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Persulfate photolysis and limited irrigation of recycled wastewater for turfgrass growth: Accumulation of pharmaceutical and personal care products and physiological responses

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ABSTRACT

Recycled wastewater effluent irrigation and implementing limited irrigation rates are two promising strategies for water conservation in agriculture. However, one major challenge is the accumulation and translocation of Pharmaceutical and Personal Care Products (PPCPs) from recycled water to crops. This study investigated the effects of UV persulfate (UV/PS) treatment of recycled water and limited irrigation rate on PPCPs accumulation and physiological responses of St. Augustine turfgrass via a 14-week field trial. Carbamazepine (CBZ), sulfamethoxazole (SMX), triclosan (TCS), fluoxetine (FLX) and diclofenac (DCF) were spiked at 0.1-1.5 µg/L into recycled water and two limited irrigation rates corresponding to 60 % and 80 % of reference Evapotranspiration (ET₀) were applied. Results showed that UV/PS removed 60 % of CBZ and > 99 % of other PPCPs from recycled water. Irrigation with UV/PS treated recycled water resulted in approximately a 60 % reduction in CBZ accumulation and complete removal of SMX, DCF, FLX and TCS in both turfgrass leaves and roots. A more limited irrigation rate at 60 % ET₀ resulted in a higher accumulation of CBZ accumulation compared to 80 % ET₀. Similarly, the canopy temperature increased under 60 % ETo irrigation rate compared to 80 % ETo, suggesting that turfgrass under 60 % ET₀ was more prone to water stress. Applying a 60 % ET₀ irrigation rate was not sufficient to maintain the turfgrass quality in the acceptable range. A negative correlation between the visual quality and cumulative mass of PPCPs in turfgrass leaves at different irrigation rates was observed, yet irrigation rate was the major driver of turfgrass overall quality and health. Insights from this study will help to integrate recycled water with treatment and limited irrigation, thereby enhancing agricultural water reuse practices.

1. Introduction

Water scarcity is a pressing global issue and a significant concern as it impacts the agriculture sector which accounts for the largest share of global water usage, often exceeding 70 % in water stressed regions (Rosegrant et al., 2002; United Nations world water development report 4: managing water under uncertainty and risk - UNESCO Digital Library [WWW Document], 2023). Insufficient water availability for irrigation can affect crop production, food security, and agricultural activities (Hanjra and Qureshi, 2010; Misra, 2014). Recycled water from municipal wastewater effluent can be a valuable alternative resource for agricultural irrigation (Jaramillo and Restrepo, 2017). For example, approximately 90 % of the wastewater was reused for agriculture

irrigation in Israel (Reich, 2020). The US has also introduced recycled water for irrigation, with approximately 1.5 million acres of crops benefiting from this practice (Use of recycled and reclaimed water sources for irrigation varies across the United States [WWW Document], 2023). In California, a drought-prone region, recycled water production has increased nearly 10 % from 2019 to 2022, with a predominant allocation towards landscape irrigation (Volumetric Annual Report of Wastewater and Recycled Water | California State Water Resources Control Board [WWW Document], 2023).

Agriculture is the primary water user in the U.S., consuming approximately half of the total freshwater resources (USDA ERS - Irrigation & Water Use [WWW Document], 2023). A significant contributor to this demand is the cultivation of turfgrass which stands as the largest

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irrigated crop in the US. Turfgrass covers over 40 million acres of land in the US, an area three times larger than any other irrigated crop (Milesi et al., 2005). In California, more than 50 % of residential water use is attributed to urban landscapes, particularly turfgrass (Colmer and Barton, 2017). This sheer magnitude of irrigation exerts a substantial strain on the existing water resources for irrigation. Thus, addressing the impact of water scarcity on agriculture requires a comprehensive approach that combines alternative water resources for irrigation and efficient irrigation practices.

While recycled water irrigation presents a promising solution to water conservation, it carries the risk of Pharmaceutical and Personal Care Products (PPCPs) accumulating in crops due to their residual presence in wastewater effluent. Several studies have indicated that conventional treatment processes, such as secondary and tertiary treatment, are ineffective in removing PPCPs from the recycled water and they can still be found in the effluent, ranging from ng/L to μ g/L levels (Boyd et al., 2003; Debroux et al., 2012; Gao et al., 2012; Snyder et al., 2003; Yang et al., 2017). Consequently, many studies have shown the plant accumulation of PPCPs from recycled water irrigation (Wu et al., 2015, 2014, 2013). These persistent organic chemicals have also been associated with increased plant stress and toxicity levels (Bartrons and Peñuelas, 2017). Therefore, an effective treatment technology is needed to remove these persistent PPCPs from recycled water for irrigation efficiently.

UV-Advanced Oxidation Processes (UV-AOP) have emerged as an efficient technology to remove PPCPs from recycled water efficiently (Guo et al., 2020). In particular, UV/persulfate (S₂O₈²⁻) has received increasing attention due to its generation of sulfate radical (SO₄[•]) from persulfate photolysis, which exhibits fast reactivity and higher selectivity with PPCPs in comparison to hydroxyl radical (*OH) (Duan et al., 2020; Guo et al., 2020). Moreover, UV/persulfate can generate secondary radicals including chlorine atom (Cl*) and carbonate radical $(CO_3^{\bullet-})$ via reactions between $SO_4^{\bullet-}$ and chloride/bicarbonate in water matrix, which can also react with PPCPs (Canonica et al., 2005; Fang et al., 2014; Lian et al., 2017). Despite the promising advantages, the application of UV/persulfate treatment for agricultural irrigation with real municipal wastewater effluent remains unexplored, and further investigation is needed to understand the radical distribution and contribution to PPCPs degradation in recycled water matrix via persulfate photolysis.

Furthermore, optimizing the irrigation rate by applying a limited rate below the evapotranspiration (ET) requirement while maintaining plant health has become an emerging irrigation practice to cope with water scarcity (Costa et al., 2007; Farré and Faci, 2009; Fereres and Soriano, 2007). Studies on water requirements for various turfgrass species have found that warm-season turfgrass species are more drought tolerant and perform relatively well under limited irrigation compared to cool-season species (Orta and Kuyumcu, 2023a). For example, 60 % reference ET (ETo: ET from a standardized surface) is often considered an adequate water requirement for warm-season turfgrass species (Colmer and Barton, 2017; Gómez-Armayones et al., 2018). Our recent research, however, revealed that 75 % ET₀ irrigation rate was needed to maintain the aesthetic values of hybrid bermudagrass (a warm-season turfgrass) in semi-arid regions of inland southern California (Haghverdi et al., 2021a). By combining the utilization of recycled water with different water quantity levels, agricultural systems could significantly impact water conservation, reduce water demand, and mitigate water scarcity challenges.

Different irrigation rates have shown various physiological responses in crops, including stomatal closure, decreased photosynthetic rates, and decreased osmotic pressure (Álvarez et al., 2009; Cameron et al., 1999; Sánchez-Blanco et al., 2002). Moreover, studies have indicated that reducing the irrigation rate can result in the accumulation of solutes in crops, including proline, amino acids and sugar (Giordano et al., 2021; Sampathkumar et al., 2014). However, to our knowledge, the fate of PPCPs in turfgrass leaves and roots using recycled water under varying

limited irrigation rate conditions in a field study remains unexplored. Furthermore, a knowledge gap exists in understanding the combined effects of recycled water and different water quantity levels on PPCPs accumulation, and overall turfgrass health and growth.

Therefore, the objectives of this study were to conduct a unique field study by irrigating St. Augustine grass, a warm-season turfgrass, with untreated and treated recycled wastewater effluent at two irrigation rates of 60 % and 80 % of the reference evapotranspiration (ET $_{\rm o}$), investigate the combined efficacy of UV/persulfate treatment and subsequent limited irrigation rate on minimizing PPCPs accumulation in turfgrass, and evaluate the overall impacts on the turfgrass aesthetic value and physiological stress.

2. Material and methods

2.1. Chemicals and materials

Five PPCPs including carbamazepine (CBZ), sulfamethoxazole (SMX), fluoxetine (FLX), diclofenac (DCF), and triclosan (TCS) were selected as the model trace organic contaminants. They are among the most commonly found PPCPs in recycled water (Benotti et al., 2012; Sengupta et al., 2014). The properties and the details of these compounds are detailed in Table S1 and Text S1. Individual stock solution of PPCP and their deuterated compounds were prepared in MilliQ water and methanol, respectively, and stored in amber glass vials at -20 °C.

Recycled water for irrigation was collected monthly from the South Coast Research and Extension Center in Irvine, CA, and stored at 4 $^{\circ}$ C within 2 h of collection for further treatment. The recycled water, produced by Irvine Ranch Water District as a municipal wastewater effluent, received tertiary treatment involving particle removal and chlorine or UV disinfection (User, S., 2023). A comprehensive analysis of the chemistry of the recycled water can be found in Table S2.

Untreated recycled water was prepared by spiking CBZ, SMX, DCF, TCS, and FLX to the freshly collected recycled water to reach an initial environmentally relevant concentration of 0.1– $1.5~\mu g/L$ for each PPCP. This concentration was selected as PPCPs are mostly found at sub- $\mu g/L$ concentration in recycled water (Kim et al., 2007). Additionally, as a negative control, potable water was collected from a hose located at the University of California Riverside Agricultural Experiment Station.

2.2. UV persulfate treatment of recycled water

A schematic diagram of the experimental setup is shown in Fig. 1. UV persulfate (UV/PS) treatment was applied to the untreated recycled water to prepare UV-treated recycled water. Fresh potassium persulfate solution was prepared daily and mixed with untreated recycled water to reach a final persulfate concentration of 14 mg/L. This dosage was selected to effectively remove PPCPs from recycled water. Furthermore, this low level of persulfate was not reported to pose any adverse effect on crop growth based on a prior study on broccoli (Vela et al., 2019). Subsequently, 3.5 L of recycled water mixture was transferred to a UV reactor (ACE Glass) equipped with three low-pressure monochromatic (λ = 254 nm; Ultra-Sun Tech) mercury lamps. The UV fluence of the UV reactor was determined using atrazine actinometry (Canonica et al., 2008). The UV exposure of recycled water lasted for 7 min, equivalent to a total UV dosage of 750 mJ/cm², a typical value used in full-scale UV/AOP water reuse treatment (Mangalgiri et al., 2019). At the end of the UV experiment, treated recycled water was collected. All three types of irrigation water (untreated, treated, and potable control) were stored at 4 °C before further analysis of residual PPCPs and field irrigation.

2.3. Field turfgrass experimental setup

A turfgrass field irrigation experiment was conducted at the Agricultural Experiment Station located at the University of California,

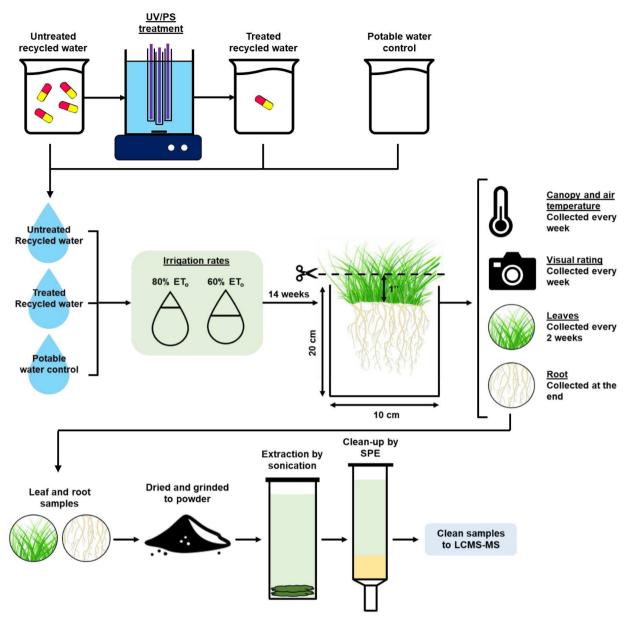


Fig. 1. Schematic diagram of experimental procedures: UV/persulfate treatment of recycled water, field irrigation of turfgrass using three types of water and two irrigation rates, turfgrass growth monitoring, turfgrass leaf and root sample collection, processing, and cleanup for PPCP analysis.

Riverside. The soil at the study site was a well-drained Hanford coarse sandy loam soil with a volumetric water content of 22.5 % (Haghverdi et al., 2021b). A well-established warm season St. Augustine grass known as Stenotaphrum secundatum (Walt.) Kuntze - was used to prepare a plot of $13.4\,\mathrm{m}^2$ to conduct 6 types of irrigation treatments for 14 weeks from July 22 to October 24, 2022. Each irrigation treatment comprised of one of the two irrigation rates (60 % and 80 % of reference crop evapotranspiration, denoted as 60 % and 80 % ETo, respectively) and one of the three irrigation water types (untreated recycled water, treated recycled water, and potable water control). Each type of irrigation treatment was conducted in triplicates with a total of 18 individual treatments. Accordingly, 18 aluminum cylinders, each with a diameter of 10 cm and a depth of 20 cm, were strategically installed, forming three blocks with six cylinders per block following a factorial randomized complete block design (Fig. S1). The cylinders were spaced approximately 30 cm apart, and the blocks were positioned 91 cm apart from each other. Irrigation frequency was set to four times a week (Fig. S2). Field Plots were covered during two light rain events in Weeks 8 and 13 to minimize the impact of rainwater and irrigation frequency

was adjusted as needed. Additionally, a single irrigation event occurred in week 14 to conclude the experiment. The total volume of irrigation water applied per week is provided in Fig. S3. Additional details on the filed irrigation trial are available in Text S2.

2.4. Sample collection and chemical analysis

Before irrigation experiments, each of the three types of water (untreated and treated recycled water, and potable control) underwent a solid-phase extraction (SPE) cleanup procedure to analyze its PPCPs concentrations. Details on the SPE process are provided in Text S3. During the irrigation field experiments, turfgrass in each cylinder of the field plot was systematically clipped to a length of 1 cm from the ground every two weeks and clipped turfgrass tissue samples were collected. At the end of the 14-week experiment, turfgrass root samples were obtained at a depth of 10 cm. The dry weights of both leaves and root samples can be found in Figs. S4 and S5. Turfgrass visual rating (VR) was measured weekly starting from week 2 following guidelines established by The National Turfgrass Evaluation Program (NTEP). The NTEP

turfgrass VR score takes into account color, density, texture, and groundcover, with a scale ranging from 1 (low quality) to 9 (high quality), and 6 representing the minimum acceptable quality (Morris and Shearman, 1998). Additionally, canopy air temperature (T_{canopy}) was measured using an infrared thermometer (Fluke 62 Max, Fluke Co., China), while air temperature (T_{air}) was measured with a precision hygro-thermometer (RH490-EXTEC, US) weekly starting from week 2. The difference between canopy and air temperature was calculated to estimate plant stress (Sapkota et al., 2023a). Both VR and temperature data were collected until week 13 and the bi-weekly moving average was calculated.

All turfgrass samples collected from the field were transported to the laboratory immediately and stored at $-20\,^{\circ}\text{C}$, followed by MQ water rinsing to remove soil particles, and dried using a paper towel. Following that, turfgrass samples were freeze dried (–50 $^{\circ}\text{C}$, 0.1 mbar) for up to 3–4 days using a FreeZone Benchtop Freeze Dryer 70020 from LABCONCO CORPORATION. The final dried turfgrass samples were ground to powder using a pestle and mortar while adding liquid nitrogen into the pestle. The resulting powder samples were weighed and stored at –20 $^{\circ}\text{C}$ until extraction.

Turfgrass sample extraction and cleanup followed an established method (Wu et al., 2012). In brief, 0.1 g of a dried turfgrass sample was spiked with five deuterated PPCP surrogates before extraction. PPCPs were extracted using acetonitrile under sonication. The extractants were dried and reconstituted in 1 mL of methanol and underwent an SPE procedure to prepare the final analytical sample, which were then injected into a HPLC-HRMS/MS (Q Exactive Hybrid Quadrupole Orbitrap; ThermoFisher Scientific) to analyze concentrations of CBZ, SMX, DCF, FLX, and TCS. Further details on the sample preparation and HPLC-HRMS/MS analysis are available in Text S3.

Statistical analyses on PPCPs accumulation and physiological responses were performed using R programming language. A two-way Analysis of Variance (ANOVA) and Tukey's Honest Significance Test (Tukey's HSD) were used to evaluate the statistical significance at a 95 % confidence interval.

3. Results and discussion

3.1. Removal of PPCPs via UV/persulfate in recycled water for irrigation

The UV/persulfate treatment effectively removed PPCPs from recycled water. Results showed that the persulfate photolysis degraded 60% of CBZ, and completely degraded SMX, DCF, FLX and TCS from the untreated recycled water (Fig. 2A). Additionally, the potable water

control contained no PPCP except for a very trace level of FLX at 0.16 μ g/L. SMX, FLX, DCF, and TCS were sensitive to UV light at 254 nm, and they were effectively removed by UV/PS treatment (Fig. S6). CBZ was degraded largely by reactive radicals via persulfate photolysis.

To investigate the percentage contributions of different reactive radicals to CBZ degradation in the recycled water via persulfate photolysis, a comprehensive calculation (Eqs. 1 and 2) was utilized:

$$f_R = \frac{\mathbf{k}_{R.CBZ}[R]_{SS}}{r_{CBZ}} \times 100\% \tag{1}$$

$$\begin{split} r_{\text{CBZ}} &= r_{\text{d}}^{\text{norm}} + k_{\bullet \text{OH,CBZ}} [\bullet \text{OH}]_{\text{SS}} + k_{\text{SO}_{4}^{\bullet-},\text{CBZ}} \big[\text{SO}_{4}^{\bullet-} \big]_{\text{SS}} + k_{\text{CI}^{\bullet},\text{CBZ}} [\text{CI}^{\bullet}]_{\text{SS}} \\ &+ k_{\text{CI}^{\bullet}_{-},\text{CBZ}} \big[\text{CI}_{2}^{\bullet-} \big]_{\text{SS}} + k_{\text{CO}_{3}^{\bullet-},\text{CBZ}} \big[\text{CO}_{3}^{\bullet-} \big]_{\text{SS}} \end{split} \tag{2}$$

where $f_{R\bullet}$ is the percentage of CBZ degradation contributed by individual reactive radicals; r_{CBZ} (s^{-1}) is the experimentally observed *pseudo* first-order degradation rate of CBZ in recycled water with UV/PS; $k_{R\bullet,CBZ}$ ($M^{-1}s^{-1}$) is the second-order rate constant between a reactive radical and CBZ; [R^{\bullet}]_{SS} (M) is the calculated steady-state radical concentration, and r_d^{norm} is the normalized direct photolysis rate (s^{-1}). The calculation was based on major reactions listed in Table S3. Further details on the calculation of radical distribution and normalized direct photolysis rate can be found in Text S4 and Text S5.

The analysis of radical distribution showed that within the UV/PS system, $SO_4^{\bullet-}$ contributed approximately 64 % to the degradation of CBZ (Fig. 2B). Furthermore, the subsequent reaction of $SO_4^{\bullet-}$ with water led to the generation ${}^{\bullet}OH$, which contributed 5 % to the degradation of CBZ. Moreover, due to the alkalinity of the recycled water, HCO_3^{-} reacted with $SO_4^{\bullet-}$, ${}^{\bullet}OH$, and $Cl_2^{\bullet-}$ radicals to generate secondary $CO_3^{\bullet-}$, which contributed approximately 26 % to CBZ degradation. There was a very minimal contribution of 3 % from $Cl_2^{\bullet-}$, due to its low steady-state concentration in the recycled water matrix. In addition, direct photolysis accounted for a negligible 1 % of total CBZ degradation within the UV/PS system. The proposed radical pathway for CBZ degradation by UV/PS in recycled water matrix can be found in Fig. S7.

3.2. Impact of UV/persulfate treatment on PPCPs accumulation in turfgrass

Over the 14-week irrigation period, the 2-week incremental CBZ concentration in turfgrass leaves irrigated with recycled water showed a gradual increase, eventually plateauing after week 12 (Fig. 3A). The plateauing phase indicated the turfgrass entered a dormant phase as the ambient temperature dropped entering into the cool season (Kimball

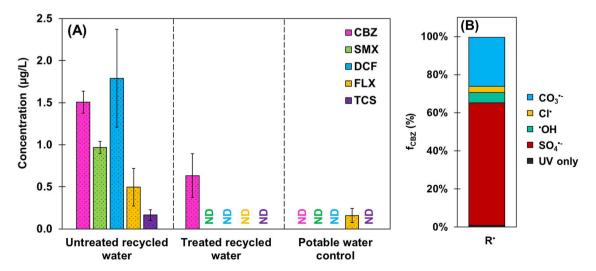


Fig. 2. (A) Initial concentration of PPCPs in three types of irrigation water, and (B) radical distribution of CBZ degradation in UV/PS system. Carbamazepine (CBZ), sulfamethoxazole (SMX), diclofenac (DCF), fluoxetine (FLX), and triclosan (TCS).

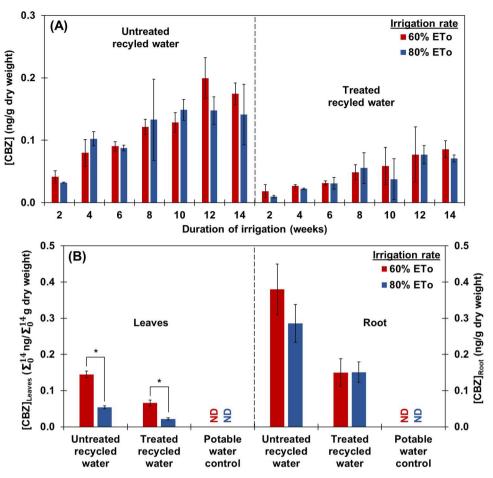


Fig. 3. Carbamazepine (CBZ) accumulation in turfgrass leaves and root using untreated and treated recycled water. (A) 2-week incremental concentration of CBZ in leaves; CBZ was not detected in potable water control, (B) 14-week normalized concentration of CBZ in leaves and final concentration in root. The star mark represents the statistical significance (p < 0.05).

et al., 2017). To further quantify the CBZ accumulation in turfgrass, the 14-week normalized CBZ concentration in turfgrass leaves was calculated by dividing the cumulative mass of CBZ measured in the leaves by the total dry weight of the leaves:

$$[CBZ]_{Leaves} = \frac{\sum_{0}^{14} M_{CBZ}}{\sum_{0}^{14} W_{Leaves}}$$
(3)

where [CBZ]_{Leaves} is in the unit of ng/g dry weight; M_{CBZ} is the cumulative mass of accumulated CBZ in leaves (ng), and W_{Leaves} is the cumulative dry weight of leaves (g). Additionally, the 14-week normalized CBZ concentration in turfgrass root (denoted as [CBZ]_{Root}) was directly measured at the end of the 14-week field trial.

Overall, turfgrass irrigated with UV/persulfate treated recycled water exhibited an approximately 60 % reduction in CBZ accumulation in leaves and roots in comparison to turfgrass irrigated with untreated recycled water (Fig. 3B). This extent of reduction in CBZ turfgrass accumulation was consistent with the level of reduction in CBZ concentration in recycled water after UV/persulfate treatment. Results showed that after UV/persulfate treatment of recycled irrigation water, the 14-week normalized CBZ concentration in turfgrass leaves decreased by 57 % from 0.14 to 0.06 ng/g, and by 60 % from 0.05 to 0.02 ng/g, at an irrigation rate of 60 % ETo and 80 % ETo, respectively (left panel of Fig. 3B). Similarly, after UV/persulfate treatment of recycled irrigation water, the 14-week normalized CBZ concentration in turfgrass roots decreased by 61 % from 0.38 to 0.15 ng/g, and by 46 % from 0.28 to 0.15 ng/g, at an irrigation rate of 60 % ETo and 80 % ETo, respectively (right panel of Fig. 3B). Turfgrass irrigated with potable water control

did not exhibit CBZ accumulation (Fig. 3B).

SMX, DCF, and FLX were detected in turfgrass leaves irrigated with untreated recycled water (Fig. S8). Conversely, when treated recycled water was used, they were not detected in the leaves (Fig. S9), as they were completely removed by UV/PS treatment from the recycled water. Interestingly, TCS was not detected in the turfgrass leaves when irrigated with untreated recycled water. This could be attributed to its hydrophobic nature (log $K_{ow} = 4.76$), which aligns with previous studies where it was not found in the leaves of leafy vegetables (Wu et al., 2014, Wu et al., 2013). However, some studies had reported the potential accumulation of TCS in leaves when soils with a spiked concentration of TCS were used for cultivation (Prosser et al., 2014; Wu et al., 2012). Furthermore, SMX, DCF, FLX, and TCS were found in the turfgrass root when irrigated with untreated recycled water, but they were not detected in the turfgrass root with irrigated with UV/PS treated recycled water (Fig. S9).

Interestingly, CBZ concentration in the turfgrass root was higher compared to that in the leaves (left vs. right panel Fig. 3B). This increase from leaves to root could be attributed to the physicochemical properties of CBZ and the root anatomy of turfgrass. Neutral compounds like CBZ have been shown to preferentially accumulate in roots where the lipid content is high (Collins et al., 2011). Additionally, the high root biomass in turfgrass grass could facilitate its localized accumulation (Qi et al., 2019). SMX and DCF exhibited a similar trend as CBZ, likely due to the high root biomass of turfgrass (left vs. right panel Fig. S9A and B). FLX showed a uniform level of accumulation in both leaves and root, which could be attributed to its very high sorption to soil (left vs. right panel Fig. S9C) (Carter et al., 2014).

3.3. Impact of limited irrigation rate on PPCPs accumulation in turfgrass

Irrigation rate significantly impacted CBZ accumulation in the leaves, with higher concentration observed at the more limited irrigation rate of 60 % $\rm ET_o$ compared to 80 % $\rm ET_o$ for both untreated and treated recycled water (left panel in Fig. 3B). This difference in CBZ accumulation in the leaves at both irrigation rates was statistically significant (left panel in Fig. 3B). A similar trend of CBZ accumulation in root was observed, although it was not statistically significant. Similarly, the accumulation of SMX, DCF, and FLX in turfgrass leaves irrigated with untreated recycled water was influenced by the irrigation rate, with higher accumulation observed at 60 % $\rm ET_o$ compared to 80 % $\rm ET_o$ (left panel of Fig. S9A–C). Similarly, the accumulation of SMX, DCF, FLX, and TCS in turfgrass root irrigated with untreated recycled water was higher at 60 % $\rm ET_o$ compared to 80 % $\rm ET_o$ when irrigated with untreated recycled water (right panel of Fig. S9A–D).

The increase in the PPCPs accumulation in turfgrass leaves when decreasing the irrigation rate from 80 % ET₀ to 60 % ET₀ can be attributed to the plant's osmotic adjustment. PPCPs are introduced to plants through irrigation water uptake, and the transport of water in plants is driven by the water potential gradient between the soil and the atmosphere (Kramer and Boyer, 1995). Variation in soil water availability and atmospheric humidity affects the water potential gradient between soil and atmosphere. Under limited water conditions, plants employ osmotic adjustment that results in the accumulation of various solutes in the cells, including inorganic ions and organic solutes such as sugars, proline, and amino acid, to maintain water potential gradient and facilitate water transport within the plant (Kramer and Boyer, 1995; Patakas et al., 2002; Plaut et al., 2004; WRIGHT et al., 1997). Similarly, the increase in root concentration could be ascribed to the root's osmotic regulation, which effectively maintains root turgor under limited water conditions (GREACEN and Oh, 1972; Osonubi and Davies, 1978; Sharp and Davies, 1979). Therefore, the accumulation of CBZ likely contributes to maintaining adequate turgor pressure, enabling the plant to regulate water flow under limited water condition and adapt to water stress.

3.4. Impact of water treatment and irrigation rate on turfgrass growth and health

VR followed a declining trend regardless of the water quality and quantity treatments, but the reduction in VR was more apparent in turfgrass plots subjected to the lower irrigation rate at 60 % than at 80 % ET₀ (Fig. 4A and B). VR is rated from 1 (low quality) to 9 (high quality), and 6 representing the minimum acceptable quality (Morris and Shearman, 1998). At 80 % ET_o irrigation rate, the minimum acceptable turfgrass VR was consistently maintained throughout the study period, regardless of the water quality type (Fig. 4B). Conversely, with a 60 % ET₀ irrigation rate, VR dropped below the minimum acceptable quality after 8 weeks of irrigation, notably with plots irrigated using untreated recycled water (Fig. 4A). However, the difference was only statistically significant in plots irrigated with untreated recycled water (Fig. 4C). These findings align with prior studies investigating the combined impacts of water quality and irrigation rates on visual quality in warm-season turfgrass species. 32,59,60 For example, previous research evaluating the impacts of 30 % and 100 % actual evapotranspiration (ET_a) rate with saline, sodic, and potable water on the quality of Tifway bermudagrass (Cynodon dactylon) reported higher turf quality at 100 % ET_a regardless of the irrigation water type (Heil et al., 2015). Similarly, another study reported no significant difference between hybrid bermudagrass quality irrigated using potable and recycled water (Lockett et al., 2008).

The canopy and air temperature variance (denoted as ΔT) was measured throughout the turfgrass irrigation trial. Negative ΔT indicates the potential contribution of irrigated landscape to evaporative cooling while drought and water stress decrease the transpiration rate and cause positive ΔT values (Henson et al., 2006; Sapkota et al., 2023b). Overall, only 80 % ET₀ irrigation rate showed ΔT close to zero,

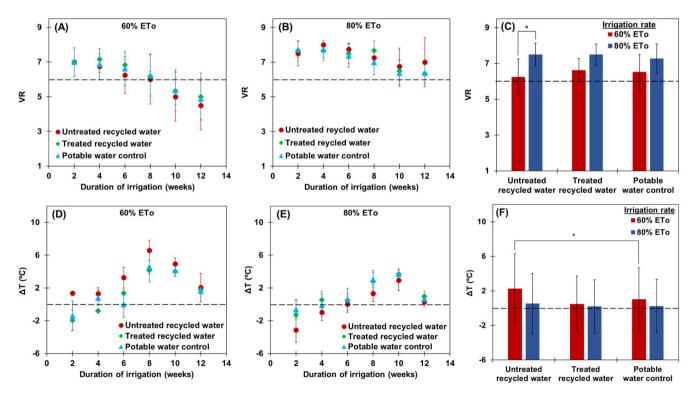


Fig. 4. Physiological responses of turfgrass when irrigated with different types of water under limited irrigation rates. The dotted lines show the minimum turfgrass acceptable quality (6) and maximum threshold of potential water stress (0 $^{\circ}$ C). (A–C) VR of turfgrass leaves, and (D-F) canopy and air temperature variance of turfgrass. The star mark represents the statistical significance (p < 0.05).

indicating less water- stress. ΔT in turfgrass followed an increasing trend regardless of irrigation treatments, and peaked after 8–10 weeks of irrigation, with relatively higher variations at 60 % ET_0 irrigation rate than at 80 % ET_0 (Fig. 4D vs. E). At 60 % ET_0 irrigation rate, plots irrigated with untreated recycled water exhibited a ΔT value that was 1.2 °C higher than plots irrigated with potable control, which was statistically significant (P < 0.05; Fig. 4F). Conversely, at an 80 % ET_0 irrigation rate, using untreated and treated recycled water resulted in a very small ΔT difference in comparison to potable water control that was not statistically significant. These findings are consistent with previous studies, which reported an increase in canopy temperature as the irrigation rate decreases, indicating plant water stress (Burgin, 2021; Haghverdi et al., 2021b; Hejl et al., 2015; Jiang et al., 2009; Orta and Kuyumcu, 2023b).

3.5. Correlation of turfgrass VR and PPCPs accumulation within irrigation rates

To evaluate the impact of irrigation rate and PPCPs accumulation on the visual quality of turfgrass leaves, the normalized cumulative mass of the five PPCPs in the turfgrass leaves during each 2-week measurement of the irrigation trial was calculated using the equation below:

$$M_{Norm} = \frac{M_{PPCPs} - M_{PPCPs}^{min}}{\Delta M_{PPCPs}}$$
 (4)

where M_{Norm} is the normalized cumulative mass of PPCPs, M_{PPCPs} is the cumulative mass of PPCPs in ng, M_{PPCPs}^{min} is the minimum cumulative mass in ng, and ΔM_{PPCPs} is the difference between maximum and minimum cumulative mass in ng.

Overall, the VR exhibited a steeper negative slope of -2.5 at 60 % irrigation rate compared to a shallower slope of -1.2 at 80 % irrigation rate (Fig. 5A vs. B). Additionally, there was no significant difference between the VR of untreated and treated recycled water at a specific irrigation rate (two data series in each of Fig. 5A or B). These results supported that limited irrigation rate strongly affected turfgrass leaf visual quality and was the primary factor influencing turfgrass health. Although prior studies have reported that the accumulation of PPCPs in plants, including wetland plants, ornamentals, and yellow lupine resulted in an increase in reactive oxygen species that inhibit the synthesis of chlorophyll pigments and damage plant tissues, reducing the greenness (yellowing) of leaves (Ravichandran and Philip, 2021; Rydzyński et al., 2017; Yan et al., 2016), our findings suggest that PPCPs accumulation was not the primary factor influencing turfgrass leaf visual quality.

4. Conclusions

This study demonstrated that UV persulfate treatment of recycled water is beneficial to reducing PPCPs accumulation in St. Augustine turfgrass, as a model urban plant and important perennial forage grass, due to its effectiveness in degrading various PPCPs. This treatment technology capitalizes on the unique photochemistry of sulfate radicals within the recycled water matrix, alongside secondary radicals generated through interactions with the water matrix. Through this advanced treatment, PPCPs are effectively removed from recycled water, making it suitable for irrigation and significantly mitigating PPCPs accumulation in turfgrass. Furthermore, changes in limited irrigation rates exhibited a significant impact on PPCPs accumulation in turfgrass, with more PPCPs accumulated at a more limited irrigation rate, which indicates the importance of optimizing the irrigation rates for crop irrigation. The research finding also suggests that under limited water irrigation conditions, the quality of water becomes critical as turfgrass accumulates more PPCPs.

Our result showed that applying the nominal suggested irrigation rate of 60 % $\rm ET_0$ is not enough to maintain the aesthetic values of St. Augustine turfgrass over summer in semi-arid environment of inland

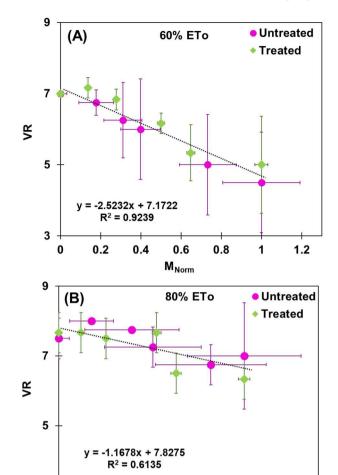


Fig. 5. Correlation of VR and cumulative mass of PPCPs in turfgrass leaves irrigated with untreated and treated recycled water at different limited irrigation rates. (A) $60 \% ET_0$ and (B) $80 \% ET_0$

M_{Norm}

0.6

0.8

1.2

1.4

southern California. Our statistical analysis also revealed that, in a short timescale, only irrigation rate, and not the presence of PPCPs, had a significant impact on turfgrass growth. Applying more water, as expected, decreased canopy temperature which indicates a higher ET rate and in turn more potential evaporative cooling benefits.

Although the duration of this field study was limited to one season, the results provide fundamental insights into the combined effect of UV/persulfate treated recycled water and changing irrigation rates on the fate and transport of PPCPs, which are critical to exploring long-term impacts. Commercially available high-intensity UV lamps and flow-through reactors can facilitate the scaling-up of the UV/PS treatment for on-site application for ready use of PPCP-free recycled water for irrigation. Future research is needed to investigate the long-term implications of UV/AOP treatment and different irrigation rates to manage recycled water and minimize PPCPs accumulation in various edible crops within a field and/or greenhouse settings. Effective management of recycled water for edible crop irrigation will ensure food safety and sustainable growth.

CRediT authorship contribution statement

Ananta Azad: Writing – review & editing, Writing – original draft, Methodology, Conceptualization. **Jean Claude Iradukunda:** Writing –

3

0.2

0.4

review & editing, Writing – original draft, Methodology, Conceptualization. Yujie Men: Methodology. Amir Verdi: Writing – review & editing, Supervision, Methodology, Funding acquisition, Conceptualization. Haizhou Liu: Writing – review & editing, Supervision, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2024.122009.

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