyses, all relevant variables were log transformed to ensure normality of distribution. Group differences between two water types were evaluated using t-test. Mean concentrations across the 5 different water types were evaluated using ANOVA. Since one of the major objectives was to compare different water types for concentrations of chemical residues, we computed median ratios of

**Table 1**

Liquid chromatography tandem mass spectrometry (LC-MS/MS) parameters, limit of detection (LOD), and percent recovery for the analytical method used in this study.

Compound Name	Precursor Ion	Product Ion	Collision Energy	Polarity	LOD	Recovery
Alachlor	270.1	238.1	10	Positive	0.63	99.2
Atrazine	216.1	174	17	Positive	0.3	102.5
Azithromycin	749.5	591.4	32	Positive	0.71	84.2
Caffeine	195	138.2	30	Positive	0.81	102.3
Ciprofloxacin	332.1	314.1	30	Positive	0.88	93.9
Erythromycin	734.5	158.2	30	Positive	0.45	82.8
Linezolid	338.2	195	28	Positive	0.67	99.8
Oxacillin	402	144	30	Positive	1.75	37.1
Oxolinic Acid	262	244	20	Positive	1.1	99.2
Penicillin G	335	159.9	30	Positive	1.36	68.1
Pipemidic Acid	304	217.4	30	Positive	0.76	83.1
Sulfamethoxazole	254	108	30	Positive	1.02	102.7
Triclocarban	313	160	10	Negative	1.46	147.8
Tetracycline	445	154.2	30	Positive	1.11	87.9
Trifluralin	336.1	236.1	30	Positive	0.03	61.7
Vancomycin	725	144	10	Positive	0.64	60.3

concentration using non-tidal freshwater creek as the reference group. We grouped these ratios into four categories: similar to reference group (median ratios between 0.5 and 1.5), higher than reference group (median ratios between 1.5 and 5.0), and considerably higher than reference group (median ratios greater than 5.0, i.e. median concentration higher than 500% of what is observed in the non-tidal freshwater creek). All analyses were performed using Stata/IC 11.2 (Stata Corp, College Station, TX).

### 3. Results

The precursor and product ions data as well as collision energy for each of the analytes are presented in Table 1. Most of the analytes, except for triclocarban, preferred positive ionization mode. The LOD ranged from 0.3 to 1.75 ng/mL for trifluralin and oxacillin, respectively (Table 1). The majority of recovery rates were in the range of 80–100% with a noted exception of oxacillin (37.1%) and triclocarban (147%). The detection frequency varied between analytes as well across sample types (Table 2). For example 100% of samples from the produce processing plant were above LOD for ciprofloxacin compared to only 32% of samples from non-tidal freshwater creeks. Likewise, 12% of tidal brackish river water samples were above LOD for vancomycin compared to 82.5% of reclaimed water samples.

The overall concentration profiles of herbicides (ALA, ATR, TRI), antibiotics (AZI, CIP, ERY, LIN, OXA, OXO, PEN, PIP, SUL, TET, VAN), disinfectant (TCC), and stimulant (CAF) across the five different water types are depicted in Fig. 1 and Table 2. Across the three untreated surface water source types (non-tidal freshwater creek, pond water, and tidal brackish river), atrazine (ATR), triclocarban (TCC), and caffeine (CAF) were present at the highest concentrations. The median concentration of ATR, TCC and CAF were 27.8, 15.3 and 6.1 ng/L, respectively, in non-tidal freshwater creeks; 135.9, 16.3 and 9.1 ng/L in pond water; and 87.1, 14.5 and 6.4 ng/L, respectively, in tidal brackish river water. The concentration profiles for reclaimed water and produce processing water differed from the three aforementioned surface water samples. In addition to ATR, TCC, and CAF, produce processing plant water had higher levels of ciprofloxacin (CIP, median 80.1 ng/L). Reclaimed water had higher concentrations of antibiotics compared to surface water samples ( $p < 0.05$ ). Notable differences included concentrations for azithromycin (AZI median concentration 215.0 ng/L vs  $< 1$  ng/L in freshwater creek, pond or the brackish river), and sulfamethoxazole (SUL median concentration 232.1 ng/L vs  $< 1$  ng/L in freshwater creek, pond or the brackish river). Similar results were also observed for vancomycin (VAN). In addition, concentrations of caffeine in the reclaimed water (median 89.4 ng/L) were higher than that observed in the freshwater creek, pond water, non-tidal brackish river

water, or the produce processing plant water; all below 11 ng/L ( $p < 0.05$ ).

Since one of our objectives was to evaluate different water types for chemical residues to inform discussion regarding the use of such non-traditional water for agricultural purposes, we compared all water types to non-tidal freshwater creek (Fig. 2). We observed that only 2 of the 16 analytes were present in higher concentration in pond water compared to the freshwater creek. In tidal brackish river water, 3 of the 16 analytes were present in higher concentrations. By comparison, 10 of the 16 analytes in reclaimed water were present at either higher (1) or considerably higher (9) concentrations compared to the non-tidal freshwater creek. Similarly, 4 of the 16 analytes were present in either higher (2) or considerably higher (2) concentrations in produce processing plant water (Fig. 2).

The seasonal variability of concentrations is depicted in Table 3 for all water types combined and separately for reclaimed water. For the combined analysis, mean ATR concentrations during summer (1191.9 ng/L), spring (596.8 ng/L), and fall (427.8 ng/L) were significantly higher than winter (36.8 ng/L) months ( $p < 0.05$ ). Likewise, mean AZI concentrations were highest during spring (171.7 ng/L) compared to winter (72.0 ng/L), summer (41.6 ng/L) or fall (64.0 ng/L), however differences were not statistically significant ( $p > 0.05$ ). Likewise, mean VAN and SUL levels were higher during spring, summer and fall compared to winter season ( $p < 0.05$ ). Similar variability was also observed when the analysis was restricted to reclaimed water alone (Table 3), with some noted differences. For example, the AZI concentration was higher ( $p < 0.05$ ) in reclaimed water during winter (694.1 ng/L) and spring (632.4) seasons compared to summer (175.8 ng/L) or fall (249.9 ng/L). Likewise, OXO level was lower ( $p < 0.05$ ) during summer (13.9 ng/L) and fall (21.3 ng/L) compared to winter (177.8 ng/L) months. VAN was higher during summer compared to winter ( $p < 0.05$ ).

### 4. Discussion

Climate change-related increases in the frequency of droughts is putting considerable stress on global freshwater supplies (Dettinger et al., 2015; IPCC, 2014a; IPCC, 2014b; Dieter et al., 2018). This underscores the need for alternate agricultural water sources, the use of which does not compromise public health. This study characterized nontraditional agricultural water sources for pharmaceuticals, herbicides, and disinfectants.

Based on the frequency of detection and concentration, atrazine was the predominant analyte detected across all five water types, while higher levels of ciprofloxacin were observed in produce processing water. An elevated level of ciprofloxacin - a broad-spectrum antibiotic -

**Table 2**  
Concentration of herbicides, antibiotics, stimulants, and disinfectants across 5 different water types.

Water Types	Herbicides (ng/L)			Antibiotics (ng/L)								Other (ng/L)			
	ALA	ATR	TRI	AZI	CIP	LIN	OXA	OXO	PEN	PIP	SUL	TET	VAN	TCC	CAF
<b>Non Tidal Freshwater Creek (N = 130)</b>															
% > LOD	28.0	100.0	97.6	22.0	32.0	21.0	6.0	49.2	71.0	27.6	51.7	94.6	16.0	88.5	86.0
Median	0.3	27.8	2.9	0.4	0.4	0.3	0.8	0.6	5.0	0.4	0.5	3.1	0.3	15.3	6.1
Max	72.6	4777.9	19.1	30.9	29.4	32.5	99.7	283.9	16.1	30.0	28.7	15.1	71.5	3155.0	469.5
Average	2.1	274.0	3.0	1.8	2.9	1.5	2.3	13.9	4.2	2.4	1.1	3.7	2.1	63.5	14.4
SD	7.0	798.4	2.8	4.5	4.8	3.8	9.2	33.8	2.7	4.8	3.1	2.3	7.1	297.6	50.8
<b>Pond Water (N = 68)</b>															
% > LOD	4.4	100.0	100.0	15.4	42.6	17.6	2.9	48.5	70.5	35.3	17.6	95.5	13.2	88.2	91.0
Median	0.3	135.9	2.7	0.4	0.4	0.3	0.8	0.6	5.0	0.4	0.5	3.1	0.3	16.3	9.1
Max	5.1	13244.4	14.3	43.9	51.8	9.3	24.3	334.6	12.4	25.5	10.0	16.7	494.8	2938.8	1389.1
Average	0.4	1464.6	3.1	4.1	5.0	1.0	1.3	13.9	4.3	3.8	1.2	4.4	9.0	80.4	34.9
SD	0.6	3296.5	3.2	9.2	9.4	1.6	3.3	41.7	2.7	6.3	1.8	3.4	60.0	360.4	169.7
<b>Tidal Brackish River (N = 66)</b>															
% > LOD	7.5	100.0	95.0	38.0	51.5	27.0	4.5	50.0	72.7	35.0	11.0	95.0	12.0	91.0	83.0
Median	0.3	87.1	2.8	0.4	2.4	0.3	0.8	2.1	5.0	0.4	0.5	3.1	0.3	14.5	6.4
Max	5.7	19066.9	18.4	28.8	24.2	8.1	52.6	596.0	20.9	47.8	5.7	18.4	1760.2	2561.9	25.0
Average	0.5	1160.3	3.5	3.4	3.7	1.4	2.2	18.9	4.6	2.8	0.9	4.4	29.1	79.9	7.0
SD	0.8	3002.4	3.7	5.7	5.1	2.0	7.2	74.5	3.5	6.3	1.2	3.3	216.6	322.5	5.0
<b>Reclaimed Water (N = 80)</b>															
% > LOD	7.5	100.0	98.7	96.0	81.0	71.0	9.0	71.0	70.0	58.7	95.0	97.5	82.5	92.5	98.7
Median	0.3	37.8	3.1	215.0	9.0	4.0	0.8	8.9	5.0	2.6	232.1	3.1	25.9	29.1	89.4
Max	2.4	1759.3	107.5	1932.8	224.0	193.4	58.0	771.6	19.7	82.7	2061.0	107.5	465.5	3490.6	67716.9
Average	0.4	124.1	6.5	350.7	17.9	12.4	2.9	39.7	5.0	7.1	451.7	6.3	65.6	103.7	2676.4
SD	0.5	233.2	13.4	430.7	28.6	25.7	8.5	102.0	4.0	13.7	475.6	12.3	88.4	435.3	9564.9
<b>Produce Processing Water (N = 13)</b>															
% > LOD	23.0	100.0	100.0	30.7	100.0	46.0	7.6	46.0	76.9	38.4	76.9	84.6	76.9	69.2	84.6
Median	0.3	102.7	2.6	0.4	80.1	0.3	0.8	0.6	5.0	0.4	10.7	3.1	0.3	15.1	10.9
Max	3.9	829.2	9.2	7.5	1535.6	7.4	31.3	88.9	23.3	59.2	38.4	9.2	7.8	72.8	145.9
Average	1.1	335.1	3.3	1.6	329.9	2.4	3.1	12.2	5.5	8.2	14.9	3.8	1.4	18.8	38.7
SD	1.6	327.8	2.6	2.2	516.0	2.6	8.4	25.7	5.7	16.6	12.8	2.7	2.3	21.8	51.0

ALA: Alachlor, ATR: Atrazine, AZI: Azithromycin, CIP: ciprofloxacin, CAF: Caffeine, LIN: linezolid, OXA: oxacillin, OXO: Oxolinic acid, PEN: Penicilli G, PIP: pipemidic acid, SUL: sulfamethoxazole, TCC: triclocarban, TET: tetracycline, TRI: triflurin.

was only identified in produce processing water, indicating that the source may be unique to this water type. While a recent study has shown wastewater from produce processing plant can be contaminated with solid and organic matter resulting from produce washing (Mundi et al., 2017), this is the first study showing elevated levels of such antibiotics. Since all 13 samples included in this study were from a single produce processing plant, future studies need to investigate this issue by including larger number of samples from multiple facilities. Similarly, reclaimed water had high levels of azithromycin, a semi-synthetic macrolide that is marketed under the brand-names Z-Pak, Zithromax, and Zmax, commonly used to treat several human bacterial infections. Most recent data suggest that azithromycin is one of the most heavily prescribed antibiotics in the U.S., with 40.3 million individuals receiving outpatient prescriptions in 2011 (Hampp et al., 2013). As expected, reclaimed water also had considerably higher concentrations of caffeine, which is excreted in the urine of coffee drinkers.

Our results show that untreated surface water sources, including pond water, non-tidal freshwater creeks as well as tidal brackish rivers, are contaminated with atrazine, the most commonly used herbicide in agricultural settings in the U.S. for controlling broad leaf weeds in crops (US EPA, 2007). National estimates of annual agricultural use during 1992–2011 demonstrate that the heavy use of atrazine and alachlor over the past decades has contaminated many rivers and streams (Ryberg and Gilliom, 2015; Stone et al., 2014). Surprisingly, atrazine was also detected in reclaimed water, although the mean concentration was lower than that observed in the three surface water types (non-tidal freshwater creek, tidal brackish river, and pond water) or the produce processing plant water. Detection of atrazine in reclaimed water may reflect widespread contamination, potentially from agricultural run-off and lawn application in urban and suburban settings, particularly in areas where combined sewer systems (that receive both raw domestic wastewater and stormwater) are still utilized (Southwick et al., 2003;

Lafrance et al., 1997; Wang et al., 2018). Atrazine has also been frequently detected in rain water samples (Brun et al., 2008; Bossi et al., 2002).

The majority of surface water samples were collected from areas dominated by agricultural fields. Atrazine is routinely applied in these fields (Denver et al., 2006) particularly during the crop growing season (late spring to early fall) to inhibit the growth of weeds by interfering with the normal function of photosynthesis (Hamilton et al., 1987). Thus, runoff from these agricultural fields during heavy precipitation events likely contributed to the distinct seasonality pattern of atrazine concentration, with the highest and lowest concentration observed during the summer and the winter months, respectively. Previous studies have suggested use of vegetative buffer strips to control such herbicide loads in runoff (Lerch et al., 2017; Stone et al., 2014). Similar to atrazine, several antibiotics such as azithromycin, oxolinic acid, and vancomycin also expressed seasonality. However the pattern was different in reclaimed water, where significantly lower concentration for azithromycin, oxolinic acid, and vancomycin were observed during summer and fall, indicating higher prescription of these antibiotics during winter and spring seasons to treat bacterial infections (Suda et al., 2014; Socan, 1998). Our findings regarding seasonality are similar to those from previous studies (Stamatis et al., 2013; Konstantinou et al., 2006) that investigated the seasonality of herbicides (atrazine) and pesticides in surface waters and observed similar trends. The different seasonality patterns observed for herbicide vs. antibiotics as well as difference that exist between different water types reflect further challenges in using these water sources for agricultural purpose. While concentration of atrazine in surface water appear to be tied to runoff during summer months, specific antibiotics in reclaimed water appears to be associated with prescriptions related to seasonal disease pattern. In light of these findings, further studies are needed to examine how such seasonal variability may be influenced by drought



Fig. 1. Distribution of herbicides, antibiotics, disinfectant and stimulant across five water types.

conditions. For instance, it remains unclear if heavy precipitation immediately following prolonged drought is worse than any set of heavy precipitation during summer months. Such data can inform if minimum “clear off period” is needed before using nontraditional water for agricultural purposes.

Our findings are in line with previously published studies. For example, Hughes et al. (2013) reviewed the distribution of PPCPs in water across the globe (Table 4). Their reported azithromycin and sulfamethoxazole concentrations are similar to the concentrations observed

in reclaimed water in the current study. Likewise, the concentrations of sulfamethoxazole and caffeine reported by Kolpin et al. (2002) and more recently by Glassmeyer and colleagues (Glassmeyer et al., 2017) are similar to the one observed for reclaimed water in our study. The concentrations of these selected antibiotics, as well as caffeine and TCC, observed in the pond water, freshwater creek and brackish river were lower than those observed by Kolpin (Kolpin et al., 2002) and Focazio (Focazio et al., 2008). Studies from India, China, South Africa, and Taiwan all reported higher concentrations of the selected antibiotics,

Water Types	ALA	ATR	TRI	AZI	CIP	ERY	LIN	OXA	OXO	PEN	PIP	SUL	TET	VAN	TCC	CAF
Non Tidal Freshwater Creek (N= 75)	Reference Group	Reference Group	Reference Group	Reference Group	Reference Group	Reference Group	Reference Group	Reference Group	Reference Group	Reference Group	Reference Group	Reference Group	Reference Group	Reference Group	Reference Group	Reference Group
Pond Water (N = 36)	Reference Group	Higher than reference group	Reference Group	Reference Group	Reference Group	Reference Group	Reference Group	Reference Group	Reference Group	Reference Group	Reference Group	Reference Group	Reference Group	Reference Group	Reference Group	Higher than reference group
Tidal Brackish River (N= 37)	Reference Group	Higher than reference group	Reference Group	Reference Group	Higher than reference group	Reference Group	Reference Group	Reference Group	Higher than reference group	Reference Group	Reference Group	Reference Group	Reference Group	Reference Group	Reference Group	Reference Group
Reclaimed Water (N= 46)	Reference Group	Reference Group	Reference Group	Higher than reference group	Reference Group	Higher than reference group	Reference Group	Higher than reference group	Higher than reference group	Reference Group	Higher than reference group	Higher than reference group	Higher than reference group			
Fruits/Vegetable Processing Water (N =13)	Reference Group	Higher than reference group	Reference Group	Reference Group	Higher than reference group	Reference Group	Reference Group	Reference Group	Reference Group	Reference Group	Reference Group	Higher than reference group	Reference Group	Reference Group	Reference Group	Higher than reference group
	Reference Group															
	Similar to Reference Group (median ratio: 0.90-1.51)															
	Higher than reference group (median ratio: 1.51-5.00)															
	Considerably higher than reference group (median ratio: >5.00)															

Fig. 2. Relative concentration profile of herbicides, antibiotics, stimulant, and disinfectant across the five water types, using non-tidal freshwater creek as a reference group.

**Table 3**  
Seasonal variability in concentration by sample type.

Sample Type	Season	Herbicides (ng/L)			Antibiotics (ng/L)								Other (ng/L)				
		ALA	ATR	TRI	AZI	CIP	LIN	OXA	OXO	PEN	PIP	SUL	TET	VAN	TCC	CAF	
All Samples Combined	Winter	N	54	54	54	54	54	54	54	54	54	54	54	54	54	54	
		Median	0.3	12.5	3.1	0.4	0.4	0.3	0.9	4.2	5.0	0.4	0.5	3.1	0.3	18.9	8.0
		Mean	1.2	36.8	3.3	72.0	5.6	2.8	1.4	27.2	4.0	2.9	17.9	4.2	1.7	41.5	39.9
	Spring	N	80	80	80	80	80	80	80	80	80	80	80	80	80	80	
		Median	0.32	48.435	3.13	0.35	0.44	0.34	0.88	6.25	5	0.38	0.51	3.13	0.32	21.86	9.66
		Mean	0.8	596.8*	4.4	171.7	6.5	5.8*	2.6	45.1	4.5	3.8	93.2*	4.1	19.8*	161.4*	1453.1*
	Summer	N	108	108	108	108	108	107	108	108	108	108	108	108	108	108	
		Median	0.3	196.7	3.1	0.4	2.9	0.3	0.9	5.2	5.0	2.4	0.5	3.1	0.3	15.9	9.3
		Mean	1.0	1191.9*	5.2*	41.6	14.1	2.7	2.0	13.4	4.0	4.1*	149.0*	4.9	26.2*	95.0	889.7*
	Fall	N	127	127	127	127	127	127	127	127	127	127	127	127	127	127	
		Median	0.3	29.3	1.7	0.4	0.4	0.3	0.9	0.6	5.0	0.4	0.5	3.1	0.3	15.8	7.7
		Mean	1.4	427.8*	2.7	64.0	33.3	4.1*	2.9	9.7	5.1*	4.5	99.8*	4.4	29.9*	27.6	46.5
Recalimed Water Only	Winter	N	5	5	5	5	5	5	5	5	5	5	5	5	5		
		Median	0.3	44.5	3.1	748.5	19.3	4.0	0.9	34.4	5.0	7.5	187.6	3.1	12.4	28.8	19.9
		Mean	0.3	41.3	5.1	694.1	17.4	24.2	0.9	177.8	4.9	6.8	173.6	4.5	9.3	32.1	115.4
	Spring	N	20	20	20	20	20	20	20	20	20	20	20	20	20	20	
		Median	0.3	55.5	3.5	360.9	10.1	9.1	0.9	15.3	5.0	3.1	286.4	3.4	40.6	33.6	42.3
		Mean	0.6	142.1*	8.1	632.4	16.4	20.3	4.3	65.1	4.8	7.2	343.1	5.3	66.9	210.0	5286.3
	Summer	N	24	24	24	24	24	24	24	24	24	24	24	24	24	24	
		Median	0.3	75.3	3.3	132.5	8.6	2.7	0.9	7.4	5.0	2.6	641.1	3.1	105.6	25.8	140.3
		Mean	0.5	133.8*	8.7	175.8#	23.4	7.4	3.0	13.9#	4.5	4.4	653.2*	7.8	105.4*	114.7	3882.2*
	Fall	N	30	30	30	30	30	30	30	30	30	30	30	30	30	30	
		Median	0.3	21.7	2.3	111.4	3.9	3.3	0.9	7.0	5.0	2.6	188.9	3.1	14.3	29.7	53.5
		Mean	0.4	121.2	4.1	249.9#	14.3	9.2	2.2	21.3#	5.2	8.9	399.1	6.2	42.4	38.5	163.9

\* Significantly higher than winter.

# Significantly lower than winter.

and caffeine (Lin et al., 2015; Agunbiade and Moodley, 2014; Zhang et al., 2017; Anumol et al., 2016; Aguilar et al., 1999).

Our findings document a considerable variability in concentration of individual analytes across different sources of nontraditional water as well as season. However, treatment technologies applied now primarily focus on microbial contaminants and not chemical residues (Wu et al., 2014, 2015). As the demand for nontraditional water grows in response to ongoing climate variability and change, novel on-farm water treatment technologies are needed that effectively remove both chemical and microbial contaminants, and are robust enough to accommodate considerable variability in matrix as well as the concentration.

**Table 4**  
Comparison of selected analytes across studies.

Study	Location	Water type	AZI	CIP	ERY	SUL	TET	CAF	TCC	ATR
Hughes et al. (2013)	Global	River	188	163	50.8	83	41	–	–	–
Kolpin et al. (2002)	USA	Stream	–	20	100	150	110	100	–	–
Focazio et al. (2008)	USA	Ground/Surface	29 <sup>a</sup>	30 <sup>a</sup>	300 <sup>a</sup>	UC	ND	270 <sup>a</sup>	–	–
Glassmeyer et al. (2017)	USA	Surface water	–	–	–	50	–	70	–	64
Lin et al. (2015)	Taiwan	Ground	–	ND	55	1820	–	9317	–	–
Agunbiade and Moodley, 2014	South Africa	River	–	1360	3180	3680	5680	3890	–	–
Zhang et al. (2017)	China	WWTP (influent)	26	98	208	316	72	–	–	–
Aguilar et al. (1999)	Spain	River	–	–	–	–	–	–	–	180
Anumol et al. (2016)	India	WWTP (influent)	–	–	–	920	–	65000	1800	ND
Present Study	USA	Reclaimed water	215	9	2	232	3	89	29	37.8
	USA	Pond	0.4	0.4	0.2	0.5	3	9	16	135.9
	USA	Tidal brackish river	0.4	2.4	0.2	0.5	3	6	15	87.1
	USA	Freshwater creek	0.4	0.4	0.2	0.5	3	6	15	27.8

UC: Unquantified; ND: Non Detect.

<sup>a</sup> Maximum concentration.

such as prolonged dermal contact in occupational settings may lead to health risks that have not yet been investigated.

There are several strengths of our study. We collectively looked at residues of common herbicides, antibiotics, as well as a stimulant (caffeine) and a disinfectant (TCC), in a range of water samples that could potentially be used for agricultural purposes. While previous studies have characterized specific water types for select groups of chemicals (e.g., antibiotics), our study provides a wider perspective (multiple chemical groups and water types) on this emerging issue. Our relatively large sample size enabled us to evaluate the seasonality of these analytes and further investigate how concentrations vary across different water types. There are several limitations to our study as well. Our study has a limited temporal coverage (2 years) so we could not evaluate long temporal trends. In addition, the vast majority of our samples were from the Mid-Atlantic region, so we could not evaluate regional differences in concentrations. While our findings regarding produce processing plant water are very interesting, we had only a limited number of samples (13) for this particular water type. Thus future studies are needed for more in-depth investigation of this issue.

## 5. Conclusion

We have characterized various water types including previously overlooked produce processing wastewater. We used monitoring data to compare concentrations observed in various water types to those present in non-tidal freshwater creek samples. Our results show considerable variability across water types and seasons. Future studies need to build on this to inform policies regarding an acceptable range of PPCPs in nontraditional water intended for agricultural use. In addition, there is a need to evaluate the effectiveness of different portable on-farm water treatment technologies that can remove these chemical contaminants.

## Conflicts of interest

None.

## Acknowledgements:

This work was supported by the United States Department of Agriculture, National Institute of Food and Agriculture (NIFA), Grant number 2016-68007-25064, awarded to the University of Maryland School of Public Health, that established CONSERVE: A Center of Excellence at the Nexus of Sustainable Water Reuse, Food and Health.

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