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Mitigating the Accumulation of Pharmaceutical and Personal Care Products in Crops Irrigated With Recycled Water: Integrating UV/Persulfate Water Treatment and Deficit Irrigation

A Dissertation submitted in partial satisfaction
of the requirements for the degree of

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by

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ABSTRACT OF THE DISSERTATION

Mitigating the Accumulation of Pharmaceutical and Personal Care Products in Crops Irrigated With Recycled Water: Integrating UV/Persulfate Water Treatment and Deficit Irrigation

by

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Global water scarcity poses a major challenge to agricultural productivity. This dissertation investigates the use of recycled water for irrigation, focusing on the occurrence of pharmaceutical and personal care products (PPCPs), their accumulation in edible crops, and the impact of irrigation water quantity on this accumulation. Analysis reveals that PPCPs, including sulfamethoxazole, are present in recycled water at concentrations ranging from 130-1400 ng/L in secondary effluent and 25-400 ng/L in tertiary effluent. The study shows that PPCP uptake and accumulation vary between leafy and fruity vegetables, with diclofenac and fluoxetine being most prevalent in each, respectively. Key factors affecting PPCP accumulation include transpiration rate and osmotic adjustments under limited water availability. The research explores two strategies: recycled wastewater effluent irrigation and limited irrigation rates, aimed at

mitigating PPCPs accumulation and conserving irrigation water. A 14-week field trial on St. Augustine turfgrass assesses the effects of UV persulfate (UV/PS) treatment and limited irrigation rates on PPCPs accumulation and plant health. Results indicate that UV/PS treatment effectively removes 60% of carbamazepine and over 99% of other PPCPs from recycled water, significantly reducing PPCP levels in turfgrass leaves and roots. Limited irrigation at 60% ET_o increases carbamazepine accumulation and canopy temperature, suggesting higher water stress compared to 80% ET_o. Additionally, greenhouse experiments with lettuce, carrot, and tomato, using PPCP-spiked recycled water, UV/PS treated recycled water, and tap water at 60%, 80%, and 100% crop evapotranspiration rates (ET_c), show that UV/PS treatment reduces PPCP accumulation by over 99%. Lettuce benefits from reduced irrigation, while carrot and tomato show increased accumulation due to osmotic adjustment. Combining UV/PS treatment with deficit irrigation conserves water, maintains crop yield, and minimizes PPCP accumulation. The findings offer valuable insights for developing strategies to safely and effectively reuse recycled water in agriculture, supporting sustainable practices and improving food safety.

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Chapter 1

Introduction

1.1 Water stress and water reuse for agricultural irrigation

Water scarcity driven by growing freshwater use and depletion of usable freshwater resources is one of the biggest challenges in the world of 21st century. Currently, 700 million people in 43 countries face water scarcity (annual supply below 1,700 m^3 per person), and by 2025, 1.8 billion people may live in conditions of absolute scarcity (below 500 m^3 per person).[1] As global water demand rises, agriculture, accounting for 70% of global water use, is particularly threatened.[2] Furthermore, agriculture is the one of the major users of water in United States, accounting for 80% nations water use.[3] Recycled water, a product of wastewater treatment plant, offers a sustainable solution for irrigation. In arid regions, it has been used for agricultural and landscape irrigation. The 2015 survey by California's State Water Resources Control Board and Department of Water Resources reported a 45,000 acre-feet increase in recycled water use since 2009, totaling 714,000 acre-feet, with 31% for agricultural and 18% for landscape irrigation.[4]

1.2 Recycled water for irrigation

Recycled water used for irrigation is primarily regulated to protect human health, as it contains pathogenic microorganisms and various organic and inorganic constituents that may lead to adverse human health effect. Over the years regulations have been modified and enforced to minimize the potential transmission of infectious diseases by microbial pathogen.[5] California has been at the forefront of establishing comprehensive laws, regulations, and policies regarding recycled water use. Title 22 of the California Code of Regulations specifies treatment requirements and permissible uses based on the treatment

level.[6] For example, food crops irrigated with recycled water, the USEPA mandates a high level of disinfection, ensuring total coliform levels are ≤2.2/100mL or fecal coliform are undetectable.[7]

1.3 Presence of pharmaceutical and personal care products (PPCPs) in recycled water

One potential challenge of promoting recycled water use for agricultural irrigation is the presence of pharmaceutical and personal care products (PPCPs). Pharmaceuticals, used to treat or prevent diseases, and personal care products, which enhance daily life quality, are excreted from human body and enter the municipal sewage system.[8] Recent studies have showed that conventional wastewater treatment (biological activated sludge, tertiary filtration and disinfection) does not efficiently remove PPCPs in the process and they are usually present in the effluent with levels ranging from ng/L to μg/L.[9–16] When this treated water is used for irrigation, PPCPs can be transferred to crops from soil through root uptake and translocate to leaves and fruits (Figure 1-1). The increasing use of PPCPs, driven by population growth and advancements in healthcare and lifestyle, exacerbates this issue. Studies have shown that residual PPCPs can reduce plant growth, increase stress and toxicity levels, and pose potential human health risks.[17,18]

1.4 UV/persulfate (UV/PS) for PPCPs removal from recycled water

UV-Advanced Oxidation Processes (UV-AOP) have emerged as an effective technology for the efficient removal of PPCPs from recycled water.[19] Conventional biological treatment processes in wastewater treatment plants are generally ineffective in removing

most PPCPs.[20] For example, traditional sewage treatment processes remove only 49-60% of anti-inflammatories, around 65% of 17β-estradiol, and 60% of sulfamethoxazole.[21] The traditional UV/H_2O_2 generates hydroxyl radicals ($^{\bullet}OH$), which degrade PPCPs rapidly.[22] However, UV/persulfate (UV/PS) has received increasing attention due to its high capability for the degradation of PPCPs. UV/PS can generate sulfate radicals ($SO_4^{\bullet-}$), which react comparatively faster with the PPCPs than $^{\bullet}OH$.[23] Additionally, UV/persulfate process is more energy saving than conventional UV/H_2O_2 process[24]. Additionally, UV/PS can produce secondary radicals like chlorine atom ($Cl^{\bullet}$) and carbonate radical ($CO_3^{\bullet-}$) via reactions between $SO_4^{\bullet-}$ and chloride/bicarbonate in water matrix that can further degrade PPCPs.[25–27] Despite its advantages, the application of UV/persulfate for treating agricultural irrigation water remains unexplored, requiring further investigation to understand its effectiveness in real municipal wastewater effluent.

1.5 Deficit irrigation for irrigation water management and its impact on PPCPs accumulation

Optimizing irrigation rates by applying water below the evapotranspiration (ET) requirement while maintaining plant health is an emerging practice to address water scarcity.[28–30] Deficit irrigation, which involves providing less water than the full crop evapotranspiration (ET_c) needs, has shown promise in conserving water and enhancing productivity. Studies indicate that warm-season turfgrass species, such as hybrid bermudagrass, are more drought-tolerant and perform well under limited irrigation compared to cool-season species.[31] For example, 60% reference ET (ET_o: ET from a standardized surface) is often considered sufficient for warm-season turfgrass species.[32,33]

Furthermore, deficit irrigation increases water productivity and profitability.[34] Nevertheless, deficit irrigation also influences various physiological responses in crops, such as stomatal closure, decreased photosynthetic rates, and decreased osmotic pressure.[35–37] Additionally, it can lead to accumulation of solutes, such as proline, amino acids, and sugars in crops.[38,39] Combining recycled water use with various irrigation levels can significantly enhance water conservation, reduce demand, and address water scarcity. However, the compound effect of deficit irrigation on crop yield and PPCP accumulation under water reuse scenarios remains unexplored and warrants further investigation.

1.6 Impact of crop type on PPCPs accumulation

The influence of crop type (e.g., leafy, root, and fruity vegetables) on the accumulation of PPCPs under deficit irrigation remains largely unexplored. Previous research has mainly examined PPCPs accumulation scenarios after these contaminants enter a crop's vascular system via root uptake.[40–42] Once inside the crop, PPCPs can translocate to different organs primarily through transpiration.[43,44] This movement of PPCPs within the plant system is influenced by the differences in water potential [45]. Leafy vegetables, root crops, and fruity vegetables may exhibit distinct behaviors in PPCP uptake and translocation due to their unique physiological characteristics. To date, a systematic and mechanistic understanding of PPCP accumulation across various crop types under water deficit conditions has not been comprehensively investigated. This knowledge is crucial for developing effective irrigation strategies and ensuring food safety when using recycled water for irrigation.

1.7 Amis and scope

The overall goal of this dissertation is to advance understanding of the impact of UV/PS on recycled water quality and deficit irrigation on the accumulation of PPCPs in turfgrass and edible crops. This research aims to enhance water use efficiency and crop safety by integrating UV/PS as an advanced water treatment technology and deficit irrigation as an optimized irrigation strategy.

To achieve this, the study begins with a comprehensive literature review aimed at evaluating the impact of recycled water quality and quantity on PPCP accumulation in various edible crops. This review covers the occurrence of PPCPs in recycled water used for irrigation, the potential for bioaccumulation in different crop types, and how irrigation water quantity influences PPCP accumulation based on crop type.

Building on this, a unique field study is conducted with St. Augustine grass, a warm-season turfgrass, which is irrigated with both untreated and treated recycled wastewater effluent at two irrigation rates (60% and 80% of reference evapotranspiration, ETo). This part of the research investigates the combined efficacy of UV/persulfate (UV/PS) treatment and limited irrigation in minimizing PPCP accumulation, while also assessing the effects on turfgrass aesthetic value and physiological stress.

Additionally, a pioneering greenhouse experiment is carried out using recycled municipal wastewater effluent under deficit irrigation conditions. This experiment aims to examine the reduction of PPCP accumulation in three types of edible crops through UV/PS treatment, integrate UV/PS treatment with deficit irrigation to enhance crop yield and

water use efficiency, and explore the distinct mechanisms of PPCP accumulation under deficit irrigation across different vegetable types.

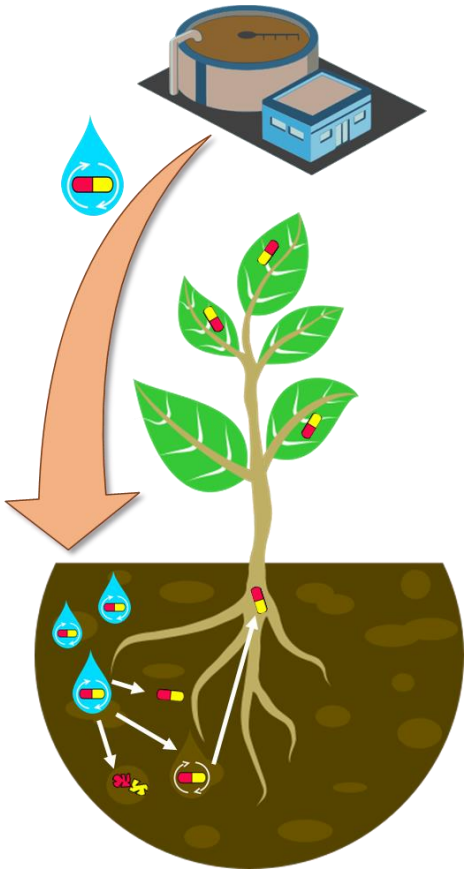

Figure 1-1 Fate of pharmaceutical and personal care products (PPCPs) in the soil-plant system.

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Chapter 2

Pharmaceutical and Personal Care Products in Recycled Water for Edible Crop Irrigation: Understanding the Occurrence, Crop Uptake, and Water Quantity Effects

Manuscript accepted on *Agriculture Water Management*

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Abstract

Global water scarcity poses a great challenge to agriculture productivity. Recycled water offers a promising alternative for agricultural irrigation, yet residual pharmaceutical and personal care products (PPCPs) in recycled water can transfer to edible crops during irrigation, and adversely affect food safety. Furthermore, irrigation water quantity can influence the accumulation of PPCPs in edible crops. This study comprehensively investigates the use of recycled water for agricultural irrigation by critically reviewing three key components: PPCPs occurrence in recycled water, their accumulation in edible crops, and the impact of water quantity on PPCPs accumulation. Literature analysis showed that PPCPs were present from 130-1400 ng/L in secondary effluent and 25-400 ng/L in tertiary effluent, with sulfamethoxazole being the most prevalent in both effluents. PPCPs uptake and accumulation varied between leafy and fruity vegetables, with diclofenac accumulating highest in leafy vegetables and fluoxetine in fruity vegetables. Furthermore, the water requirement of leafy and fruity crops vary throughout the growing season. In leafy vegetables, PPCPs accumulation in leaves is influenced by transpiration rate, with reduced accumulation occurring under limited water availability due to slower transpiration. In fruity vegetables, osmotic adjustment drives the water transport in fruits, leading to increased PPCPs accumulation under limited water conditions. This study contributes insights into PPCPs occurrence, accumulation, and irrigation water quantity, aiding in the development of effective strategies for recycled water use in agriculture.

Keywords: Recycled water irrigation, occurrence, crop accumulation, water quantity.

2.1 Introduction

Water scarcity poses a great challenge for global food production and food security. The agriculture sector accounts for 70% of global water use, and is constantly competing with municipal and industrial sectors for a limited water supply.[1,2] In the United States, agriculture is the major user of fresh water, accounting for more than 40% of the national total fresh water withdrawals in 2015.[3] Faced with severe fresh water scarcity, recycled water from municipal wastewater effluent can be a valuable alternative resource for agricultural irrigation. Historically, recycled water has been used for irrigation in many arid regions.[4] For example, 85% of treated wastewater is recycled for agricultural irrigation in Israel.[5] California and Florida also have been using recycled water to irrigate selective crops.[6] Globally 20 million hectares in 50 countries are estimated to practice recycled water irrigation, accounting for 10% of total irrigated land.[7]

One pressing challenge on recycled water irrigation is the risk of pharmaceutical and personal care products (PPCPs) accumulation in food and food safety. Pharmaceuticals are medicinal drugs to treat or prevent human and animal disease, and personal care products are used to improve the quality of daily life. PPCPs enter the municipal sewage system, after human consumption.[8] In agro-food system, recycled water is the primary source of PPCPs.[9,10] Recent studies have shown that conventional wastewater treatment processes, such as secondary and tertiary treatment, do not completely remove PPCPs and they are usually present in the effluent with levels ranging from ng/L to μg/L.[11–18] The secondary effluent is treated by a conventional activated sludge process.[19,20] The tertiary effluent receives advanced treatment including membrane filtration (*e.g.*,

microfiltration) and/or followed by disinfection (chlorine or UV).[21,22] When treated wastewater effluent is used for irrigation, PPCPs can transfer from irrigation water to crops via root uptake, and translocate to leaves and fruits.[23] These persistent trace organic chemicals have also been reported to substantially reduce plant growth, increase plant stress and induce toxicity.[24,25]

Water quantity emerges as a critical factor significantly impacting agricultural irrigation and exerting profound effects on crop growth, yield, and overall productivity.[26] Different crops have varying water requirements at different growth stages and a reduced water amount can impact the balance in a negative way.[27] Beyond these visible impacts, limited water quantity can trigger the accumulation of inorganic and organic solute in crops posing potential harm. The intricate relationship between limited water quantity and physiological responses in crops can lead to stomatal closure, decreased photosynthetic rates, and decreased osmotic pressure.[28–30] Moreover, studies have indicated that limited water quantity can also lead to the accumulation of critical solutes, including proline, amino acids, and sugars in crops.[31,32]

Comprehensive insight into the impact of irrigation water quality and quantity on PPCPs accumulation and crop health are important. First, the beneficial use of recycled water for irrigation depends on the extent of treatment and the residual PPCPs levels. For example, Title 22 of California Code of Regulations describes tertiary recycled water can be used for unrestricted irrigation of food crops, while the use of secondary recycled water is restricted to surface irrigation only to avoid contact with the edible crops.[33] Despite

previous reports on the occurrence, [19,21,22,34–39] there lacks a critical synthesis of the occurrence of PPCPs in recycled water for irrigation. Second, although the accumulation of PPCPs in different crops when irrigated with recycled water was previously reported, [40,41] differences in crop species, crop lipid content, metabolism system and transpiration rate can affect the uptake and translocation of PPCPs.[42–45] Understanding the accumulation of PPCPs in different crops such as leafy and fruity crops will provide valuable insight to food safety using recycled water irrigation.

Finally, PPCPs uptake in plants has been evaluated where PPCPs enter a plant's vascular system via root uptake.[46–48] Once within the system, PPCPs have the potential to translocate to different organs primarily influenced by transpiration.[49,50] This movement of PPCPs in the plant system is linked to water driven by water potential difference.[51] Despite this understanding, a knowledge gap exists regarding the influence of various types of crops (e.g., leafy, fruity) on the uptake of PPCPs with varying water quantities.

Thus this study aims to assess the impact of recycled water quality and quantity on PPCPs accumulation in different edible crops by evaluating existing literature to understand the occurrence of PPCPs in recycled water for irrigation, bioaccumulation potential of PPCPs in various crops, and finally the impact of irrigation water quantity on PPCPs accumulation as a function of crop type.

2.2 Methods and Materials

Eight widely occurring PPCPs were selected as candidate compounds, including carbamazepine (CBZ), diclofenac (DCF), fluoxetine (FLX), gemfibrozil (GMF),

naproxen (NPX), sulfamethoxazole (SMX), triclosan (TCS), and trimethoprim (TRM).[52–54] These chemicals presented a wide range of hydrophobicity (K_{ow}) and acidity (pK_a) values.[23,55,56] The natural logarithmic value of K_{ow}, expressed as logK_{ow}, is a crucial parameter for predicting the accumulation of contaminants in various environmental compartments, including water, soil, and plants. They are also among the top most prescribed PPCPs in the US. Data on the chemical properties and prescription numbers of the PPCPs are provided in Table S1 of the Supporting Information (SI).

To compile data on PPCPs occurrence, concentrations of these compounds in secondary and tertiary wastewater effluent from various global studies were analyzed. These studies include data from countries such as the USA, Spain, Canada, Sweden, Austria, Japan, Switzerland, the UK, Australia, and Germany. were Both secondary and tertiary effluents were evaluated due to their common use in agricultural, landscape, and golf course irrigation.[57] For sites with multiple sampling events, data from each sampling event were collected, and the mean concentration was calculated for analysis. Detailed data on the occurrence of selected PPCPs in secondary and tertiary effluent are presented in Table S3 and S4.

To quantify the bioaccumulation effects of PPCPs in crops, data from prior studies on PPCPs accumulation in crops grown in hydroponic systems were evaluated. Detailed bioaccumulation data are provided in Table S5. A total of 9 vegetables were investigated in this study, including 6 leafy vegetables (*i.e.*, lettuce, spinach, cabbage, collard, Wisconsin fast plant, and cauliflower) and 3 fruity vegetables (*i.e.*, cucumber, pepper,

and pea). Because hydroponic systems have been utilized as a standard method for plant biology research[58], which provides insights into the influence of PPCPs physiochemical properties on crop uptake without the complicating factors of soil properties.[59] It was reported that a majority of prior studies examining PPCPs uptake and accumulation in plants were conducted using hydroponic systems.[60] In addition, the bioconcentration factor (BCF) for each PPCPs in leafy and fruity vegetables was obtained from prior literature that used environmentally relevant concentrations of PPCPs in the growth medium. BCF is the ratio of the PPCPs concentration in the plant tissue to its concentration in the growth medium.[61] Two BCF values were calculated from prior literature, representing accumulation in root (BCF_{root}) and the above-root tissues of leaf and steam combined ($BCF_{leaf/stem}$).

To understand the impact of recycled water quantity and crop type on the accumulation of PPCPs, a systematic analysis of peer-reviewed literature was conducted. The methodology employed a snowballing approach to identify major studies focusing on several key concepts: (1) water transport and water potential difference in plant system, (2) nutrient uptake at different water quantity, (3) solute accumulation in plant leaves and roots at various water quantity levels, and (4) impact of water quantity on transpiration rate. Furthermore, the monthly water quantity requirements of leafy and fruity vegetables were calculated as crop evapotranspiration: $ET_C = ET_o * K_{c;}$ where ET_C is the crop evapotranspiration in unit of mm, ET_o (mm) is the reference evapotranspiration collected from the California Irrigation Management Information System (CIMIS) for at Riverside, California in 2023 as an example (station 44), and K_c is the average crop coefficient of

each crop. The K_c values and corresponding water requirements of the plants are provided in Tables S2 and Figure S7. Due to limited information regarding the K_c values of collards and Wisconsin fast plants, these crops were excluded from water requirement analysis, as collards are considered specialty crops and Wisconsin fast plants are primarily used in education and research settings.

2.3 Results and Discussion

2.3.1 PPCPs occurrence in treated wastewater effluent

The mean concentration of the eight selected PPCPs in the secondary wastewater effluent ranged between 130 and 1400 ng/L, with SMX exhibiting the highest concentration and fluoxetine the lowest concentration (Figure 1A). Concentrations of NPX, GMF, and TRM ranged between 500 and 800 ng/L, followed by concentrations of CBZ, DCF, and TCS ranging between 200 and 400 ng/L. The ranking of the PPCP occurrence in the secondary wastewater effluent followed the order of SMX > NPX > GMF > TRM > CBZ > DCF > TCS > FLX (Figure 1A). The mean concentration of PPCPs in the tertiary wastewater effluent ranged between 25 and 400 ng/L (Figure 1B). Compared to the secondary wastewater effluent, an additional 37%-93% of PPCPs were removed by tertiary treatment processes (Figure S1). For example, NPX concentration decreased by 93% to 55 ng/L in the tertiary effluent. Accordingly, PPCP occurrence in the tertiary wastewater effluent followed the order of SMX > TRM > GMF > CBZ > TCS > NPX > DCF > FLX (Figure 1B). The detailed range of PPCPs occurrence in secondary and tertiary effluent is provided in Table S6.

Activated sludge is the most common biological secondary wastewater treatment. PPCPs are mainly removed via biological degradation and adsorption by the activated sludge.[62–65] Chemicals with low octanol-water partition coefficients ($\log K_{ow} < 3.0$) were reported to have low adsorption capacity to sludge, which leads to low removal efficiency.[66] For example, SMX has the lowest octanol-water partition coefficient ($\log K_{ow} = 0.89$) and exhibited the highest concentration in the secondary effluent, while FLX has the highest octanol-water partition coefficient ($\log K_{ow} = 4.05$) and exhibited the lowest concentration in the secondary effluent (Figure S2). The lower removal efficiency for NPX can be ascribed to less hydrophobic nature ($\log K_{ow} \approx 3$).[67]

Tertiary effluent received membrane filtration and/or followed by UV or chlorine disinfection as a part of the treatment process. The removal of PPCPs during membrane filtration was reported to be associated with hydrophobicity ($\log K_{ow}$) of PPCP, where compounds with $\log K_{ow} < 3$ had low removal efficiency and compounds with $\log K_{ow} > 3$ had higher removal efficiency.[68,69] For example, the high residual concentration of SMX, TRM, and CBZ in tertiary effluent could be attributed to their low hydrophobicity ($\log K_{ow} < 3$) (Figure S3). Similarly, TCS, NPX, DCF, and FLX were found at low concentration in the tertiary effluent due to high affinity to the membrane ($\log K_{ow} > 3$) during the tertiary treatment (Figure S3). Additionally, PPCPs can be degraded via UV or chlorine disinfection process.[70,71]

2.3.2 Bioaccumulation of PPCPs in various vegetable crops

Overall, the accumulation of PPCPs in leafy vegetable crops is higher than that in fruity vegetable crops. The bioaccumulation analysis of leafy vegetables showed the potential of PPCPs accumulation in leafy vegetables followed the order of DCF > NPX > FLX > TCS > CBZ > TRM > GMF > SMX (Figure 2A). In contrast, the bioaccumulation of PPCPs in fruity vegetables exhibited a different trend compared to leafy vegetables, following the order of FLX > TRM > CBZ > NPX > GMF > DCF > SMX > TCS (Figure 2B). Leafy vegetables accumulated higher levels of PPCPs than fruity vegetables, most likely due to their minimal barrier to PPCPs translocation from roots to the edible parts *i.e.*, the leaves themselves, resulting in higher concentration of PPCPs in the leaves.[72] Moreover, this difference can be attributed to the ionizable nature of PPCPs, facilitating their movement from xylem to phloem and vice versa, and predominantly following the direction of the transpiration stream and accumulating mostly in transpiring organs, *i.e.*, leaves.[73,74]

The accumulation of PPCPs also exhibited variability depending on the type of vegetable crops. For example, DCF demonstrated the highest accumulation in leafy vegetables (Figure S4A-B), while it exhibited the lowest accumulation in fruity vegetables (Figure S5A-B). Additionally, the accumulation of PPCPs was influenced by the location within the vegetables (*i.e.*, root *vs*. leaf/stem), as analyzed by BCF values in different sections of the leafy and fruity vegetables (denoted as BCF_{root} *vs*. $BCF_{leaf/stem}$). For example, DCF displayed a remarkably high accumulation potential in the root of leafy vegetables, while its accumulation potential in the leaf/steam was comparatively low (Figure 4A-B). The

variation in PPCP uptake by different parts of vegetables can be influenced by various biological and physicochemical factors, as well as the environmental conditions in the hydroponic system. Hydrophilic compounds are prone to translocate from root to other regions in the plant, while hydrophobic compounds tended to remain in the roots, mainly due to the sorption of PPCPs.[61] For example, hydrophobic DCF (logK_{ow} = 4.51) mostly accumulated in the roots of leafy vegetables (Figure S4). In contrast, hydrophilic CBZ (logK_{ow} = 2.45) was found in leaf/steam at higher concentrations than in root (Figures S4-S5). Additionally, root lipid content was reported as a good indicator for root uptake and it was positively correlated with root concentration.[75,76] Another study reported a linear relationship between the crop root uptake of neutral insecticides with logK_{ow} in the range of 2-5.[77] Both leafy and fruity vegetables showed a positive correlation between values of log BCF_{root} and logK_{ow} for all PPCPs (Figure S6A-B). Moreover, the physiological properties and the ionic properties of PPCPs can also influence their uptake in different plants.[60,78]

2.3.3 Water quantity requirements and its effects on PPCPs accumulation across plant types

The uptake of PPCPs is also impacted by the recycled water quantity during irrigation of crops. The water requirements of crops are influenced by both crop species and prevailing climatic conditions. For example, leafy and fruity crops exhibit their highest ET_C in summer, peaking at around 190 mm, before gradually declining to 76 mm as the temperature cools down throughout the season annually (Figure S7). The amount of applied water relative to required ET_C plays a crucial role in crop cultivation, impacting

plants' ability to uptake organic and inorganic solutes, as well as PPCPs, which varies across different plant types.

PPCPs are introduced to plants through water uptake via the irrigation water, and the transport of water in plants is driven by the difference in water potential between the media and the atmosphere.[79] Water potential, denoted by Ψ, is the sum of osmotic, matric, gravimetric, pressure, and overburden potentials.[80] Variation in water availability in the media and atmospheric humidity modulate the water potential gradient between the media and atmosphere. Accordingly, water potential gradient changes within different plant parts including root, stem, and leaves. Therefore, the movement of water from the growing media to the air via crops follows the gradient of water potential (Figure 3) as $\Psi_{media} > \Psi_{root} > \Psi_{stem} > \Psi_{leaves} > \Psi_{air}$, where Ψ_{media}, Ψ_{root}, Ψ_{stem}, Ψ_{leaves}, Ψ_{air} is the water potential of the media, root, stem, leaves, and air, respectively.

In leafy crops, PPCPs accumulation can be attributed to transpiration, a fundamental process of influencing water flow to the leaves (Figure 3). Transpiration effectively generates a negative water potential in the leaves, prompting the flow of water through the xylem towards the site of evaporation in leaves.[81,82] Therefore, under normal condition, the accumulation of solutes and nutrients can increase via increased transpiration rate.[83] Conversely, under limited water availability, solute accumulation is reduced due to slower transpiration rate. Our recent study a similar trend that CBZ accumulation in lettuce was lower under deficit irrigation at 60% ET_C compared to full irrigation at 100% ET_C due to reduced transpiration rate.[84]

Additionally, the water flow in leafy plants via transpiration is also maintained by the stomata in the leaves. Anisohydric leafy plants like lettuce has the ability to keep the stomata open under limited water condition to sustain growth.[85] Consequently, this physiological trait leads to lower solute accumulate mainly due to slower transpiration rate.[86,87] Conversely, isohydric leafy plants close their stomata under limited water conditions to prevent water loss from transpiration pathways.[88] In the absence of stomatal activity under limited water quantity, these plants employ osmotic adjustment to maintain the water potential gradient and facilitate increased solute accumulation. This adaptive response encompasses the accumulation of various solutes, including inorganic ions and organic solutes such as sugars, proline, and amino acids.[89–91] For example, spinach has been showed to have increased proline accumulation due to stomatal closure under limited water conditions via osmotic adjustment.[92]

In fruity crops, similar to leafy crops, the maintenance of a negative water potential gradient for water transport is essential, facilitated by water loss to the air through the fruit surface due to transpiration (Figure 3).[93] However, a challenge arises in certain fruits where the absence of stomata impedes the maintenance of water potential gradient through transpiration.[94] In response to this, fruity crops employ osmoregulation as a mechanism to sustain water transport, resulting in increased organic and inorganic solute accumulation under limited water availability. For example, fruity vegetables can accumulate solutes via osmotic adjustment when water availability is limited.[95] Our recent study also demonstrated that carrot and tomato accumulated more CBZ under deficit irrigation at 60% ET_C compared to full irrigation at 100% ET_C, due to osmotic

adjustment.[84] Another study has demonstrated a tenfold increases in free proline accumulation in peas under conditions of limited water.[96] Therefore, the uptake of PPCPs is impacted by the irrigation water quantity and depends on the type of crops species and prevailing climatic conditions that affect the evapotranspiration rate.

2.4 Conclusion

The presence of PPCPs in recycled water underscores a potential risk to irrigation water quality, as these compounds are prevalent in recycled water and have the potential to accumulate in various crops. The bioaccumulation of PPCPs in vegetable crops raises concern about food safety as higher accumulation was observed in leafy vegetables compared to fruity vegetables. Additionally, the quantity of irrigation water impacts PPCPs accumulation, with variations observed across crops type due to differences in transpiration rate and osmotic adjustment.

To address these issues, an effective water treatment technology needs to be developed to efficiently remove PPCPs from recycled water for irrigation and consequently reduce the accumulation of PPCPs in food crops. Additionally, there is a critical need for comprehensive and systematic monitoring of PPCPs in recycled water to accurately assess irrigation water quality and the effectiveness of treatment processes. Further research is required to elucidate PPCPs accumulation patterns across different crop types. While this study provides valuable insights into the occurrence and fate of PPCPs in water-crop systems, future research should focus on closing the existing research gaps. Prioritizing the development of advanced water treatment technologies, such as UV-advanced oxidation processes, will be essential to enhance the removal of PPCPs from

recycled water for irrigation. Controlled field and greenhouse studies across a range of leafy, fruity, and root crops are needed to better understand crop-specific accumulation patterns. Additionally, future research should investigate irrigation rate optimization as a strategy to conserve irrigation water while assessing its impact on PPCPs uptake. These studies will provide crucial data to inform sustainable irrigation practices and mitigate potential food safety risks associated with PPCPs in crops irrigated with recycled water.

Acknowledgement

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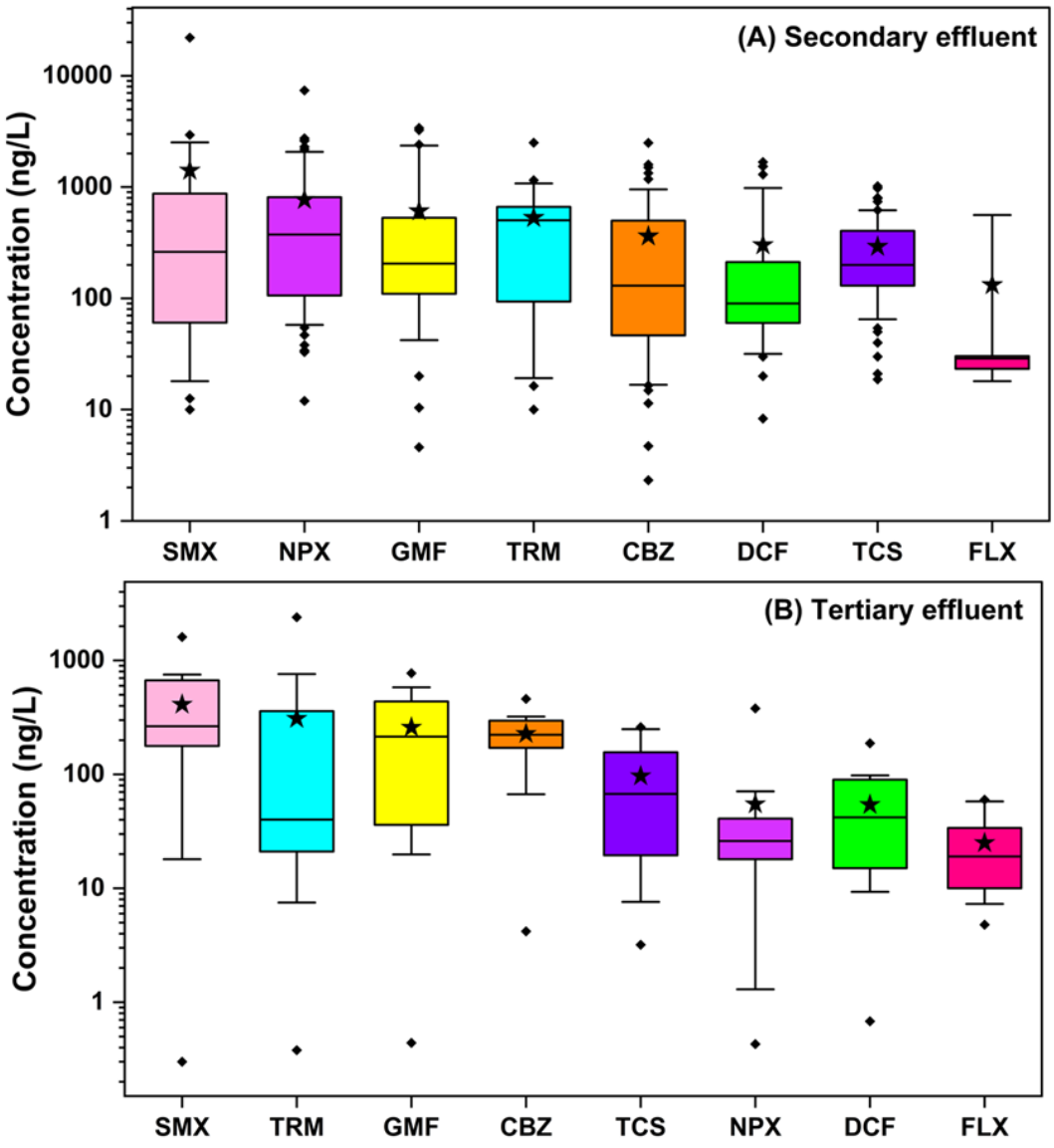

Figure 2-1 Occurrence of PPCPs in municipal wastewater effluents. (A) Secondary effluent; (B) Tertiary effluent. The top and bottom whiskers represent 90th and 10th percentile. The ends of the box are 1st and 3rd quartile. The median is marked by the horizontal line inside the box. Top and bottom diamonds are the outliers. Star represents the mean concentration. Sulfamethoxazole (SMX), trimethoprim (TRM), gemfibrozil (GMF), carbamazepine (CBZ), triclosan (TCS), naproxen (NPX), diclofenac (DCF), and fluoxetine (FLX).

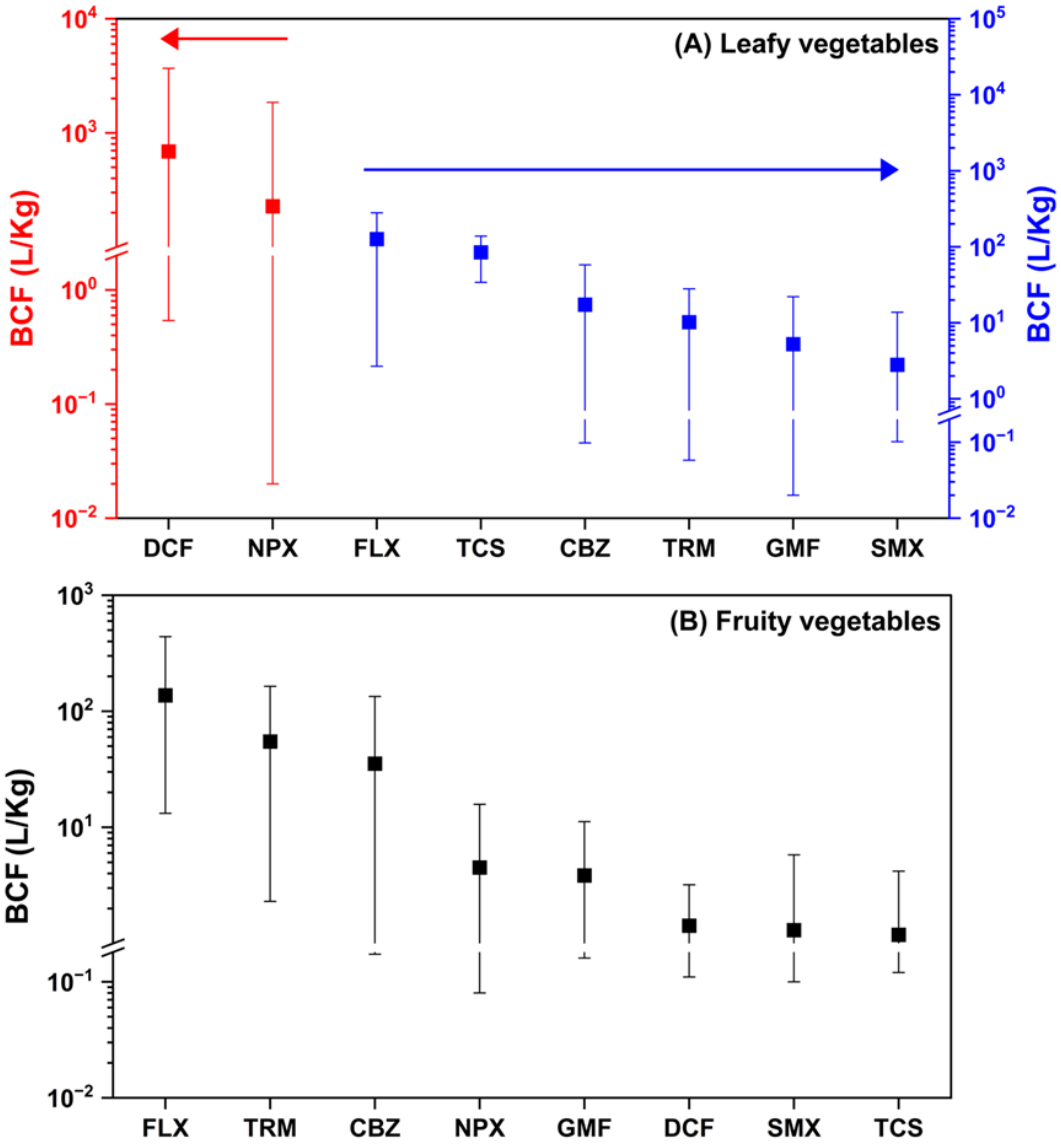

Figure 2-2 The bioconcentration factors (BCF) of PPCPs in edible crops in hydroponic systems. (A) leafy and (B) fruity vegetables. The error bars represent the maximum and minimum of the dataset. Sulfamethoxazole (SMX), trimethoprim (TRM), gemfibrozil (GMF), carbamazepine (CBZ), triclosan (TCS), naproxen (NPX), diclofenac (DCF), and fluoxetine (FLX).

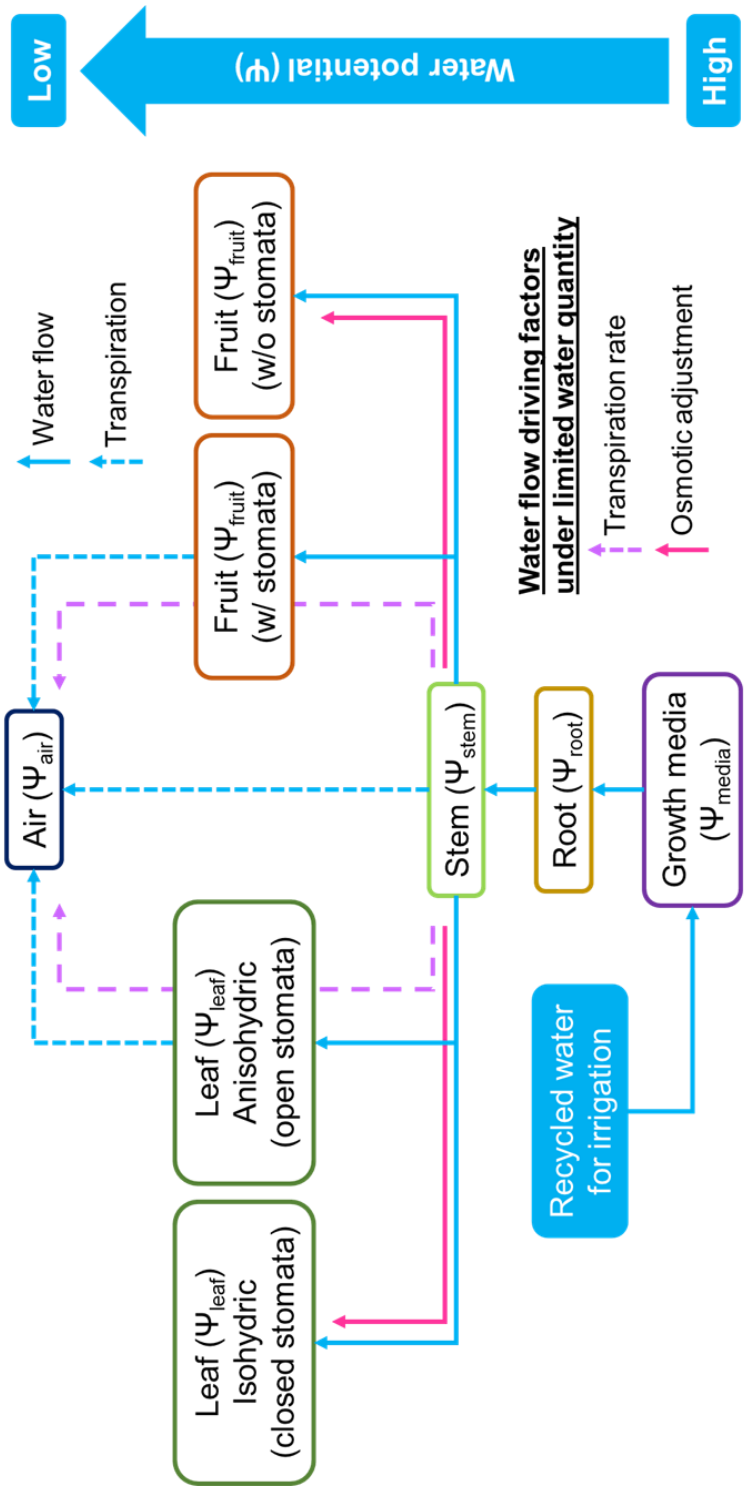

Figure 2-3 A schematic diagram of water transport system in leafy and fruity crops that follows the water potential gradient.

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Chapter 3

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 PPCP 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 (ET_o) 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% ET_o resulted in a higher accumulation of CBZ accumulation compared to 80% ET_o. Similarly, the canopy temperature increased under 60% ET_o irrigation rate compared to 80% ET_o, suggesting that turfgrass under 60% ET_o was more prone to water stress. Applying a 60% ET_o 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 that 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.

Keywords: PPCPs accumulation, turfgrass, UV persulfate, irrigation rates, reference evapotranspiration, field trial, physiological responses.

3.1 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.[1,2] Insufficient water availability for irrigation can affect crop production, food security, and agricultural activities.[3,4] Recycled water from municipal wastewater effluent can be a valuable alternative resource for agricultural irrigation.[5] For example, approximately 90% of the wastewater was reused for agriculture irrigation in Israel.[6] The US has also introduced recycled water for irrigation, with approximately 1.5 million acres of crops benefiting from this practice.[7] In California, a drought-prone region, recycled water production has increased nearly 10% from 2019 to 2022, with a predominant allocation towards landscape irrigation.[8]

Agriculture is the primary water user in the U.S., consuming approximately half of the total freshwater resources.[9] A significant contributor to this demand is the cultivation of turfgrass which stands as the largest 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.[10] In California, more than 50% of residential water use is attributed to urban landscapes, particularly turfgrass.[11] 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 µg/L levels.[12–16] Consequently, many studies have shown the plant accumulation of PPCPs from recycled water irrigation.[17–19] These persistent organic chemicals have also been associated with increased plant stress and toxicity levels.[20] 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.[21] In particular, UV/persulfate ($S_2O_8^{2-}$) has received increasing attention due to its generation of sulfate radical ($SO_4^{\bullet-}$) from persulfate photolysis, which exhibits fast reactivity and higher selectivity with PPCPs in comparison to hydroxyl radical ($^{\bullet}OH$).[21,22] Moreover, UV/persulfate can generate secondary radicals including chlorine atom ($Cl^{\bullet}$) and carbonate radical ($CO_3^{\bullet-}$) via reactions between $SO_4^{\bullet-}$ and chloride/bicarbonate in water matrix, which can also react with PPCPs.[23–25] 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 PPCP 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.[26–28] 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.[29] For example, 60% reference ET (ET_o: ET from a standardized surface) is often considered an adequate water requirement for warm-season turfgrass species.[11,30] Our recent research, however, revealed that 75% ET_o irrigation rate was needed to maintain the aesthetic values of hybrid bermudagrass (a warm-season turfgrass) in semi-arid regions of inland southern California.[31] 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.[32–34] Moreover, studies have indicated that reducing the irrigation rate can result in the accumulation of solutes in crops, including proline, amino acids and sugar.[35,36] 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_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.

3.2 Material and Methods

3.2.1 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.[37,38] 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°C within 2 hours 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.[39] 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 µg/L for each PPCP. This concentration was selected as PPCPs are mostly found at sub-µg/L concentration in recycled water.[40] Additionally, as a negative control, potable water was collected from a hose located at the University of California Riverside Agricultural Experiment Station.

3.2.2 UV persulfate treatment of recycled water

A schematic diagram of the experimental setup is shown in Figure 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.[41] Subsequently, 3.5 L of recycled water mixture was transferred to a UV reactor (ACE Glass) equipped with three low-pressure monochromatic ($\lambda = 254$ nm; Ultra-Sun Tech) mercury lamps. The UV fluence of the UV reactor was determined using atrazine actinometry.[42] The UV exposure of recycled water lasted for 7 mins, equivalent to a total UV dosage of 750 mJ/cm^2, a typical value used in full-scale UV/AOP water reuse treatment.[43] 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.

3.2.3 Field turfgrass experimental setup

A turfgrass field irrigation experiment was conducted at the Agriculture Experiment Station located at the University of California, Riverside. The soil at the study site was a well-drained Hanford coarse sandy loam soil with a volumetric water content of 22.5%.[44] A well-established warm season St. Augustine grass – known as *Stenotaphrum secundatum* (Walt.) Kuntze – was used to prepare a plot of 13.4 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% ET_o, 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 (Figure 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 (Figure 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 Figure S3. Additional details on the filed irrigation trial are available in Text S2.

3.2.4 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 PPCP 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 Figure S4-5. 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.[45] 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.[46] 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°C, followed by MQ water rinsing to remove soil particles, and dried using a paper towel. Following that, turfgrass samples were freeze dried (-50ºC,

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°C until extraction.

Turfgrass sample extraction and cleanup followed an established method.[47] 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.

3.3 Results and Discussion

3.3.1 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 (Figure 2A). Additionally, the potable water control contained no PPCP except for a very trace level of FLX at 0.16

μg/L. SMX, FLX, DCF, and TCS were sensitive to UV light at 254 nm, and they were effectively removed by UV/PS treatment (Figure 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 (Equations 1-2) was utilized:

$$f_{R\cdot} = \frac{k_{R\cdot,CBZ}[R\cdot]_{SS}}{r_{CBZ}} \times 100\% \quad \text{(Equation 1)}$$

$$r_{CBZ} = r_d^{norm} + k_{\bullet OH,CBZ}[\bullet OH]_{SS} + k_{SO_4^{\bullet-},CBZ}[SO_4^{\bullet-}]_{SS} + k_{Cl\cdot,CBZ}[Cl^{\bullet}]_{SS} + k_{Cl_2^{\bullet-},CBZ}[Cl_2^{\bullet-}]_{SS} + k_{CO_3^{\bullet-},CBZ}[CO_3^{\bullet-}]_{SS} \quad \text{(Equation 2)}$$

where $f_{R\cdot}$ 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 (Figure 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 $Cl^{\bullet}$, 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 Figure S7.

3.3.2 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 (Figure 3A). The plateauing phase indicated the turfgrass entered a dormant phase as the ambient temperature dropped entering into the cool season.[48] 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:

$$[\mathrm{CBZ}]_{\mathrm{Leaves}} = \frac{\sum_0^{14} \mathrm{M_{CBZ}}}{\sum_0^{14} \mathrm{W_{Leaves}}} \qquad \text{(Equation 3)}$$

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 (Figure 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% ET_o and 80% ET_o, respectively (left panel of Figure 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% ET_o and 80% ET_o, respectively (right panel of Figure 3B). Turfgrass irrigated with potable water control did not exhibit CBZ accumulation (Figure 3B).

SMX, DCF, and FLX were detected in turfgrass leaves irrigated with untreated recycled water (Figure S8). Conversely, when treated recycled water was used, they were not detected in the leaves (Figure 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.[17,18] However, some studies had reported the potential accumulation of TCS in leaves when soils with a spiked concentration of TCS were used for cultivation.[49,50] 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 (Figure S9).

Interestingly, CBZ concentration in the turfgrass root was higher compared to that in the leaves (left *vs.* right panel Figure 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.[51] Additionally, the high root biomass in turfgrass grass could facilitate its localized accumulation.[52] SMX and DCF exhibited a similar trend as CBZ, likely due to the high root biomass of turfgrass (left *vs.* right panel Figure S9A-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 Figure S9C).[53]

3.3.3 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% ET_o compared to 80% ET_o for both untreated and treated recycled water (left panel in Figure 3B). This difference in CBZ accumulation in the leaves at both irrigation rates was statistically significant (left panel in Figure 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% ET_o compared to 80% ET_o (left panel of Figure S9A-C). Similarly, the accumulation of SMX, DCF, FLX, and TCS in turfgrass root irrigated with untreated recycled water was higher at 60% ET_o compared to 80% ET_o when irrigated with untreated recycled water (right panel of Figure S9A-D).

The increase in the PPCP accumulation in turfgrass leaves when decreasing the irrigation rate from 80% ET_o to 60% ET_o 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.[54] 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.[54–57] Similarly, the increase in root concentration could be ascribed to the root's osmotic regulation, which effectively maintains root turgor under limited water conditions.[58–60] 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.

3.3.4 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% ET_o (Figure 4A-B). VR is rated from 1 (low quality) to 9 (high quality), and 6 representing the minimum acceptable quality.[45] At 80% ET_o irrigation rate, the minimum acceptable turfgrass VR was consistently maintained throughout the study period, regardless of the water quality type (Figure 4B). Conversely, with a 60% ET_o irrigation rate, VR dropped below the minimum acceptable quality after 8 weeks of irrigation, notably with plots irrigated using untreated recycled water (Figure 4A). However, the difference was only statistically significant in plots irrigated with untreated

recycled water (Figure 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.[61] Similarly, another study reported no significant difference between hybrid bermudagrass quality irrigated using potable and recycled water.[62]

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.[63,64] Overall, only 80% ET_o irrigation rate showed ΔT close to zero, 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_o irrigation rate than at 80% ET_o (Figure 4D *vs*. Figure 4E). At 60% ET_o irrigation rate, plots irrigated with untreated recycled water exhibited a ΔT value that was 1.2℃ higher than plots irrigated with potable control, which was statistically significant ($P < 0.05$; Figure 4F). Conversely, at an 80% ET_o 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.[44,61,65–67]

3.3.5 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:

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

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 (Figure 5A *vs*. 5B). 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 Figure 5A or 5B). 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[68–70], our findings suggest that PPCPs accumulation was not the primary factor influencing turfgrass leaf visual quality.

3.4 Conclusions

This study demonstrated that UV persulfate treatment of recycled water is beneficial to reducing PPCP 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 PPCP 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% ET_o is not enough to maintain the aesthetic values of St. Augustine turfgrass over summer in semi-arid environment of inland 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.

Supporting Information

Properties of PPCPs, field layout and irrigation scheduling, analysis of turfgrass and water samples, calculation of the fate of radical species, and proposed pathway of CBZ degradation by UV/PS.

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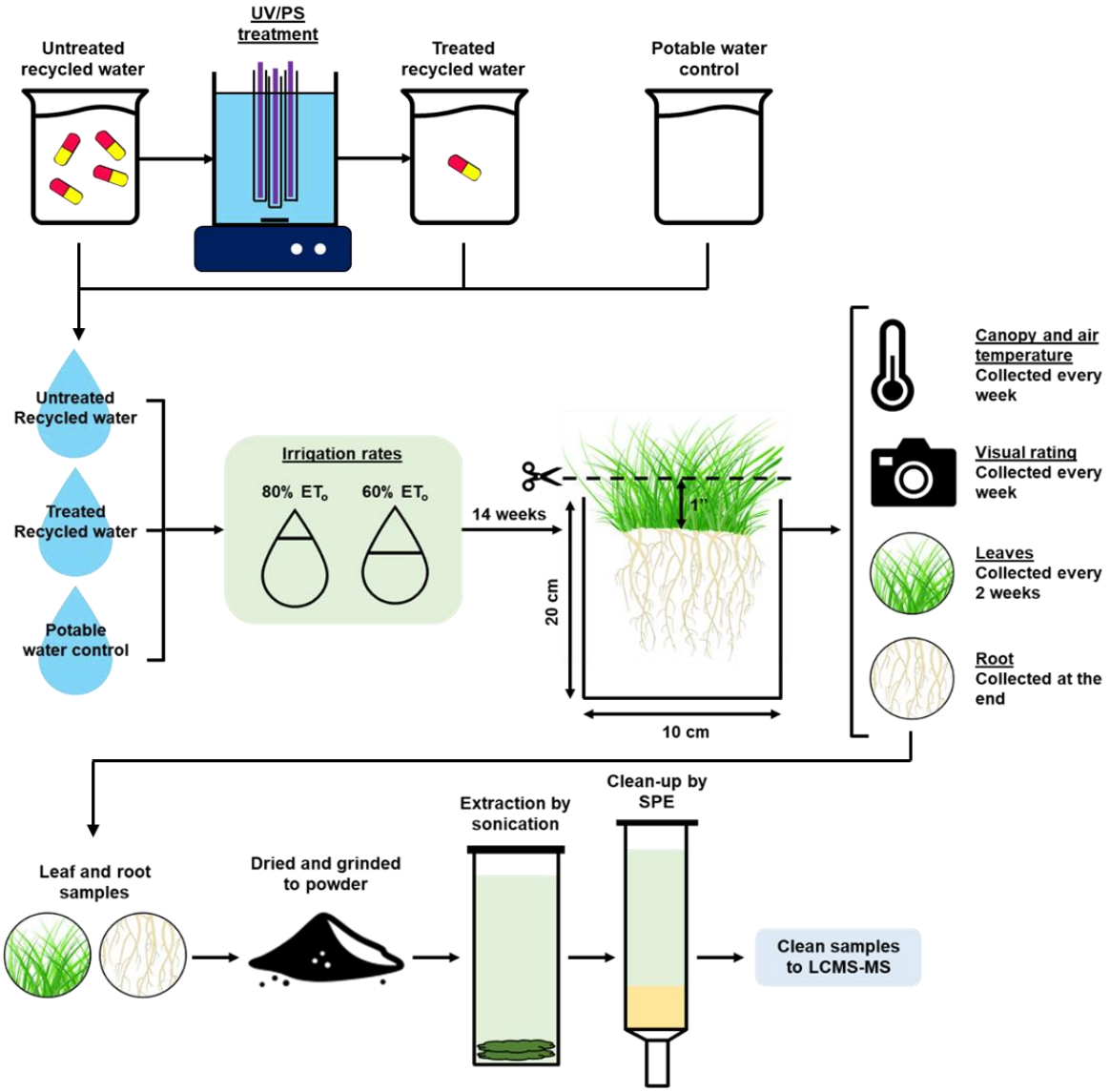

Figure 3-1 Schematic diagram of experimental procedures: UV/persulfate treatment of recycled water, field irrigation of turfgrass using three types of water and two irrigation rates, turfgrass growth monitoring, turfgrass leaf and root sample collection, processing, and cleanup for PPCP analysis.

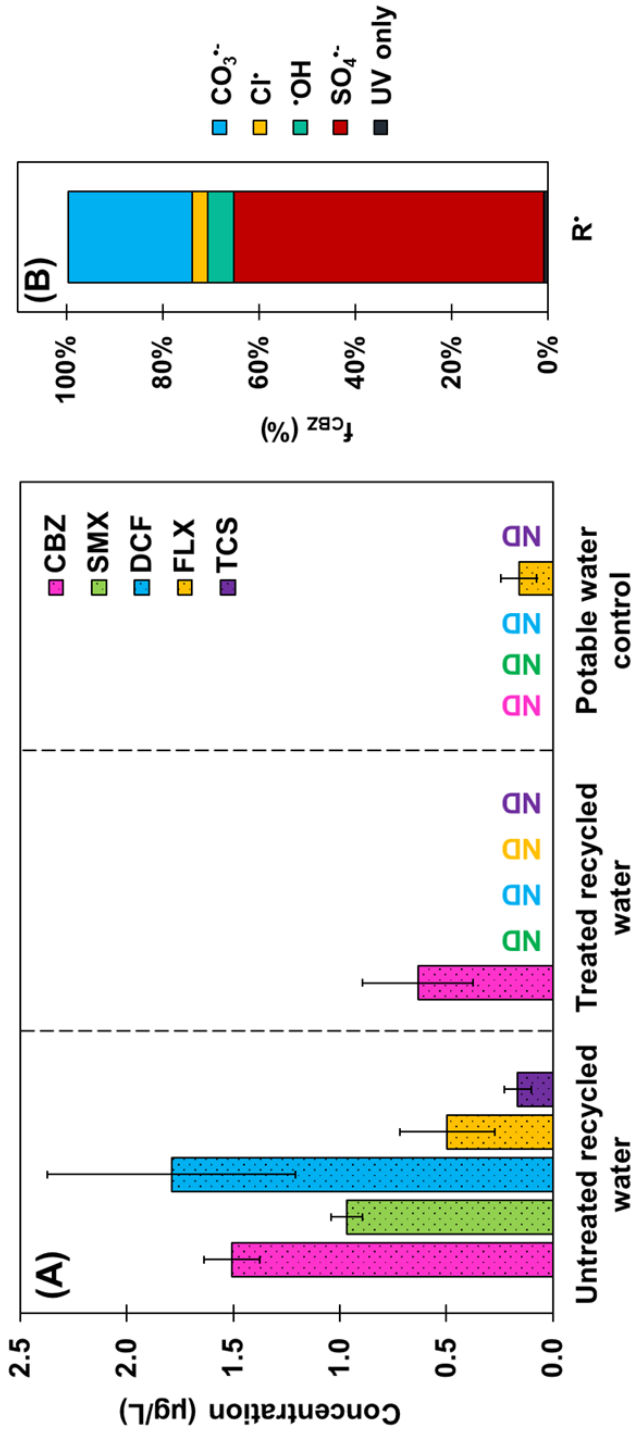

Figure 3-2 (A) Initial concentration of PPCPs in three types of irrigation water, and (B) radical distribution of CBZ degradation in UV/PS system. Carbamazepine (CBZ), sulfamethoxazole (SMX), diclofenac (DCF), fluoxetine (FLX), and triclosan (TCS).

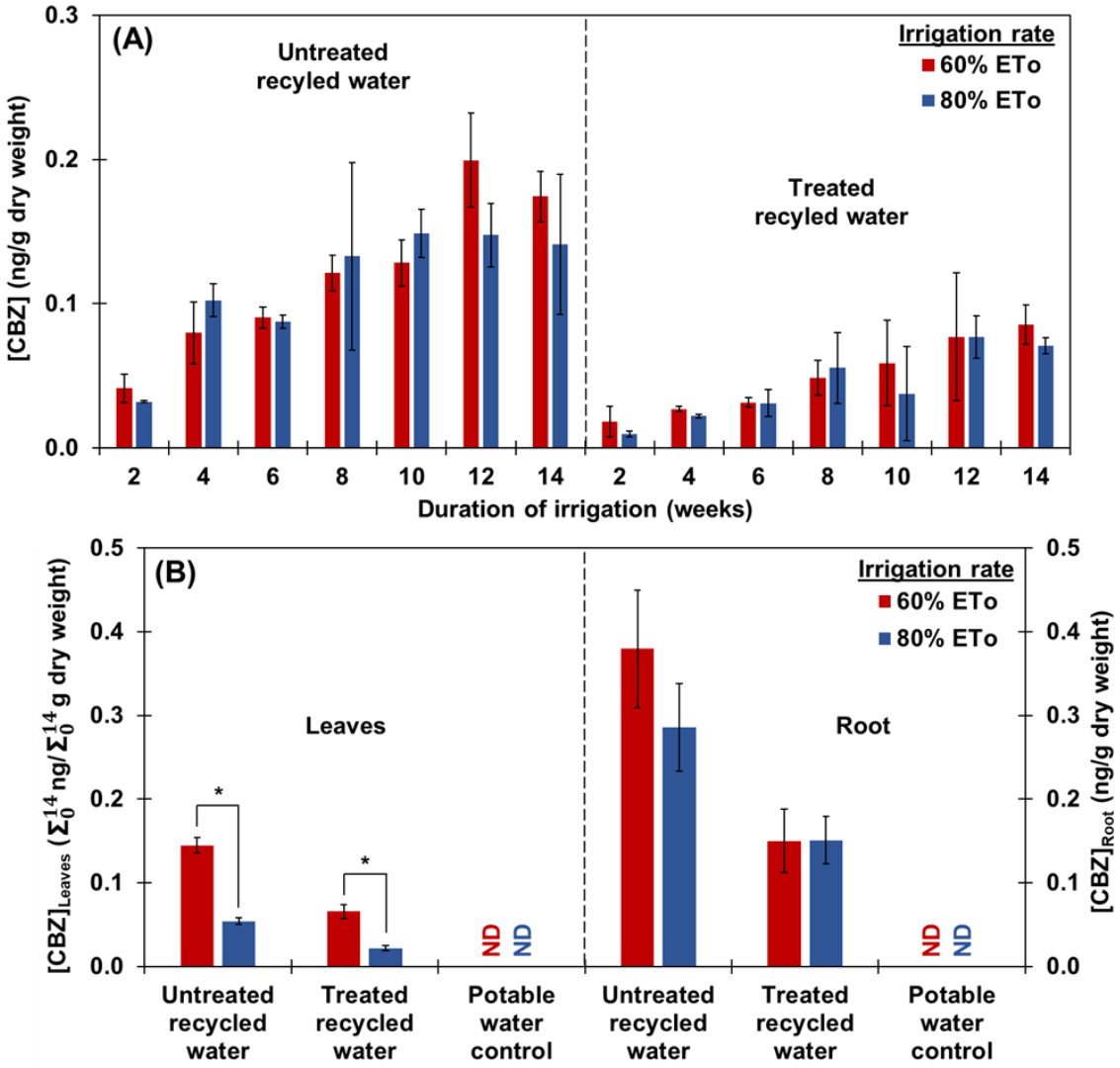

Figure 3-3 Carbamazepine (CBZ) accumulation in turfgrass leaves and root using untreated and treated recycled water. (A) 2-week incremental concentration of CBZ in leaves; CBZ was not detected in potable water control, (B) 14-week normalized concentration of CBZ in leaves and final concentration in root.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

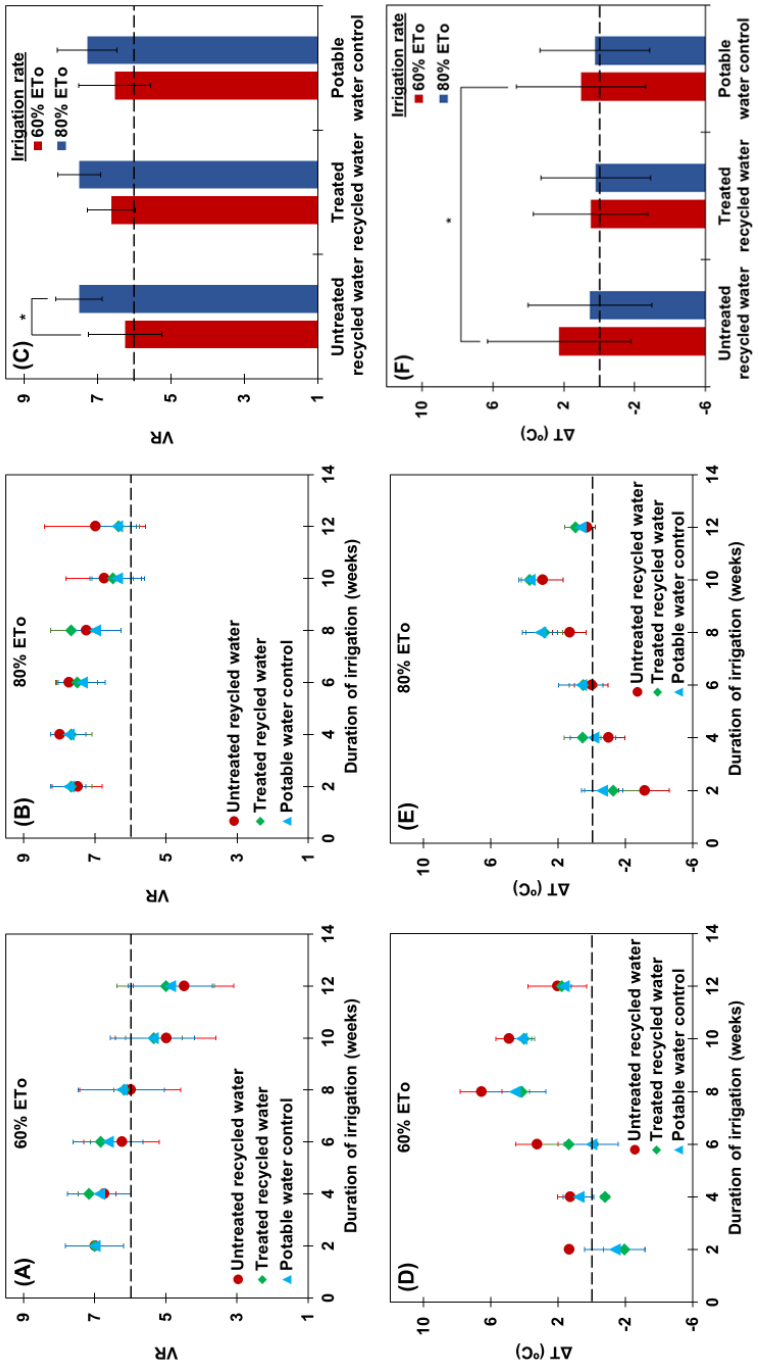

Figure 3-4 Physiological responses of turfgrass when irrigated with different types of water under limited irrigation rates. The dotted lines show the minimum turfgrass acceptable quality (6) and maximum threshold of potential water stress (0ºC). (A-C) VR of turfgrass leaves, and (D-F) canopy and air temperature variance of turfgrass. The star mark represents the statistical significance ($p < 0.05$).

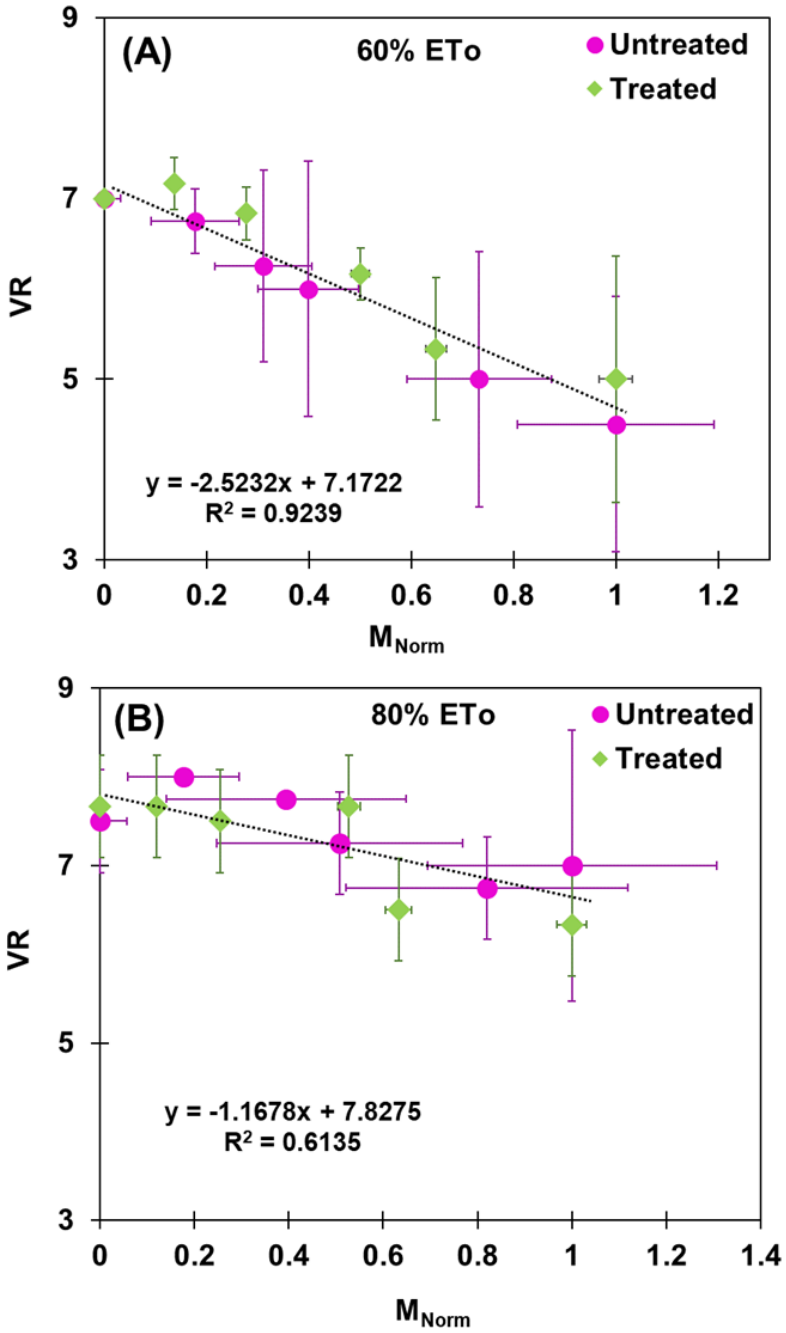

Figure 3-5 Correlation of VR and cumulative mass of PPCPs in turfgrass leaves irrigated with untreated and treated recycled water at different limited irrigation rates. (A) 60% ET_o and (B) 80% ET_o.

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Chapter 4

Integrating UV/Persulfate and Deficit Irrigation of Recycled Water: Strategy to Minimize Crop Accumulation of Trace Organic Contaminants and Enhance Crop Yield

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Abstract

This study investigated the combination of UV persulfate (UV/PS) treatment of recycled water and deficit irrigation to minimize pharmaceutical and personal care products (PPCPs) accumulation and improve crop quality. Lettuce, carrot, and tomato, commonly consumed raw, were cultivated in a greenhouse using PPCP spiked recycled water, UV/PS treated recycled water, and tap water control, under irrigation rates at 60%, 80% and 100% of crop evapotranspiration (ET_C) rates. UV/PS removed ≥99% of carbamazepine, diclofenac, and fluoxetine from spiked recycled water. Post-treatment, carbamazepine accumulation in harvested lettuce, carrot, and tomato was reduced by 96-99%, 35-70% and 72-93%, respectively. Minimal accumulation of diclofenac and fluoxetine occurred in edible crops due to their existence as dissociated ions. Three edible crops exhibited distinct trends of PPCPs accumulation in response to irrigation rates. Lettuce exhibited a decreasing PPCPs accumulation with a reduced irrigation rate, which was attributed to slower transpiration. In contrast, carrot and tomato exhibited increased PPCP accumulation due to osmotic adjustment. Lettuce and carrot exhibited higher irrigation water utilization efficiency at deficit irrigation, while the opposite was observed for tomato. This study highlights the beneficial integration of UV/PS with deficit irrigation to conserve water, maintain crop yield, and minimize PPCP accumulation.

Keywords: UV/persulfate, deficit irrigation, PPCPs, edible crop, recycled water, ET_C.

4.1 Introduction

Agriculture irrigation consumes over 70% of global fresh water in water stressed regions and more than 40% in the U.S.[1–3] To cope with water scarcity and climate impact, recycled water can be a valuable alternative resource.[4,5] For example, 90% of recycled water is used for agriculture in Israel, and its use for irrigation in California increased by 10% between 2019 and 2022.[6,7] However, recycled water contains residual pharmaceutical and personal care products (PPCPs). For example, carbamazepine (CBZ), diclofenac (DCF), and fluoxetine (FLX) are three commonly found PPCPs in recycled water, ranging from ng/L to μg/L[8–10], leading to a major risk of PPCP accumulation in crops.[11–13] Therefore, it is urgent to develop an effective water treatment and management strategy to minimize PPCPs from recycled water before irrigation application.

UV/persulfate (UV/PS), a UV-based Advanced Oxidation Process (UV/AOP), stands out as an efficient approach to remove PPCPs from wastewater effluent.[14,15] Persulfate photolysis generates $SO_4^{\bullet-}$, which exhibits higher selectivity compared to $^{\bullet}OH$.[16–18] Moreover, UV/PS offers distinct advantages in recycled water systems due to the generation of secondary radicals including $Cl^{\bullet}$ and $CO_3^{\bullet-}$ that can selectively react with PPCPs.[19,20] However, the beneficial effects of UV/PS treatment in agricultural irrigation, especially regarding the fate of PPCPs in edible crop production during recycled water irrigation remains unknown.

Optimizing water quantity is critical to water reuse in agriculture. Deficit irrigation, a promising water conservation practice, involves applying less water than full crop water requirements (i.e., crop evapotranspiration, ET_C). Growers might practice deficit

irrigation by deliberately under-irrigating crops to maximize net farm income. Deficit irrigation can boost crop profitability by increasing irrigation water use efficiency, reducing irrigation cost, and enabling irrigation of more land with the same amount of water.[21,22] Furthermore, in semiarid and arid regions, deficit irrigation may become inevitable due to water scarcity, especially during droughts and climate change. Studies show it can help conserve water and increase irrigation water use efficiency without significantly reducing yield.[23,24] Nevertheless, deficit irrigation affects various physiological responses in crops, including stomatal closure, decreased photosynthetic rates, and decreased osmotic pressure.[25–27] Moreover, it can accumulate solutes, such as proline, amino acids, and sugars in crops.[28,29] The compound effect of deficit irrigation on crop yield under water reuse scenarios remains unexplored.

Furthermore, the impact of crop type (*e.g.*, leafy, root, and fruity vegetables) on the accumulation of PPCPs under deficit irrigation remains unexplored. Prior studies on PPCP accumulation mainly evaluated the scenarios after PPCPs enter a crop's vascular system via root uptake.[30–32] Once taken up by the crop, PPCPs can potentially translocate to different organs primarily through transpiration.[33,34] This movement of PPCPs within the plant system is driven by differences in water potential.[35] To date, a systematic mechanistic understanding of PPCPs accumulation via water flow under water deficit conditions across various crop types has not been investigated.

Therefore, by conducting the first of its kind crop growth greenhouse experiment using recycled municipal wastewater effluent under deficit irrigation, the objectives of this study were to: (1) investigate the reduction of PPCPs accumulation in three different

types of edible crops by UV/PS treatment of recycled water; (2) integrate UV/PS treatment and deficit irrigation optimization of recycled water to enhance crop yield and irrigation water use efficiency; (3) understand the distinct mechanisms of PPCPs accumulation under deficit irrigation condition in different vegetables.

4.2 Materials and Methods

A schematic illustration of the experimental procedure is shown in Figure 1. Recycled water for irrigation was collected monthly from the South Coast Research and Extension Center in Irvine, CA. Spiked recycled water was prepared by adding CBZ, DCF, and FLX at an environmentally relevant concentration of 1.5 μg/L, reflecting typical sub-μg/L concentration in recycled water.[36] Additionally, clean tap water control was sourced from a municipal water supply in Riverside, CA. Chemical properties of chemical information are provided in Text S1 and Table S1.

The spiked recycled water underwent UV/persulfate treatment to produce treated recycled water (Figure 1). Freshly prepared persulfate solution was added to 21 L of spiked recycled water to achieve an initial persulfate dosage of 35 mg/L. This level of persulfate posed no significant adverse effects on edible crops based on prior literature on crop growth.[37] Additionally, the pH change with 35 mg/L of persulfate in recycled water was minimal, with a variation of only 0.5 units. The spiked water was then transferred to a 3.5-L UV reactor equipped with three low-pressure lamps (λ = 254 nm; Ultra-Sun Tech.) for 12 mins of exposure corresponding to a UV dosage of 1100 mJ/cm^2. The UV fluence was determined using atrazine actinometry.[38] This UV dosage level is similar to full-scale municipal potable water reuse treatment.[39] The combined persulfate and UV

dosage aimed to achieve 2-log removal of PPCPs from the spiked recycled water. In our experiment, an average of 55-60% persulfate remained after UV treatment. Both treated and spiked recycled water were stored at 4°C until utilized for chemical analysis and subsequent greenhouse irrigation.

A crop irrigation trial was conducted in a factorial randomized complete block design in the greenhouse facility at UCR for 4 months from February to June 2023 (Figure S1). The trial employed 3 water types and 3 irrigation rates with 3 replications on 3 different edible crops, including leafy crop romaine lettuce (*Lactuca sativa* L. var. 'Vivian'), root crop carrot (*Daucus carota* L. var. 'Danvers 126'), fruity crop tomato (*Lycopersicon esculentum* Mill. var. 'Siletz'). Water types included spiked recycled water, UV/PS-treated recycled water, and tap water control, while irrigation levels were set at 100% ET_C, 80% ET_C and 60% ET_C (Figure 1). The total irrigation volume of each crop is summarized in Figure S2. Individual one-gallon containers delivered irrigation water to the plants via dripping pipes. Reference ET (ET_o) was estimated using an ET gauge (Spectrum Technologies) installed inside the greenhouse. Crop ET_C ($ET_C = ET_o * K_c$) was then calculated by obtaining crop coefficient (K_c) values from the literature for each crop. Edible parts of lettuce, carrot and tomato were collected 65, 66, and 99 days after the initiation of the irrigation experiment, respectively, and immediately preserved at -20°C in the lab for further processing. The details of the greenhouse trial are given in Text S2.

Crop samples were washed to remove soil particles, dried using a paper towel, weighed for its fresh mass, freeze dried for 3-4 days using a freeze dryer (Labconco Corp.), and

ground into fine powder using a published method.[40] Both crop and irrigation water samples underwent solid phase extraction (Figure 1). Final samples were injected into an HPLC-HRMS/MS (Q Extractive Hybrid Quadrupole Orbitrap; ThermoFisher Scientific) for PPCP analysis. The recovery of CBZ, DCF, and FLX in biomass was 65-96%, 91-145%, and 29-49%, respectively. Similarly, their recovery in recycled water was 80-121%, 99-134%, and 42-45%, respectively. Details on sample processing and chemical analysis are provided in Text S3. Statistical analyses on PPCPs accumulation and crop yield were conducted using Origin Pro Software. One-way analysis of variance (ANOVA) and the Tukey test were applied at a significant level of 0.05.

4.3 Results and discussion

4.3.1 Impact of UV/PS treatment on minimizing PPCPs accumulation in edible crops

A comprehensive analysis of the chemistry of recycled water is available in Table S2. No PPCP was detected in tap water control. UV/PS treatment removed ≥99% of CBZ, DCF, and FLX from spiked recycled water for irrigation. Consequently, the concentration of these PPCPs in treated recycled water was reduced to 3-17 ng/L from an initial average of 1.5 µg/L (Figure S3A). DCF and FLX were directly photolyzed by 254-nm photons and CBZ was degraded predominantly by reactive radical species (Figure S4). The contribution of reactive radical species to CBZ degradation in recycled water was further calculated based on radical chain reactions (detailed list of reactions and calculations are shown in Table S3 and Texts S4-5). $SO_4^{\bullet-}$ contributed approximately 65% to CBZ degradation (Figure S3B). $^{\bullet}OH$ and $Cl^{\bullet}$ that were generated through the reactions of $SO_4^{\bullet-}$ with water and chloride, respectively, contributed to less than 10% of CBZ degradation.

$CO_3^{\bullet-}$, generated via HCO_3^- reacting with $SO_4^{\bullet-}$, $^{\bullet}OH$, and $Cl_2^{\bullet-}$, contributed approximately 25% to CBZ degradation. Furthermore, no significant contribution from direct photolysis toward CBZ degradation was observed (≤0.2%).

The accumulation of CBZ in all three edible crops was significantly reduced when irrigated with UV/PS-treated recycled water compared to spiked recycled water. Specifically, irrigation of treated recycled water led to a reduction of CBZ accumulation by 96%-99% in lettuce, 35%-70% in carrot, and 72%-93% in tomato regardless of irrigation rate (left *vs*. middle panel in Figure 2A, 2B and 2C, respectively). The accumulation of CBZ in crops after treated recycled water irrigation is minimal and on par with that observed with tap water irrigation control (middle *vs.* right panel in Figure 2A, 2B, and 2C, respectively). The trace levels following treated recycled water application are likely attributed to the background PPCPs level in soil, as PPCPs were detected in crops irrigated with tap water control (right panel in Figure 2A-C). In addition, the accumulation of DCF was minimal in all crops regardless of the type of irrigation water. Similar trends were observed for FLX in lettuce and carrot, while FLX accumulated in tomato was significantly reduced when irrigated with treated recycled water.

The uptake of PPCPs from soil into crops depends on their molecular charge. Ionic PPCP update was reported to be low due to their slow crossing via the crop cell membrane.[41] DCF is carboxylate and negatively charged in recycled water (pK_a = 4.15). FLX is a secondary amine and positively charged in recycled water (pK_a=10.09). CBZ features an amide functional group, maintaining a neutral molecule in recycled water (pK_a = 2.3 and

13.9). This is consistent with the experimental observation that non-ionic CBZ accumulated more compared to ionic DCF and FLX (Figure 2).

Crop type significantly affected the accumulation of CBZ. Lettuce exhibited a CBZ accumulation four times higher than carrot and 20 times higher than tomato when irrigated with spiked recycled water (left panel in Figure 2A-C). Non-ionic CBZ was reported to traverse plant cell membranes, favoring transportation towards transpiring streams and resulting in their higher accumulation in leaves.[34,42] This preferentially favors CBZ accumulation in leafy vegetables such as lettuce. In comparison, CBZ accumulation in carrot was lower than in lettuce, consistent with a previous report suggesting that root tends to accumulate less PPCPs compared to leaves.[11,43] The lowest CBZ accumulation in tomato is associated with the crop difference in transpiration rate. Tomato lacks stomata, which results in a very low transpiration rate and consequently decreases the accumulation of CBZ.[44,45]

4.3.2 Impact of irrigation rate on PPCPs accumulation in edible crops

Irrigation rate significantly impacted CBZ accumulation in edible crops, and the extent of accumulation depended on crop types. When irrigated with spiked recycled water, lettuce exhibited a significant decrease in CBZ accumulation, dropping from 0.46 to 0.15 ng/g as the irrigation rate decreased. In contrast, both carrot and tomato exhibited a significant increase in CBZ accumulation, rising from 0.02 to 0.1 ng/g and 0.006 to 0.02 ng/g, respectively, with decreasing irrigation rate (left panel in Figure 2). When irrigated with treated recycled water, lettuce and carrot exhibited a similar significant trend in CBZ accumulation. In tomato, no significant trend was observed due to the trace level of CBZ

accumulation (middle panel in Figure 2). Additionally, no distinguishable trend was observed for DCF and FLX in all crops, as both PPCPs only accumulated at trace levels. In leafy lettuce, CBZ accumulation is associated with transpiration that influences water flow. Transpiration induces a negative water potential in the leaves, driving water movement towards the evaporative sites in the leaves.[46,47] As the irrigation rate decreased from 100% ET_C to 60% ET_C, the transpiration rate decreased and slowed down the movement of water towards lettuce leaves, consequently reducing the translocation and accumulation of CBZ in lettuce. This mechanism was supported by prior observations on lettuce's ability to regulate transpiration rate in response to water deficit conditions.[48–50] In root vegetable carrot, the increased CBZ accumulation with reduced irrigation rate is linked to osmotic adjustment needed to maintain a desirable water potential gradient. Water scarcity triggers osmotic adjustment in carrot, which accumulates solutes including sugars, proline, and amino acids to maintain the water potential gradient in the root.[51–54] A similar trend is observed in fruity vegetable tomato, and it can be attributed to tomato's ability to reduce water potential within the fruit through solute accumulation. Solute accumulation of tomato under water deficit conditions was observed before.[55] Moreover, the absence of stomata in tomato skin poses challenges in maintaining water potential gradient through transpiration, further emphasizing the reliance on the solute accumulation mechanism.[44]

4.3.3 Water Use Efficiency and crop yield of recycled water irrigation

Irrigation Water use efficiency (IWUE, kg ha^{-1} m^{-1}), an indicator of crop production based on irrigation water quantity, was calculated as following:

$$\mathrm{IWUE} = \frac{\mathrm{Y_{Crop}}}{\mathrm{V_I}} \quad \text{(Equation 5)}$$

where Y_{Crop} is crop yield as the fresh weight of the harvested crops (kg/ha), and V_I is the volume of the applied irrigated water normalized to the plot surface area (m^3/m^2). Results showed that the IWUE value varied depending on the crop type and irrigation rates. Interestingly, the IWUE was significantly higher for lettuce under the 60% ET_C deficit irrigation rate than the 100% ET_C irrigation rate (Table 1), indicating that lettuce maintained a relatively high yield even under severe deficit irrigation conditions. Carrot exhibited a similar trend but was not statistically significant. In contrast, the IWEU of tomato was significantly lower under deficit irrigation (60% *vs*. 100% ET_C). This is likely associated with the fruity crop's inherent dependence on water to maximize yield.[56,57] The IWEU of lettuce, carrot, and tomato using spiked recycled water and tap water control followed similar trends. The yield of all three crops decreased as the irrigation rate was reduced from 100% ET_C to 60% ET_C across the three different types of water (Table 1).

4.4 Conclusions

Integration of persulfate photolysis with deficit irrigation of recycled wastewater effluent can lead to minimal PPCPs accumulation and better IWUE for crops, thus conserving water while maintaining crop quality. In lettuce, employing a 60% ET_C irrigation rate is advantageous to minimize CBZ accumulation while increasing IWUE. For carrot

cultivation, irrigation rates of 80% or 100% ET_C are suitable, ensuring relatively lower CBZ accumulation. Finally, tomato yield can be maximized while minimizing CBZ accumulation at 100 ET_C, considering the minimal observed accumulation of CBZ in tomato. Overall, these insights lead to better water quality and quantity management strategies for water reuse for agriculture. The impact of PPCPs (spiked recycled water) on crop yield was not consistent across crops and irrigation rates. Further studies on long-term irrigation trials are needed to better understand and quantify the impact of PPCPs on the yield quantity of various crops. Furthermore, natural organic matter (NOM) can be found in tertiary treated recycled water at the level up to 5 mg C/L. Despite this concentration, the steady-state concentrations of major radicals remains unchanged in the system (Table S6). The impact of NOM is not expected to significantly affect PPCPs accumulation or crop yield, which are primarily influenced by feedwater treatment extent, irrigation rate, and crop type.

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Supporting Information

Properties of PPCPs, greenhouse setup, volume of irrigation water, analysis of carrot, lettuce, tomato and water samples, calculation of the fate of radical species for CBZ degradation by UV/PS.

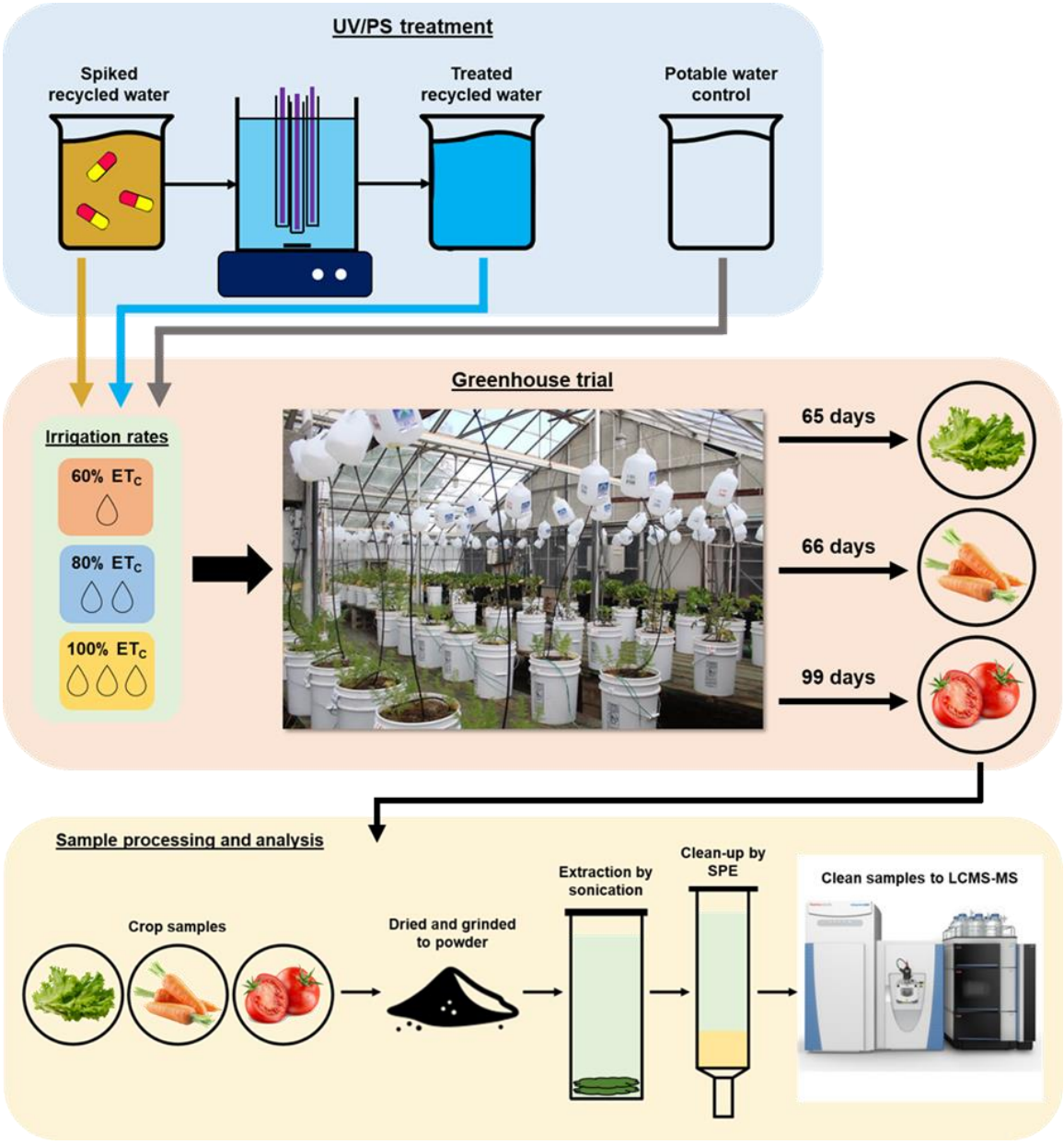

Figure 4-1 Schematic diagram of experimental procedures: UV/persulfate treatment of recycled water, Greenhouse trail of lettuce, carrot, and tomato using three types of water and three irrigation rates, crop sample collection, processing, and cleanup for PPCP analysis.

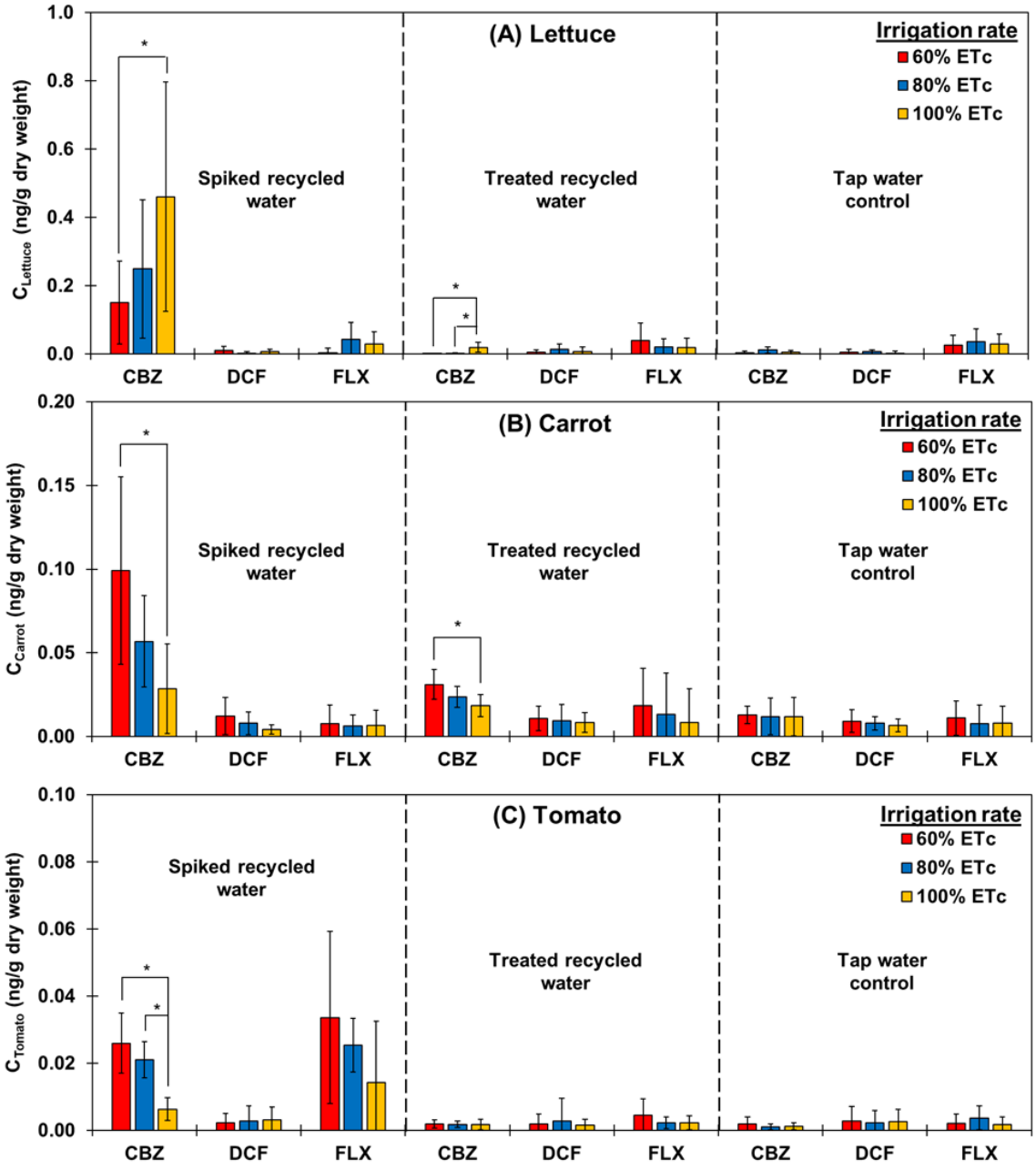

Figure 4-2 Accumulation of PPCPs in edible crops when irrigated with spiked and treated recycled water and tap water control at different irrigation rates. (A) lettuce, (B) carrot, and (C) tomato. The star mark represents the statistical significance ($p < 0.05$). Carbamazepine (CBZ), diclofenac (DCF), and fluoxetine (FLX).

Table 4-1 Yield and IWUE of different crops irrigated with spiked and treated recycled water at three different irrigation rates. Statistical significance ($P < 0.05$) is represented by symbol a for 60% and 100% ET_C, b for 60% and 80% ET_C, and c for 80% and 100% ET_C.

Spiked recycled water						
	Yield (kg ha^{-1})			**IWUE (kg ha^{-1} m^{-1})**		
Crop/ET_C	**60%**	**80%**	**100%**	**60%**	**80%**	**100%**
Lettuce	3150 ± 1126	3678 ± 1908	4220 ± 2314	47 ± 15^{a}	36 ± 19^{c}	33 ± 18^{ac}
Carrot	3941 ± 1121	3473 ± 1702	4212 ± 2748	48 ± 17	41 ± 19	39 ± 22
Tomato	4567 ± 361^{a}	7711 ± 2204^{c}	19397 ± 3452^{ac}	37 ± 3^{a}	47 ± 14^{c}	95 ± 17^{ac}
Treated recycled water						
	Yield (kg ha^{-1})			**IWUE (kg ha^{-1} m^{-1})**		
Crop/ET_C	**60%**	**80%**	**100%**	**60%**	**80%**	**100%**
Lettuce	3355 ± 1178	3339 ± 1481	4219 ± 2617	49 ± 15^{ab}	36 ± 15^{bc}	31 ± 21^{ac}
Carrot	3177 ± 1556	3618 ± 1748	5589 ± 2688	52 ± 24	40 ± 22	38 ± 24
Tomato	7276 ± 1230^{a}	9985 ± 2416^{c}	20820 ± 3806^{ac}	59 ± 10^{a}	61 ± 15^{c}	102 ± 19^{ac}
Tap water control						
	Yield (kg ha^{-1})			**IWUE (kg ha^{-1} m^{-1})**		
Crop/ET_C	**60%**	**80%**	**100%**	**60%**	**80%**	**100%**
Lettuce	3037 ± 1568^{ab}	3226 ± 1803^{bc}	4923 ± 2818^{ac}	40 ± 21^{b}	32 ± 18^{bc}	39 ± 22^{c}
Carrot	3401 ± 2202	4271 ± 1721	5095 ± 2445	51 ± 33	49 ± 20	46 ± 22
Tomato	5813 ± 1068^{a}	8542 ± 3291^{c}	20603 ± 3824^{ac}	47 ± 9^{a}	52 ± 20^{c}	101 ± 19^{ac}

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Chapter 5

Conclusions and Broader Impacts

The research presented in this dissertation underscores the critical need for effective water treatment technologies to mitigate the accumulation of pharmaceutical and personal care products (PPCPs) in crops irrigated with recycled water. The presence of PPCPs in recycled water poses significant risks to food safety, particularly in leafy vegetables, and necessitates the continuous monitoring of irrigation water quality and quantity to minimize their bioaccumulation. Additionally, the study highlights the influence of irrigation water quantity on PPCP accumulation in crops, emphasizing the importance of optimized water management practices to ensure the safe use of recycled water in agriculture.

The investigation into UV persulfate treatment revealed its efficacy in degrading PPCPs, thus reducing their accumulation in turfgrass. This advanced oxidation process leverages the photochemistry of sulfate radicals to achieve significant reductions in PPCP levels, making recycled water more suitable for irrigation. The findings also underscore the importance of proper irrigation rates, as limited irrigation increases PPCP accumulation in plants. The study's insights into the combined effects of UV treatment and irrigation rates provide a foundation for future research on long-term impacts and the scaling-up of UV/PS treatment technologies for practical applications.

Furthermore, the integration of persulfate photolysis with deficit irrigation strategies demonstrated the potential to enhance irrigation water use efficiency (IWUE) while minimizing PPCP accumulation in various edible crops such as lettuce, tomato, and carrot. The research identified optimal irrigation rates for different crops, ensuring lower PPCP levels and better water conservation without compromising crop yield. This study

highlights the necessity of understanding the interactions between PPCP-contaminated recycled water, irrigation practices, and crop types to develop sustainable water reuse strategies for agriculture.

The broader impact of this research lies in its contribution to sustainable agricultural practices and water resource management. By addressing the challenges posed by PPCPs in recycled water, this dissertation provides critical insights into improving water quality for agricultural reuse, thus ensuring food safety and environmental protection. The findings have significant implications for policymakers, farmers, and water management authorities, offering a scientific basis for developing guidelines and regulations for the safe use of recycled water in agriculture. Moreover, the advanced treatment technologies and irrigation strategies explored in this research can be applied to various agricultural settings, promoting the sustainable use of water resources and supporting the global efforts towards water conservation and food security.

In the turfgrass experiments, higher accumulation of Carbamazepine was observed under water-stressed conditions, while in greenhouse experiments with lettuce, lower accumulation was detected under similar water stress. Despite both turfgrass and lettuce being leafy plants, these contrasting trends highlight the importance of crop-specific responses to water deficit. The differential accumulation patterns can be attributed to the distinct water transport mechanisms in plants under stress. For instance, lettuce, classified as an anisohydric plant, tends to keep its stomata open during water deficit, maintaining higher transpiration rates. In contrast, turfgrass exhibits isohydric behavior, closing stomata to conserve water. These physiological responses lead to different defense

mechanisms being deployed under stressed conditions, which in turn influence PPCP accumulation. Understanding these crop-specific behaviors is crucial for optimizing irrigation strategies and mitigating the risks associated with PPCP accumulation in crops irrigated with recycled water.

This research provides valuable insights into the feasibility of scaling up UV treatment for real-time irrigation water purification. Our findings demonstrate that a UV dosage of 1100 mJ/cm² in conjunction with 35 mg/L of persulfate can effectively degrade ≥99% of PPCPs in recycled water. To implement this technology at a small-scale farm, a pilot-scale UV reactor could be designed to treat 27,530 gallons of water per acre, which is the estimated irrigation requirement for a 1-inch application. Commercial UV lamps typically offer a dosage of around 800 mJ/cm² in a flow-through reactor with a residence time of 30 seconds. A preliminary design suggests a pilot-scale reactor with a volume of 6.7 gallons and a flow rate of 10 gallons per minute (GPM), achieving a residence time of 40 seconds to deliver the required 1100 mJ/cm² dosage. This pilot-scale reactor could serve as a valuable tool for optimizing the UV treatment process and informing the design of larger-scale reactors for on-site implementation.

Our research, conducted in both field and greenhouse settings, provides significant insights into the accumulation patterns of PPCPs within complex soil-plant systems, in contrast to hydroponic studies. We have observed trace amounts of PPCP accumulation in food crops, which is crucial for understanding these patterns. This information is crucial for assessing the potential risks associated with the use of recycled water for irrigation. Furthermore, our results provide a foundation for future research on other

emerging contaminants, such as per- and polyfluoroalkyl substances (PFAS), which may have lower toxicity thresholds. By investigating the accumulation patterns of these compounds in agricultural systems, we can develop more effective strategies for managing their presence in recycled water and ensuring the safety of our food supply. Through this research, a framework has been established for future investigations into the long-term implications of using treated recycled water for irrigation. The studies conducted provide a foundation for understanding the dynamic interactions between water quality, irrigation practices, and crop health. This comprehensive approach ensures that the agricultural sector can move towards more sustainable practices, addressing the dual challenges of water scarcity and contamination. The integration of advanced water treatment technologies with optimized irrigation strategies offers a pathway to achieving higher crop yields, improved food safety, and more efficient water use, ultimately contributing to the sustainability and resilience of agricultural systems worldwide.

Write about the implication of UV/PS and deficit irrigation as a function of crop type

Appendix A

Supporting information for Chapter 2

Accepted on Agricultural Water Management

Azad A., Liu H., Pharmaceutical and Personal Care products in Recycled Water for Edible Crop Irrigation: Understanding the Occurrence, Crop Uptake, and Water Quantity Effects, *Agricultural Water Management*, 2024, (accepted).

Table S1 Properties of PPCPs in this study; chemical structure, class information, $\log_{10}$ transformation of the octanol-water partition coefficient (log K_{ow}), $\log_{10}$ transformation of the acid dissociation constant (pK_a), and number of prescriptions.

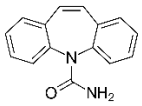
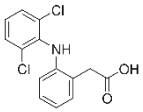
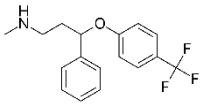
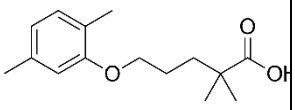
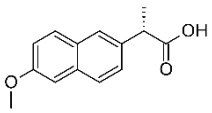
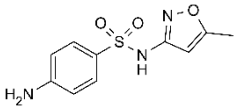
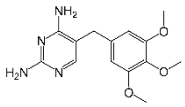
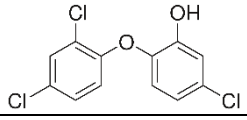
PPCPs	**Chemical Structure**[1]	**Class**	**log K_{ow}** [2]	**pK_a**[2]	**No. of Prescriptions (in millions) (2019)**[3]
Carbamazepine		Anticonvulsant	2.45	2.30	2.8
Diclofenac		Anti-inflammatory	4.51	4.15	10.1
Fluoxetine		Antidepressant	4.05	10.09	27.1
Gemfibrozil		Cholesterol medication	4.77	4.75	2.4
Naproxen		Anti-inflammatory	3.18	4.15	11.7
Sulfamethoxazole		Antibiotics	0.89	1.85	6.6 (Sulfamethoxazole and Trimethoprim are used together in medicinal drugs)
Trimethoprim		Antibiotics	0.91	7.12	
Triclosan		Antimicrobial agent	4.76	7.90	Used in personal care products

Table S2 Crop coefficient of leafy and fruity crops [4,5].

Leafy/fruity crops	**K_C initial**	**K_C middle**	**K_C end**	**Avg K_C**
Lettuce	0.7	1	0.95	0.88
Spinach	0.7	1.05	0.95	0.90
Cabbage	0.7	1.05	0.95	0.90
Cauliflower	0.7	1.05	0.95	0.90
Cucumber	0.6	1	0.75	0.78
Pea	0.5	1.15	1.1	0.92
Pepper	0.86	1.55	1.4	1.27

Table S3 PPCPs occurrence (ng/L) in secondary effluent.

Ref	CBZ	DCF	FLX	GMF	NPX	SMX	TRM	TCS	Location
[6]	270	130		3250	2300	920	620	790	USA
[7]		395, 315		3393, 1373	2602, 725				USA
[8]		68, 83			38, 34, 12			82, 54, 65	USA
[9]						700, 200, 480, 460	2500, 300, 580, 590		USA
[10]								130, 170, 350	USA
[11]					106			21	USA
[12]								240, 410	USA
[13]	76, 111, 34	8, 32, 177		42, 84		472, 274, 79			USA
[14]								171, 181	USA
[15]	23					22000, 580, 1400	1000, 22, 760		USA
[16]					1850, 2600, 800	250			Spain
[17]		70, 60, 210, 190, 50, 30, 90, 70, 70, 70, 80, 70, 120, 70,		110, 110, 540, 530, 180, 180, 200, 210, 140, 150, 80, 80, 320, 220,	570, 510, 790, 770, 700, 680, 980, 980, 590, 600, 370, 350, 1110, 650,			160, 140, 190, 190, 160, 160, 200, 210, 130, 130, 110, 130, 740, 600,	Canada

		60, 60, 20, 40, 20, 70, 60, 60		220, 230, 20	620, 560, 210, 310, 370, 810, 740, 720			520, 550, 40, 50, 30, 120, 150, 150	
[18]	1180	120		180	250	70	40	160	Sweden
[19]	1594, 1337, 952, 690, 465	1536, 1533, 1680, 1300, 780				50, 18, 91, 51			Austria
[20]	32, 24, 119, 17, 270, 116, 51, 52, 148, 61, 80, 100, 56, 15, 17, 49				162, 103, 230, 81, 173, 138, 98, 61, 145, 164, 116, 68, 89, 73, 55, 38			381, 296, 618, 620, 978, 518, 803, 1020, 541, 352, 387, 404, 434, 219, 262, 346	Japan
[21]		140, 194		255, 246	351, 452			106, 108	Canada
[22]		90		130	380			250	USA
[23]	65		560			140	120		USA
[24]	130	900						200	Spain
[25]					99				Japan
[20]	2, 11, 21, 46				74, 47, 33, 85	40	16	298, 360, 238, 158	Japan
[26]	290, 500, 320,				2620, 1180, 1830,				Spain

	370				1960				
[27]							76, 111		Switzerland
[28]	2499	98			370	10	1152		UK
[29]						50	10		Australia
[30]	740								Germany
[31]		485			340				Sweden
[32]	1500	670		230	330	71	520	410	Switzerland
[33]	147, 5, 25			63, 5, 10		829, 13			USA

Table S4 PPCPs occurrence (ng/L) in tertiary effluent.

Ref	CBZ	DCF	FLX	GMF	NPX	SMX	TCS	TRM	Location
[34]	4	0.7	10	0.4	0.4	0.3	3	0.4	USA
[35]	322	9	16	123	32	753	60	40	USA
[36]	257	71	34	20	22	1612	63	35	USA
[37]	210, 460, 320							120, 760, 38	USA
[38]	67					670		21	USA
[39]		90		130	380			250	USA
[7]		188, 98		581, 258	55, 71				
[40]					31, 23		72, 47, 28		USA
[9]						680, 220, 500, 380		2400, 210, 540, 360	
[41]			60, 56				129, 163		USA
[42]							110		USA
[10]							260, 150, 180		
[43]	223, 269, 297	18, 42, 47	20, 18, 22	438, 773, 215	18, 41, 11	18, 180, 265	11	59, 25	USA
[44]	155					178			USA
[45]	205, 171	15, 17	5, 10	36, 270	26, 1.3	265, 33	7.6, 11	15, 7.5	USA

Table S5 PPCPs bioaccumulation factors (L/kg) in various crops.

PPCPs		Lettuce	Spinach	Collards	Cabbage	Wisconsin fast plant	Cauliflower	Cucumber	Pepper	Pea	Ref
CBZ	**Root**	26 19.6	7.2 9.6		10	0.5 (whole plant)		19.2 11.6 1.6	14.4 13	0.2	46–49
	Leaves	58 50	5.8 4.6		0.01			48 32 45.3	134 104	2.2	
SMX	**Root**	ND 0.6	ND 0.3		13.8	1.9 (whole plant)		5.8 1.4	1 1.3	1.7	46,47,49
	Leaves	ND ND	ND 0.2		0.1			0.1 ND	0.2 0.1	0.1	
TRM	**Root**	26 28	22 18.4		8.9	0.8 (whole plant)		54 28	48 54	2.3	46,47,49
	Leaves	2.2 2	2.2 1.8		0.06			20 11.8	14.8 24	1.2	
NPX	**Root**	19.8 28 1853	0.4 0.8	399				5 5.8	6.6 15.8		46,50
	Leaves	ND 0.02 62	0.08 0.04	139				0.4 0.08	1.2 1.2		
FLX	**Root**	260 280	190 182					440 220	52 46		46,51
	Leaves	44 52	68 60				2.7	13.2 24	138 164		
GMF	**Root**	17.6 22	1 0.5					7.4 11.2	2.4 5.4		46
	Leave	0.4	0.4					0.2	0.2		

	s	0.1	0.02					ND	0.2		
TCS	**Root**	138 112	54 34					4.2 4.2	0.4 0.6		[46]
	Leaves	ND ND	ND ND					0.4 0.1	0.2 0.3		
DCF	**Root**	4.2 4 3677	ND 0.5	942				0.6 0.4	2.8 3.2	0.1	[46,49,50]
	Leaves	ND ND 75	ND ND	115				ND ND	ND ND	ND	

Table S6 The range of PPCPs occurrence in secondary and tertiary effluent.

	Secondary effluent			Tertiary effluent		
PPCPs	**Mean (ng/L)**	**10^{th} percentile (ng/L)**	**90^{th} percentile (ng/L)**	**Mean (ng/L)**	**10^{th} percentile (ng/L)**	**90^{th} percentile (ng/L)**
SMX	1400	33	2455	400	23	731
NPX	770	60	1982	55	3	68
GMF	608	48	2141	259	20	581
TRM	529	21	1015	309	11	672
CBZ	361	17	952	228	85	322
DCF	301	35	947	55	9	98
TCS	292	68	614	97	9	215
FLX	130	20	348	25	9	56

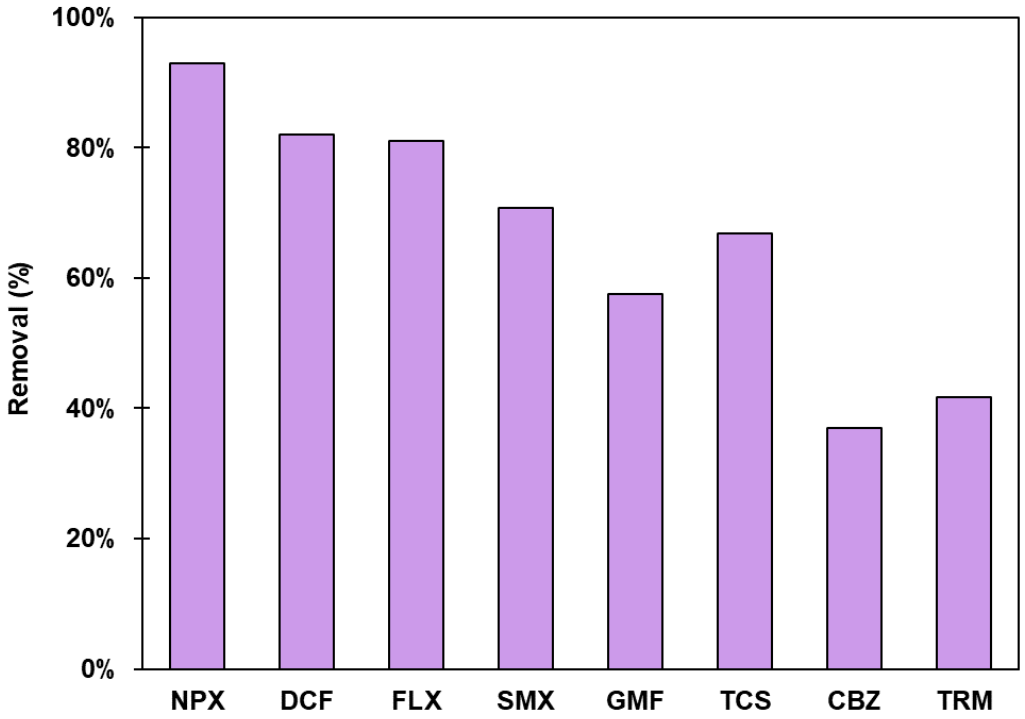


Figure S1 The average removal of PPCPs from wastewater effluent by tertiary treatment processes. The mean concentration of secondary and tertiary effluent was used to calculate the percentage overall removal.

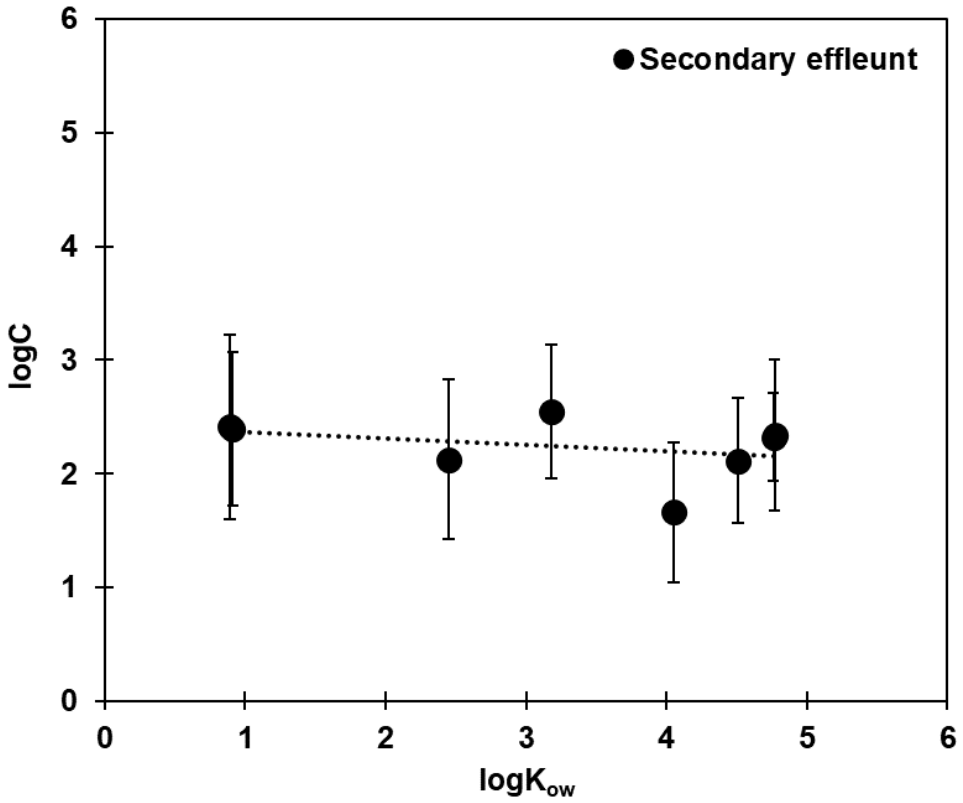


Figure S2 Relationship between logC vs logK_{ow} of selected PPCPs in the secondary effluent.

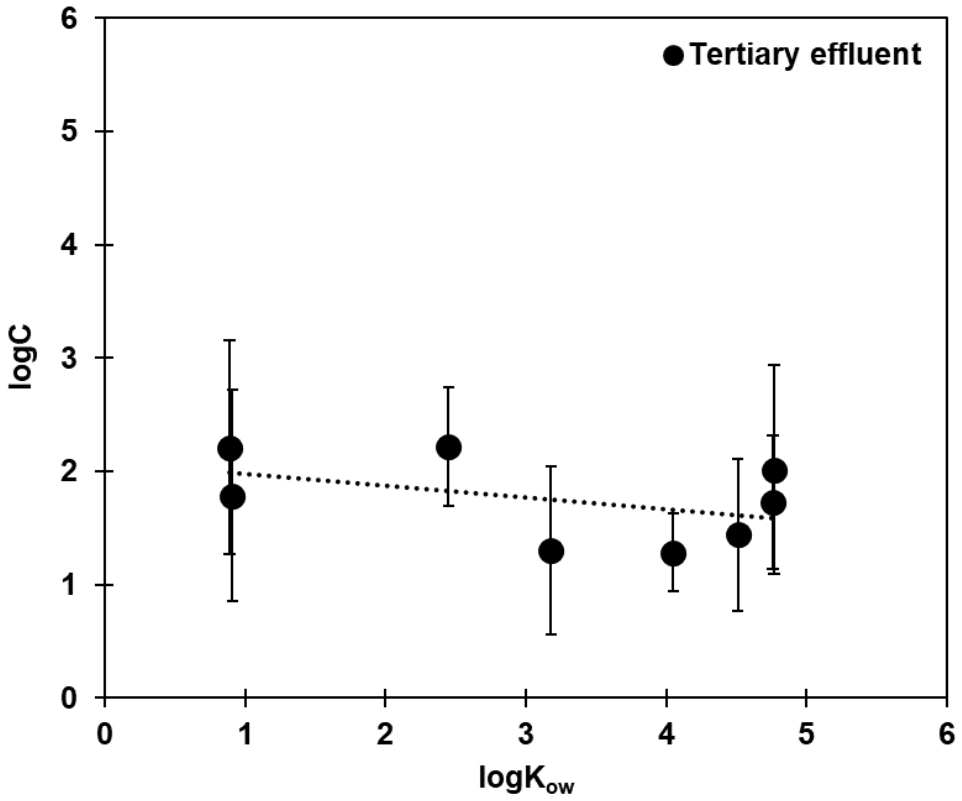


Figure S3 Relationship between logC vs logK_{ow} of selected PPCPs in the tertiary effluent.

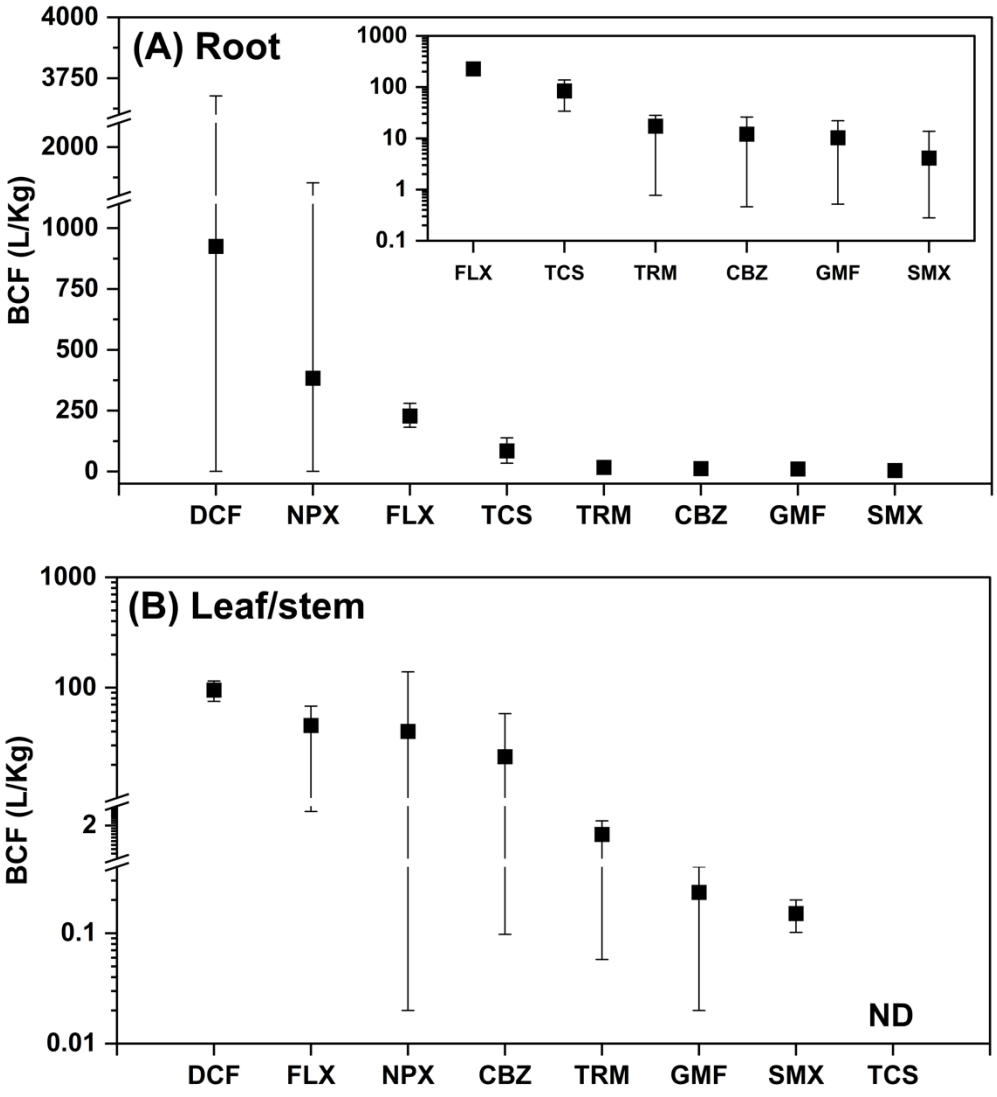


Figure S4 The mean bioconcentration factors (BCF) of PPCPs in different parts of leafy vegetables in hydroponic system. (A) Root and (B) Leaf/stem. The error bars represent the maximum and minimum of the dataset.

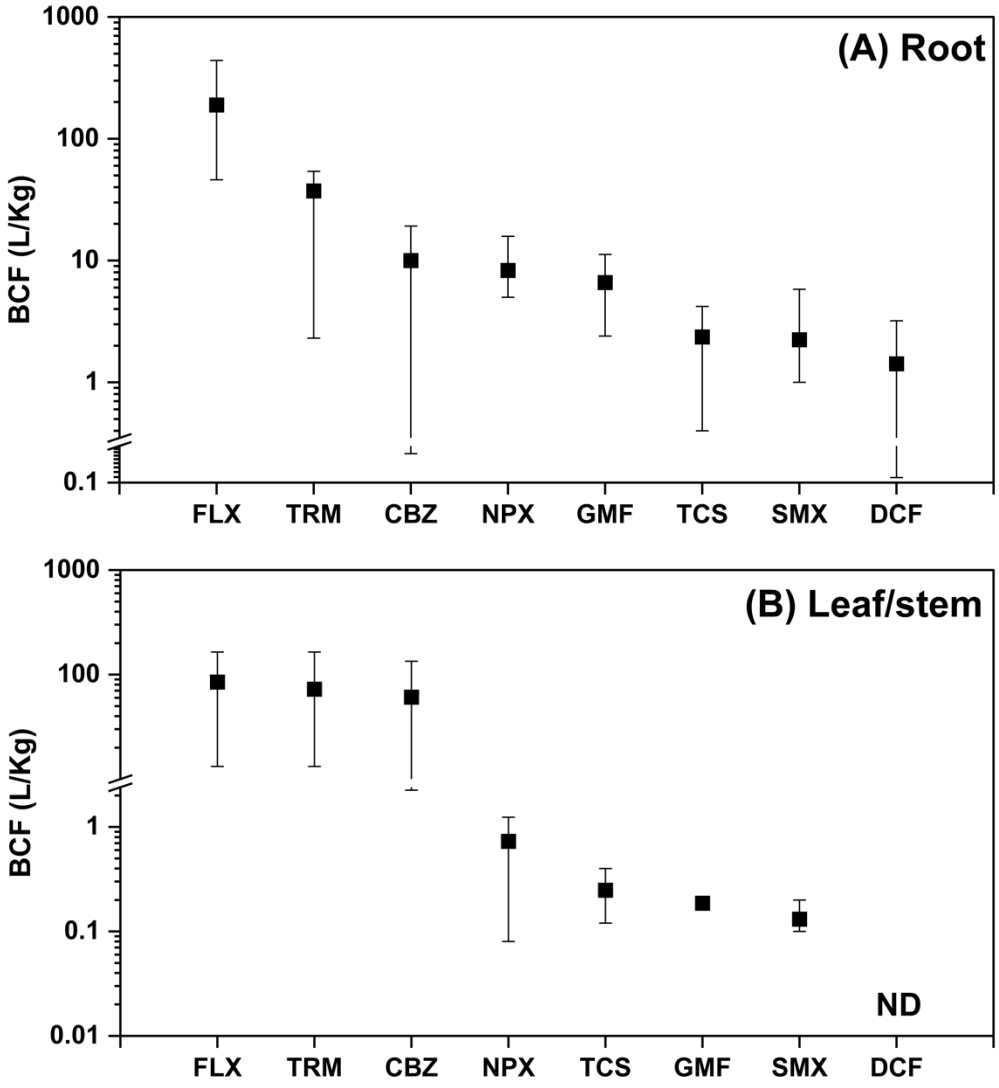


Figure S5 The mean bioconcentration factors (BCF) of PPCPs in different parts of fruity vegetables in hydroponic system. (A) Root and (B) Leaf/stem. The error bars represent the maximum and minimum of dataset.

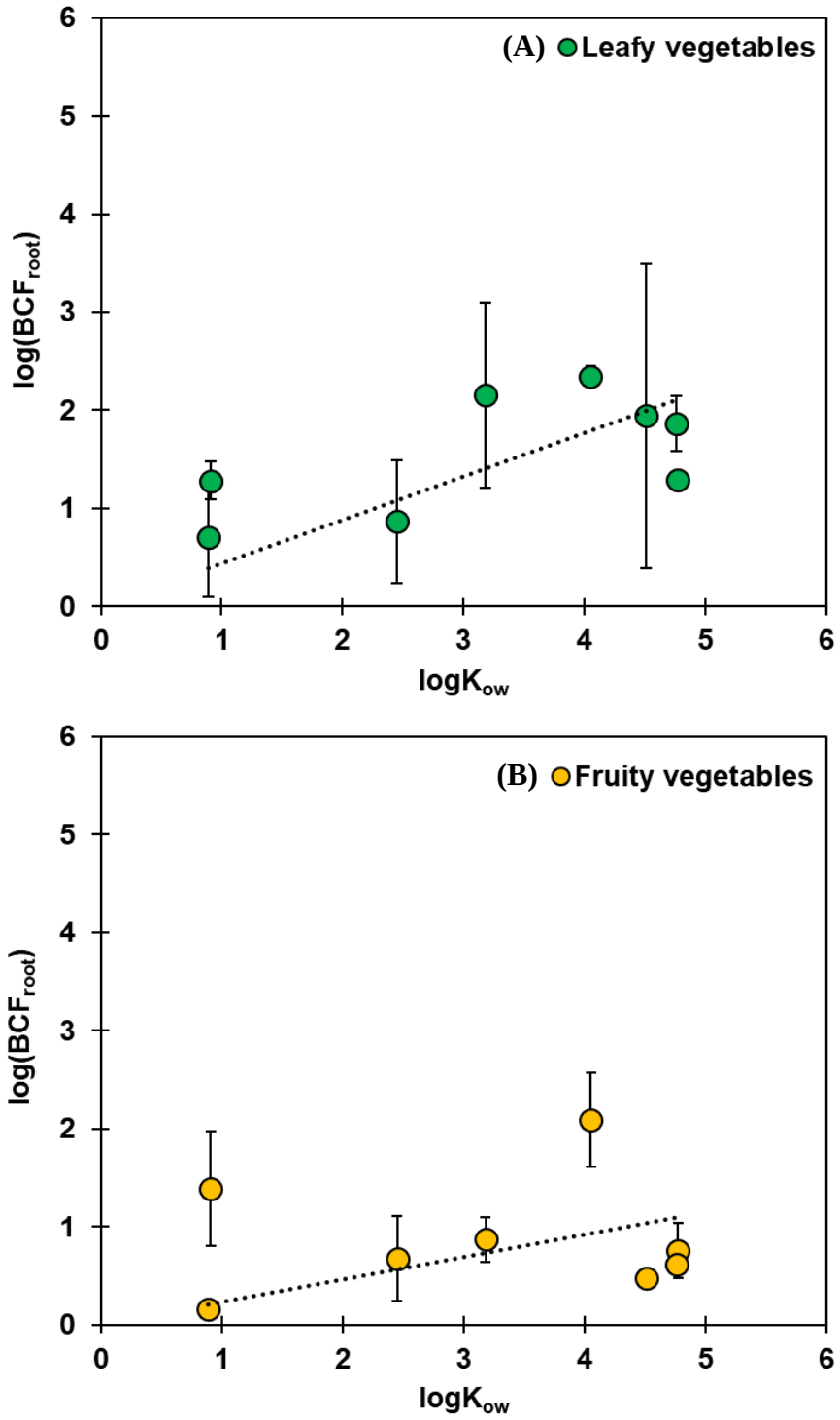


Figure S6 The relationship of logK_{ow} and log(BCF$_{root}$) in edible crops. (A) Leafy vegetables and (B) Fruity vegetables.

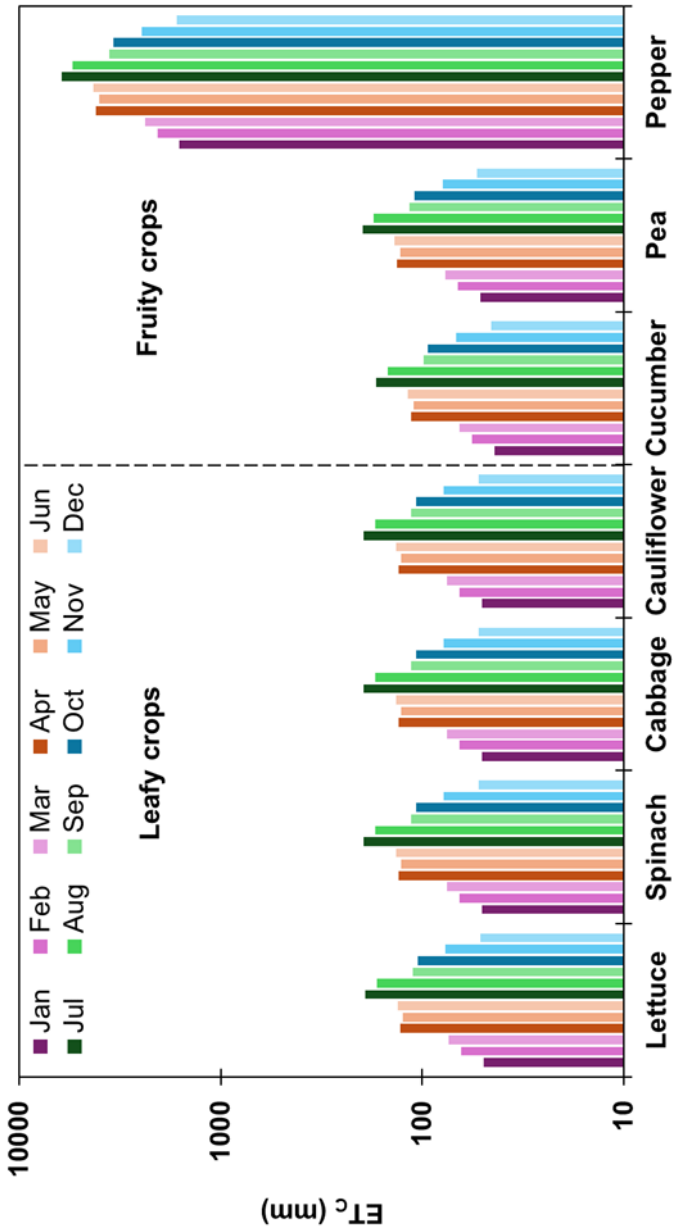


Figure S7 The annual crop evapotranspiration (ET_C) of leafy and fruity vegetables. Data were calculated using the year of 2023 as an example and based on reference evapotranspiration collected from the California Irrigation Management Information System (CIMIS) for at Riverside, California (Station 44).

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Appendix B

Supporting information for Chapter 3

Previously published on Water Research

Azad A., Iradukunda J., Men Y., Verdi A., Liu H., Persulfate Photolysis and Limited Irrigation of Recycled Wastewater for Turfgrass Growth: Accumulation of Pharmaceutical and Personal Care Products and Physiological Responses, *Water Research*, 2024, DOI: https://doi.org/10.1016/j.watres.2024.122009

Table S1 Properties of PPCPs in this study; chemical structure, class information, $\log_{10}$ transformation of the octanol-water partition coefficient (log K_{ow}), $\log_{10}$ transformation of the acid dissociation constant (pK_a).

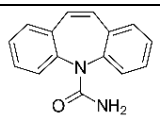
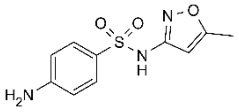
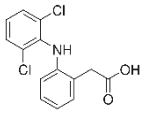
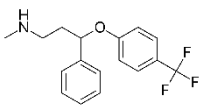
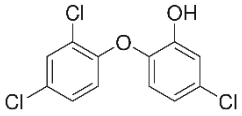
PPCPs	**Chemical Structure**	**Class**	**log K_{ow}**[1]	**pK_a**[1]
Carbamazepine		Anticonvulsant	2.45	2.30
Sulfamethoxazole		Antibiotics	0.89	1.85
Diclofenac		Anti-inflammatory	4.51	4.15
Fluoxetine		Antidepressant	4.05	10.09
Triclosan		Antimicrobial agent	4.76	7.90

Table S2 Recycled water quality for turfgrass irrigation.

Chemical Constituents	**Unit**	**Range**
pH		7.5
Cl^-	mg/L	143.59 ± 2.71
NO_3^- (as N)	mg/L	4.05 ± 0.01
NO_2^- (as N)	mg/L	0.06 ± 0.01
SO_4^{2-}	mg/L	195 ± 1.18
Alkalinity (as $CaCO_3$)	mg/L	111.75 ± 1.75
NH_3 (as N)	mg/L	0.91 ± 0.02

Table S3 Reactions and rate constants of radicals in recycled water for carbamazepine degradation.

No.	Reaction	Rate constant	Ref.
1	$SO_4^{\bullet-} + S_2O_8^{2-} \rightarrow S_2O_8^{-\bullet} + SO_4^{2-}$	$6.6\times10^5\ M^{-1}s^{-1}$	[2]
2	$SO_4^{\bullet-} + H_2O \rightarrow {}^{\bullet}OH + HSO_4^{2-}$	$6.6\times10^2\ s^{-1}$	[3]
3	$SO_4^{\bullet-} + Cl^- \leftrightarrow Cl^{\bullet} + SO_4^{2-}$	$k_+ = 3.2\times10^8\ M^{-1}s^{-1}$ $k_- = 2.1\times10^8\ M^{-1}s^{-1}$	[4]
4	$SO_4^{\bullet-} + HCO_3^- \rightarrow CO_3^{\bullet-} + SO_4^{2-} + H^+$	$1.6\times10^6\ M^{-1}s^{-1}$	[4]
5	$SO_4^{\bullet-} + NO_3^- \rightarrow NO_3\bullet + SO_4^{2-}$	$2.1\times10^6\ M^{-1}s^{-1}$	[5]
6	$SO_4^{\bullet-} + NO_2^- \rightarrow {}^{\bullet}NO_2 + SO_4^{2-}$	$9.8\times10^8\ M^{-1}s^{-1}$	[6]
7	$SO_4^{\bullet-}$ + CBZ → product	$1.9\times10^9\ M^{-1}s^{-1}$	[7]
8	${}^{\bullet}OH + S_2O_8^{2-} \rightarrow S_2O_8^{-\bullet} + OH^-$	$1.4\times10^7\ M^{-1}s^{-1}$	[8]
9	${}^{\bullet}OH + NO_2^- \rightarrow {}^{\bullet}NO_2 + HO^-$	$1.2\times10^{10}\ M^{-1}s^{-1}$	[6]
10	${}^{\bullet}OH + Cl^- \leftrightarrow ClOH^{\bullet-}$	$k_+ = 4.3\times10^9\ M^{-1}s^{-1}$ $k_- = 6.1\times10^9\ s^{-1}$	[5]
11	${}^{\bullet}OH + HCO_3^- \rightarrow CO_3^{\bullet-} + H_2O$	$8.5\times10^6\ M^{-1}s^{-1}$	[5]
12	${}^{\bullet}OH$ + CBZ → product	$8.8\times10^9\ M^{-1}s^{-1}$	[9]
13	$Cl^{\bullet} + S_2O_8^{2-} \rightarrow S_2O_8^{-\bullet} + Cl^-$	$8.8\times10^6\ M^{-1}s^{-1}$	[10]
14	$Cl^{\bullet} + Cl^- \rightarrow Cl_2^{\bullet-}$	$8.5\times10^9\ M^{-1}s^{-1}$	[11]
15	$Cl^{\bullet} + H_2O \leftrightarrow ClOH^{\bullet-} + H^+$	$k_+ = 2.5\times10^5\ s^{-1}$ $k_- = 2.1\times10^{10}\ M^{-1}s^-$	[12]

		[1]	
16	$Cl^{\bullet} + HCO_3^- \rightarrow Cl^- + CO_3^{\bullet-}$	$2.2\times10^8\ M^{-1}s^{-1}$	[13]
17	$Cl^{\bullet} + NO_2^- \rightarrow Cl^- + {}^{\bullet}NO_2$	$8.8\times10^9\ M^{-1}s^{-1}$	[5]
18	$Cl^{\bullet} + CBZ \rightarrow$ Product	$2.7\times10^9\ M^{-1}s^{-1}$	[14]
19	$Cl_2^{\bullet-} + S_2O_8^{2-} \rightarrow S_2O_8^{\bullet-} + 2Cl^-$	$6.0\times10^5\ M^{-1}s^{-1}$	[15]
20	$Cl_2^{\bullet-} + H_2O \rightarrow HClOH^{\bullet} + Cl^-$	$1.3\times10^3\ s^{-1}$	[16]
21	$Cl_2^{\bullet-} + HCO_3^- \rightarrow 2Cl^- + H^+ + CO_3^{\bullet-}$	$8.0\times10^7\ M^{-1}s^{-1}$	[17]
22	$Cl_2^{\bullet-} + NO_2^- \rightarrow Cl^- + Cl^- + {}^{\bullet}NO_2$	$2.5\times10^8\ M^{-1}s^{-1}$	[5]
23	$Cl_2^{\bullet-} + CBZ \rightarrow$ Product	$2.2\times10^6\ M^{-1}s^{-1}$	[14]
24	$CO_3^{\bullet-} + NO_2^- \rightarrow CO_3^{2-} + {}^{\bullet}NO_2$	$6.6\times10^5\ M^{-1}s^{-1}$	[5]
25	$CO_3^{\bullet-} + CBZ \rightarrow$ Product	$2.51\times10^6\ M^{-1}s^{-1}$	[7]

Table S4 The calculated steady-state concentrations of radical species during UV/PS photolysis treatment of recycled water used in this study.

Radicals	**[$^{\bullet}$R]ss (M)**
$SO_4^{\bullet-}$	7.40×10^{-13}
$^{\bullet}OH$	1.32×10^{-14}
$Cl^{\bullet}$	2.69×10^{-14}
$Cl_2^{\bullet-}$	4.79×10^{-12}
$CO_3^{\bullet-}$	2.23×10^{-10}

Table S5 Recoveries of target analytes in biomass and water.

Compounds	LOQ* (ng/mL)	Linearity (R^2)	Recovery (%)				
			Leaves	Root	Spiked recycled water	Treated recycled water	Potable water
Carbamazepine	0.9	0.9997	56 ± 8	63 ± 18	67 ± 7	57 ± 7	NA
Sulfamethoxazole	1.0	0.9963	11 ± 4	40 ± 8	42 ± 4	NA	NA
Diclofenac	0.9	0.9997	66 ± 16	52 ± 23	51 ± 17	NA	NA
Fluoxetine	0.9	0.9995	16 ± 7	12 ± 4	22 ± 5	NA	23 ± 1
Triclosan	0.9	0.9986	NA	47 ± 4	54 ± 3	NA	NA

*LOQ, limit of quantification

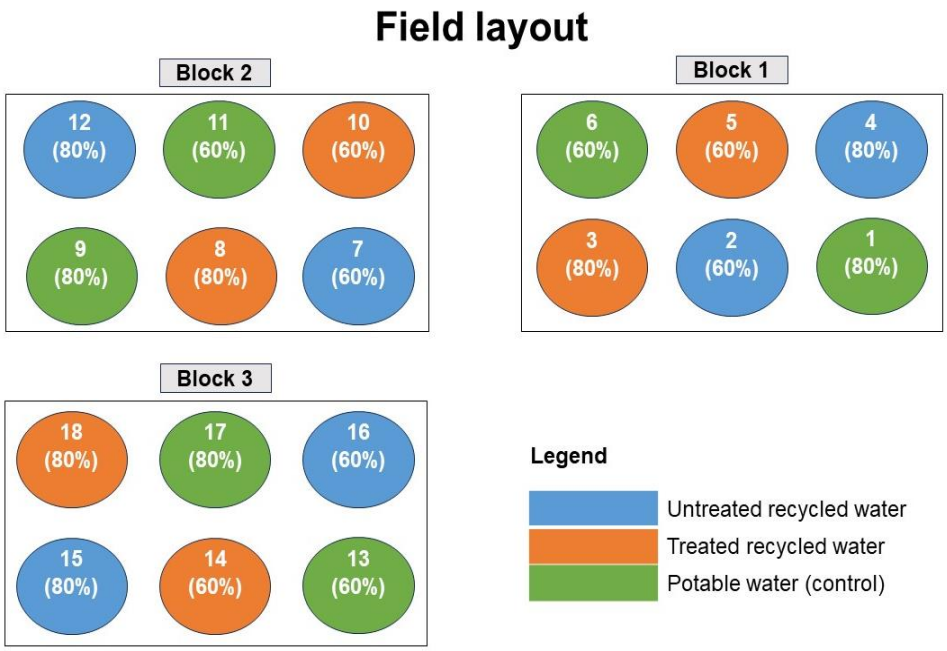


Figure S1 The field layout of the turfgrass irrigation experiment.

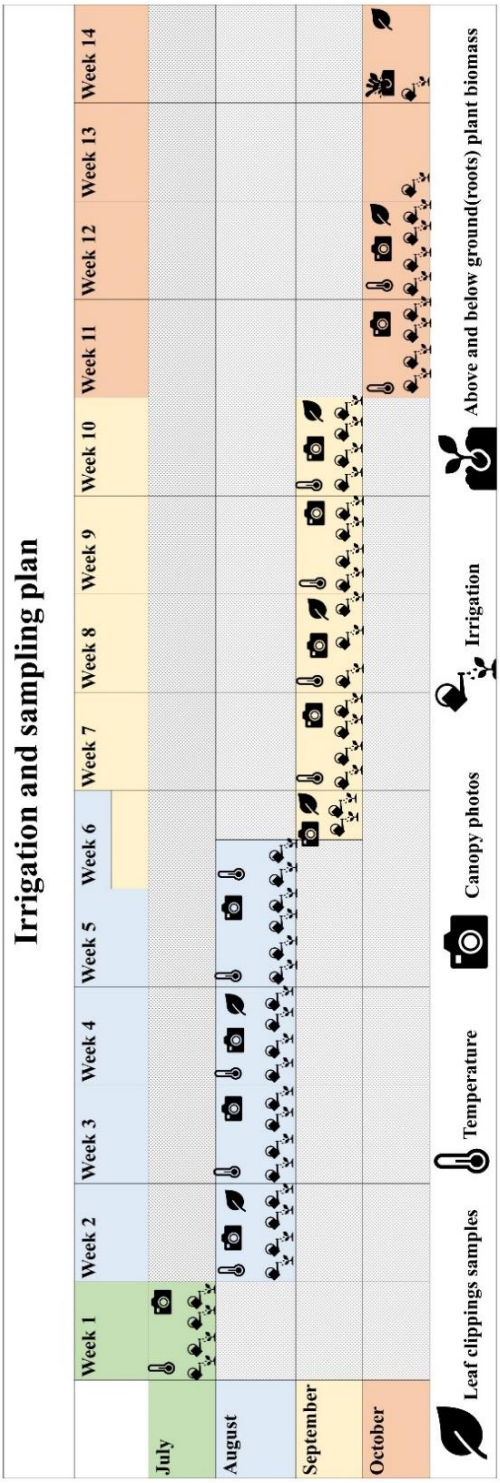


Figure S2 Irrigation schedule of the 14-week turfgrass field experiments from July 2022 to October 2022.

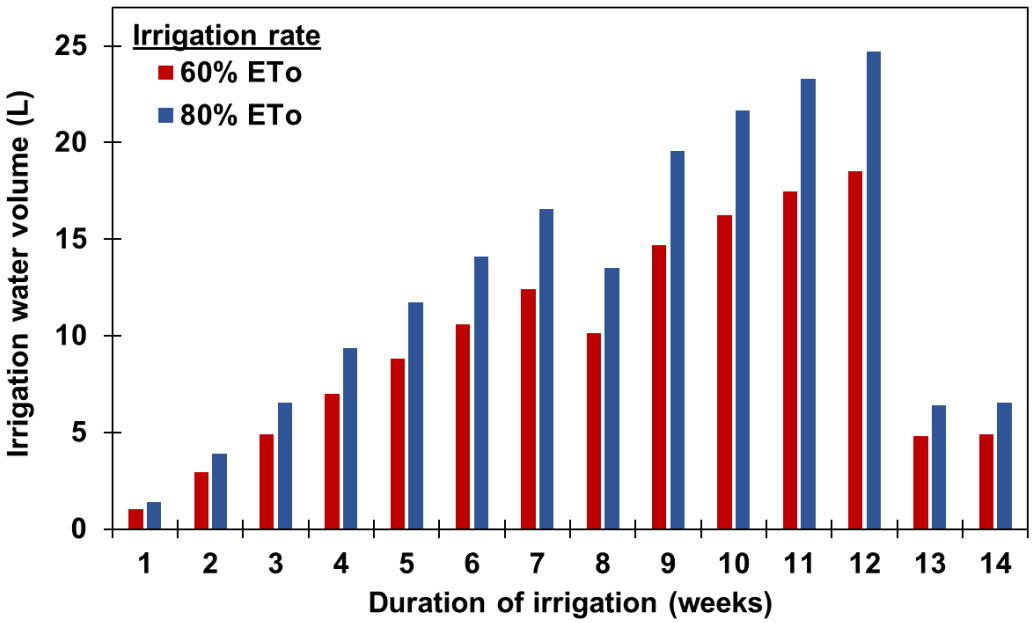


Figure S3 The total volume of irrigation water under different irrigation scenarios.

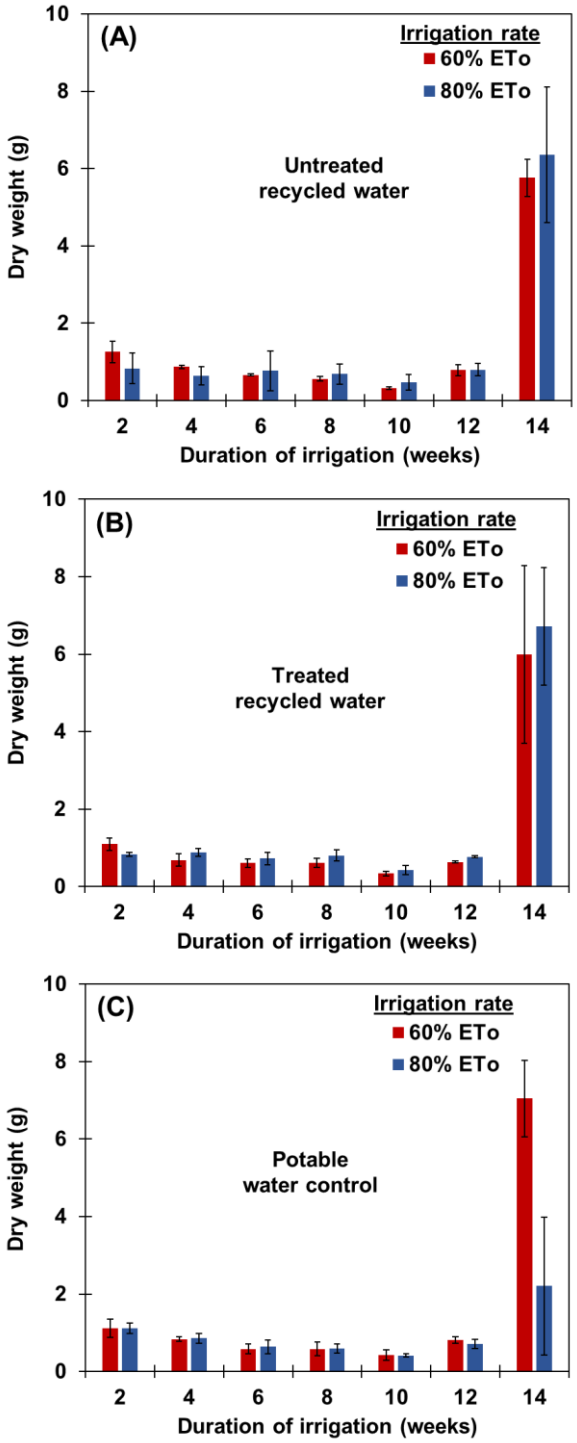


Figure S4 Dry weight of leaf sample collected when irrigated with different types of irrigation water. (A) untreated recycled water, (B) treated recycled water, (C) potable water control.

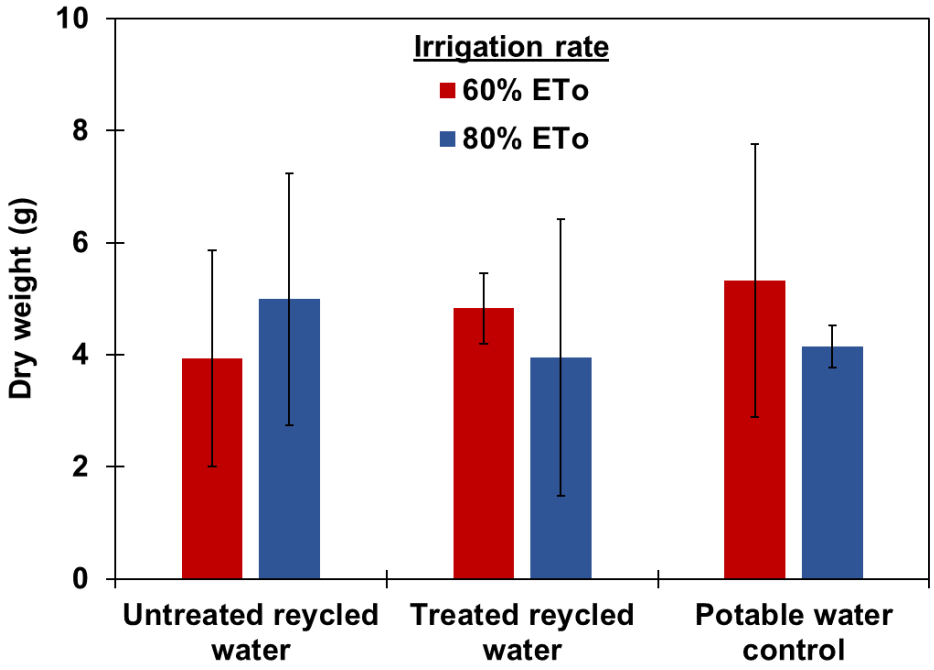


Figure S5 Dry weight of root sample collected when irrigated with different types of irrigation water.

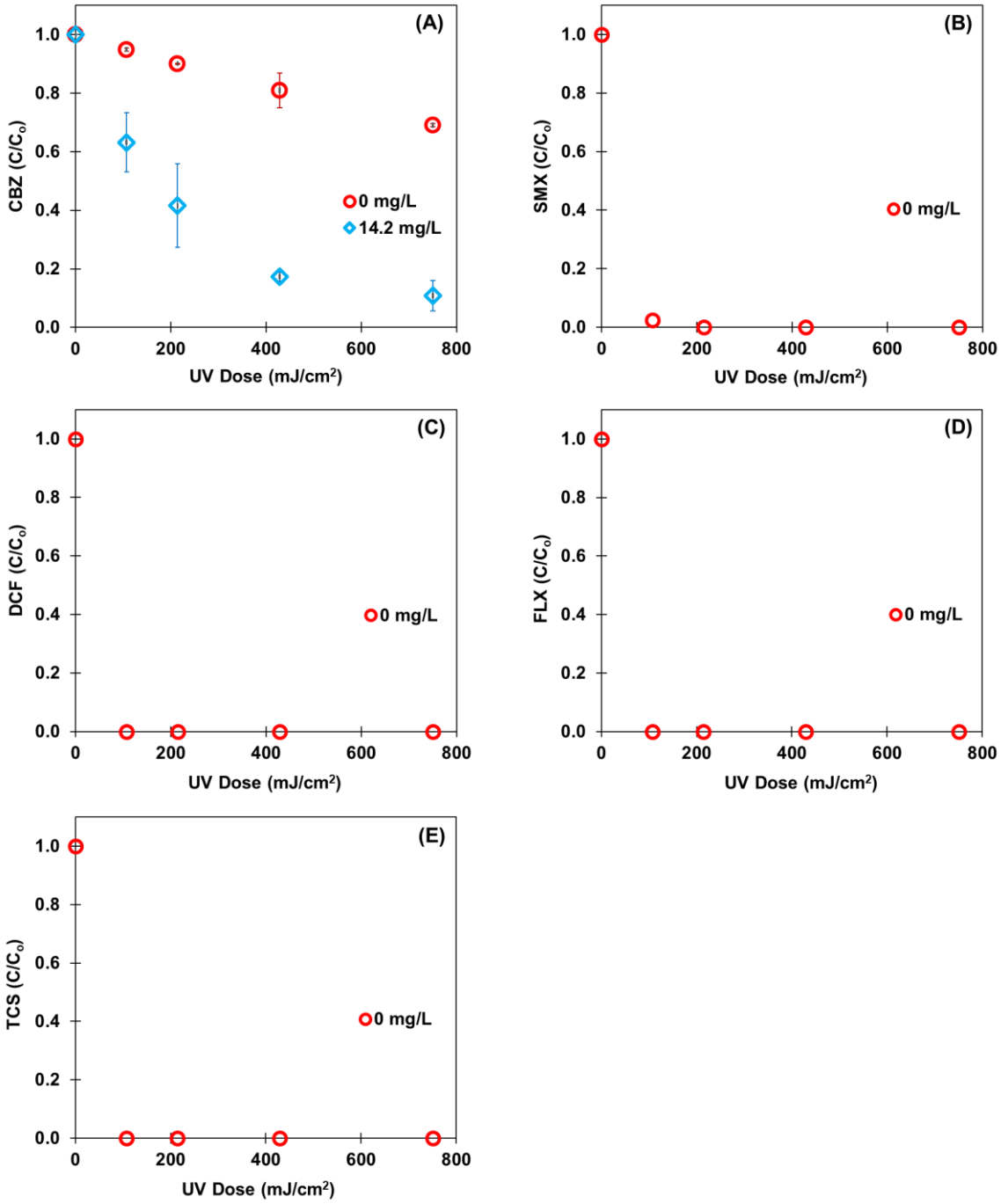


Figure S6 Degradation of PPCPs with varying concentrations of $S_2O_8^{2-}$ in untreated recycled water. (A) carbamazepine (CBZ), (B) sulfamethoxazole (SMX), (C) diclofenac (DCF), (D) fluoxetine (FLX), and (E) triclosan (TCS).

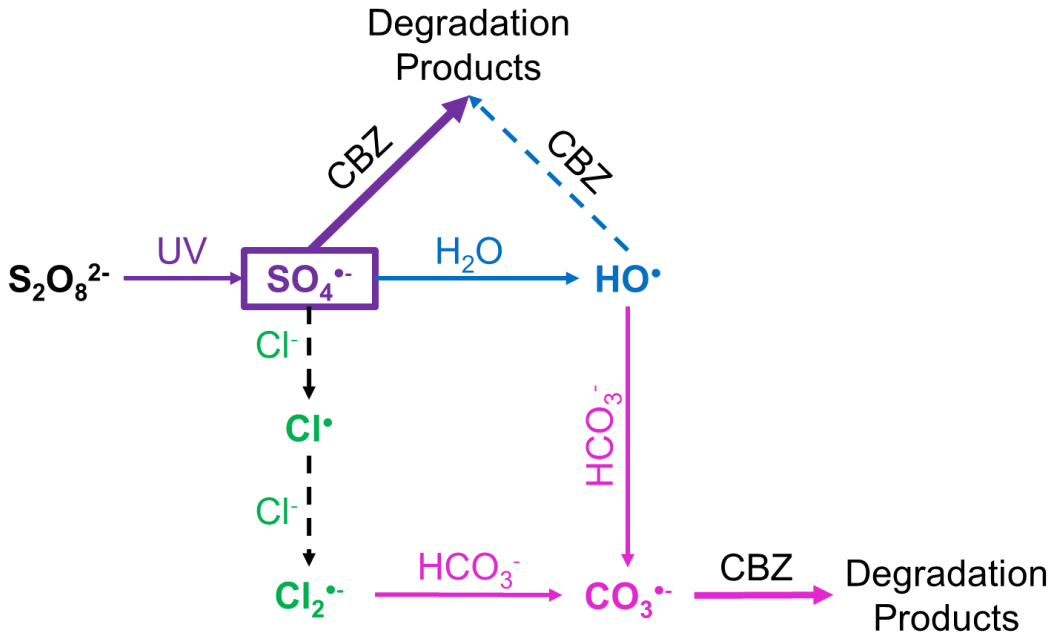


Figure S7 Proposed radical pathway for carbamazepine (CBZ) degradation by UV/PS in recycled water. All reactions are listed in Table S3.

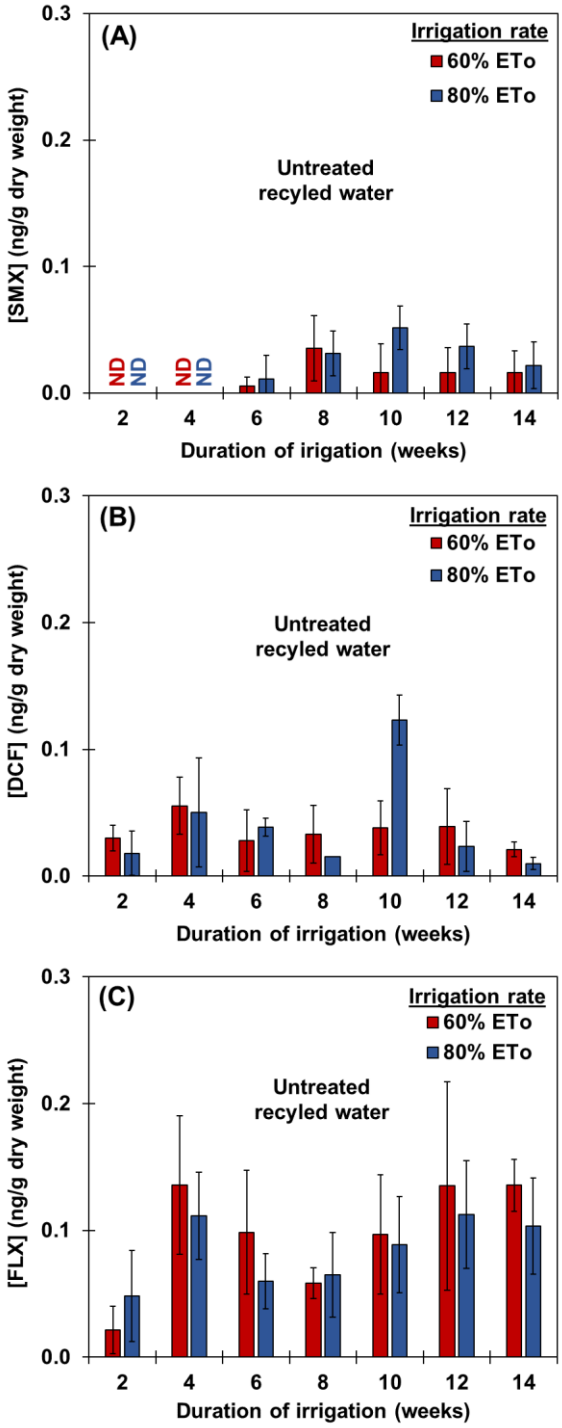


Figure S8 PPCPs accumulation in turfgrass leaves over 14 weeks when irrigated with untreated recycled water at two different irrigation rates. (A) sulfamethoxazole (SMX), (B) diclofenac (DCF), and (C) fluoxetine (FLX).

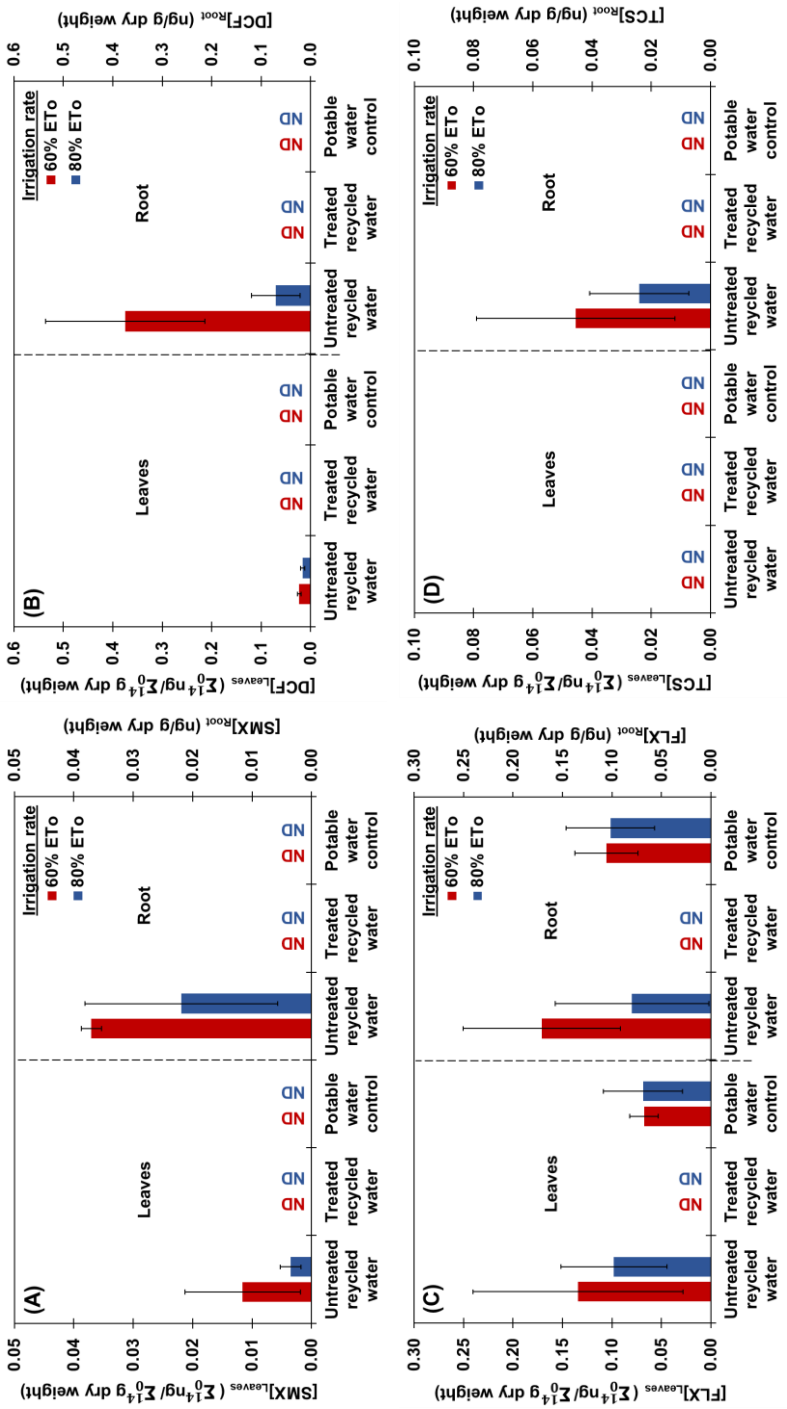


Figure S9 14-week normalized concentration of PPCPs turfgrass leaves and final concentration in roots when irrigated with untreated recycled water at two different irrigation rates. (A) Sulfamethoxazole (SMX), (B) diclofenac (DCF), (C) fluoxetine (FLX), and (D) triclosan (TCS).

Text S1. Chemicals and materials

Carbamazepine was purchased from Acros Organics, sulfamethoxazole was purchased from TCI, Diclofenac-Na salt and fluoxetine-HCl were purchased from Alfa Aesar, triclosan (Irgasan) was purchased from Sigma. Carbamazepine-d_{10}, sulfamethoxazole-d_4, diclofenac-d_4 sodium, fluoxetine-d_5 hydrochloride, and triclosan-d_3 were purchased from TRC (Toronto Research Chemicals). Potassium Persulfate was purchased from J.T.Baker. Deionized water (DI) (resistivity >18.2 MΩ) was prepared using a Millipore system.

Text S2. Field irrigation trial

The turfgrass field irrigation experiment was conducted at the University of California Riverside Agriculture Experiment Station (33°57′ 47.0″N 117°20′ 13.4″W) in Riverside, California. The grass was established with sod in a 3.5 m × 3.5 m plot in June 2021. Full irrigation was applied to facilitate establishment using four-quarter cycle pop-up heads controlled using a solenoid valve (Hunter, CA). Full irrigation was applied again in May 2022 to help plants recover from dormancy until July 2022 before starting the experiment. The ET_o data were obtained from the California Irrigation Management Information Systems (CIMIS) weather station located at the University of California Riverside Agricultural Operations, situated just 250 meters away from the experimental site.

Text S3. Analysis of PPCPs

Irrigation water samples. A 5 mL water sample was spiked with deuterated surrogates to reach a predetermined concentration of 1 µg/L. The water sample was then loaded onto the HLB cartridges (150 mg, Waters) that were preconditioned with 7 mL methanol and 7 mL DI water. After the extract passed through the cartridge, 15 mL methanol was used to elute the analytes. The methanol extract was further dried under nitrogen gas and reconstituted in 1 mL methanol. The final samples were centrifuged at 16,000g for 30 minutes and injected into HPLC-HRMS/MS for analysis.

Turfgrass tissue samples. 0.1 grams of plant tissue samples were placed in a 50 mL centrifuge tube and spiked with 50 µL of 400 µg/L of deuterated surrogates before the extraction. PPCPs in plant tissue samples (leaves and roots) were extracted using 20 mL of acetonitrile in an ultrasonic water bath for 30 minutes, followed by centrifugation at 10,000 rpm for 10 min. The supernatant was pooled after centrifugation. The plan tissue samples were extracted once more with 20 mL of acetonitrile and then centrifuged. The combined extracts were dried under nitrogen gas using a nitrogen evaporator (N-EVAP 111, Organomation) and redissolved in 1 mL methanol followed by mixing with 20 mL DI water. The aqueous solution was loaded onto HLB cartridges (150 mg, Waters) that were preconditioned with 7 mL methanol and 7 mL DI water. After the extract passed through the cartridge, 15 mL methanol was used to elute the analytes. The methanol extract was further dried under nitrogen gas and reconstituted in 1 mL methanol. The final samples were centrifuged at 16,000g for 30 min and filtered through 0.22 µm polytetrafluoroethylene (PTFE) membrane filters to remove solids. Final samples were

injected into HPLC-HRMS/MS for analysis. The spiked deuterated surrogates were used to determine the overall analyte recovery for the entire extraction and clean up procedure. Recoveries of deuterated compounds are in Table S5.

Post-SPE cleanup, samples were subjected to analysis using a high-resolution liquid chromatography from ThermoFisher Q Exactive Hybrid Quadrupole Orbitrap (HPLC-HRMS/MS) with a HESI-II and ESI source. Analyte separation was performed at 30°C using a Waters XBridge C18 column (2.1 mm × 50 mm × 3.5 µm). The mobile phase A was LC-MS grade water and B was pure methanol, both amended with 1% formic acid. The flow rate was 0.35 mL/min with the following gradient: 5% A: 0-1 min, 5-95% A: 1-16 min, 95% A: 16-21 min, and 5% A: 21-26 min. For HRMS detection, both the positive and negative electrospray ionization was used with a resolution of 70,000 @ *m/z* 200 for the full scan (*m/z* 50 - 750) and 17,500 @ *m/z* 200 for the data dependent MS^2 scan. Carbamazepine, sulfamethoxazole, and fluoxetine were analyzed in positive mode while diclofenac and triclosan were analyzed in negative mode.

Text S4. Calculation of the fate of each reactive radical species

All the reactions and citations of rate constants for this calculation are listed in Table S3.

Fate of $^{\bullet}OH$ in UV/$S_2O_8^{2-}$

$^{\bullet}OH$ was generated via the following reaction:

$SO_4^{\bullet-} + H_2O \rightarrow {}^{\bullet}OH + HSO_4^{2-}$ $k_2 = 6.6\times10^2\ s^{-1}$

Once $^{\bullet}OH$ was generated, it participated in the following reactions:

$^{\bullet}OH + S_2O_8^{2-} \rightarrow S_2O_8^{\bullet-} + OH^-$ $k_8 = 1.4\times10^7\ M^{-1}s^{-1}$

$^{\bullet}OH + NO_2^- \rightarrow {}^{\bullet}NO_2 + HO^-$ $k_9 = 1.2\times10^{10}\ M^{-1}s^{-1}$

$^{\bullet}OH + HCO_3^- \rightarrow CO_3^{\bullet-} + H_2O$ $k_{11} = 8.5\times10^6\ M^{-1}s^{-1}$

$^{\bullet}OH$ + CBZ → product $k_{12} = 8.8\times10^9\ M^{-1}s^{-1}$

Therefore, the theoretical $[^{\bullet}OH]_{SS}$ can be expressed as:

$$[OH^{\cdot}]_{SS} = \frac{k_2\,[SO_4^{\cdot-}]_{SS}}{k_8[S_2O_8^{2-}]+k_9[NO_2^-]+k_{11}[HCO_3^-]+k_{12}[CBZ]} \quad \text{(Equation S6)}$$

Under the experimental condition of 7.39×10^{-2} mM of $S_2O_8^{2-}$, 1.30×10^{-3} mM of NO_2^-, 2.40 mM of HCO_3^-, and 6.35×10^{-6} mM of CBZ, the ratio of steady-state concentrations of $^{\bullet}OH$ to $SO_4^{\bullet-}$ based on Equation S1 was calculated as:

$$\frac{[OH^{\cdot}]_{SS}}{[SO_4^{\cdot-}]_{SS}} = 1.78\times10^{-2} \quad \text{(Equation S7)}$$

Fate of $Cl^{\bullet}$ in UV/$S_2O_8^{2-}$

$Cl^{\bullet}$ was generated via the following reaction:

$SO_4^{\bullet-} + Cl^- \leftrightarrow Cl^{\bullet} + SO_4^{2-}$ $k_{+3} = 3.2\times10^8\ M^{-1}s^{-1}$, $k_{-3} = 2.1\times10^8\ M^{-1}s^{-1}$

$Cl^{\bullet}$ reacted with chemical constituents via the following reactions:

$Cl^{\bullet} + S_2O_8^{2-} \rightarrow S_2O_8^{\bullet-} + Cl^-$ $k_{13} = 8.8\times10^6\ M^{-1}s^{-1}$

$Cl^{\bullet} + Cl^{-} \rightarrow Cl_2^{\bullet-}$ $k_{14} = 8.5\times10^{9}\ M^{-1}s^{-1}$

$Cl^{\bullet} + H_2O \leftrightarrow ClOH^{\bullet-} + H^{+}$ $k_{+15} = 2.5\times10^{5}\ s^{-1}$, $k_{-15} = 2.1\times10^{10}\ M^{-1}s^{-1}$

$Cl^{\bullet} + HCO_3^{-} \rightarrow Cl^{-} + CO_3^{\bullet-}$ $k_{16} = 2.2\times10^{8}\ M^{-1}s^{-1}$

$Cl^{\bullet} + NO_2^{-} \rightarrow Cl^{-} + {}^{\bullet}NO_2$ $k_{17} = 8.8\times10^{9}\ M^{-1}s^{-1}$

$Cl^{\bullet} + CBZ \rightarrow$ Product $k_{18} = 2.7\times10^{9}\ M^{-1}s^{-1}$

For $Cl^{\bullet}$ reactions with water (Reaction 9 above), the pseudo first-order rate constant for the reverse reaction at pH 7.5 was calculated to be $6.64\times10^{2}\ s^{-1}$, significantly lower (by three orders of magnitude) than the forward rate constant ($2.5\times10^{5}\ s^{-1}$). Consequently, for this calculation, the reverse reaction was considered negligible.

Therefore. the theoretical $[Cl^{\bullet}]_{SS}$ can be expressed as:

$$[Cl^{\cdot}]_{SS} = \frac{k_{+3}[SO_4^{\bullet-}]_{SS}\,[Cl^{-}]}{k_{13}[S_2O_8^{2-}]+k_{14}[Cl^{-}]+k_{+15}+k_{16}[HCO_3^{-}]+k_{17}[NO_2^{-}]+k_{18}[CBZ]+k_{-3}[SO_4^{2-}]} \quad \text{(Equation S8)}$$

Under the experimental condition of 7.39×10^{-2} mM of $S_2O_8^{2-}$, 1.30×10^{-3} mM of NO_2^{-}, 2.40 mM of HCO_3^{-}, 4.06 mM of Cl^{-}, 2.03 mM of SO_4^{2-}, and 6.35×10^{-6} mM of CBZ, the ratio of steady-state concentrations of $Cl^{\bullet}$ to $SO_4^{\bullet-}$ based on Equation S3 was calculated as:

$$\frac{[Cl^{\cdot}]_{SS}}{[SO_4^{\bullet-}]_{SS}} = 3.64\times10^{-2} \quad \text{(Equation S9)}$$

Fate of $Cl_2^{\bullet-}$ in UV/$S_2O_8^{2-}$

$Cl_2^{\bullet-}$ was generated via the following reaction:

$Cl^{\bullet} + Cl^{-} \rightarrow Cl_2^{\bullet-}$ $k_{14} = 8.5\times10^{9}\ M^{-1}s^{-1}$

$Cl_2^{\bullet-}$ participated in the following reactions:

$Cl_2^{\bullet-} + S_2O_8^{2-} \rightarrow S_2O_8^{\bullet-} + 2Cl^{-}$ $k_{19} = 6.0\times10^{5}\ M^{-1}s^{-1}$

$Cl_2^{\bullet-} + H_2O \rightarrow HClOH^{\bullet} + Cl^-$ $k_{20} = 1.3\times10^3\ s^{-1}$

$Cl_2^{\bullet-} + HCO_3^- \rightarrow 2Cl^- + H^+ + CO_3^{\bullet-}$ $k_{21} = 8.0\times10^7\ M^{-1}s^{-1}$

$Cl_2^{\bullet-} + NO_2^- \rightarrow Cl^- + Cl^- + {}^{\bullet}NO_2$ $k_{22} = 2.5\times10^8\ M^{-1}s^{-1}$

$Cl_2^{\bullet-} + CBZ \rightarrow Product$ $k_{23} = 2.2\times10^6\ M^{-1}s^{-1}$

Therefore, the theoretical $[Cl_2^{\bullet-}]_{SS}$ can be expressed as:

$$[Cl_2^{\bullet-}]_{SS} = \frac{k_{14}\,[Cl^-]\,[Cl^{\cdot}]_{SS}}{k_{19}[S_2O_8^{2-}]+k_{20}+k_{21}[HCO_3^-]+k_{22}[NO_2^-]+k_{23}[CBZ]} \qquad \text{(Equation S10)}$$

Under the experimental condition in this study, the ratio of steady-state concentrations of $Cl_2^{\bullet-}$ to $Cl^{\bullet}$ based on Equation S5 was calculated as:

$$\frac{[Cl_2^{\bullet-}]_{SS}}{[Cl^{\cdot}]_{SS}} = 1.78\times10^{-2} \qquad \text{(Equation S11)}$$

Substituting equation S4 in equation S6, the following relationship is generated:

$$\frac{[Cl_2^{\bullet-}]_{SS}}{[SO_4^{\cdot-}]_{SS}} = 6.48 \qquad \text{(Equation S12)}$$

Fate of $CO_3^{\bullet-}$ in UV/$S_2O_8^{2-}$

$CO_3^{\bullet-}$ was generated via the following reactions:

$SO_4^{\bullet-} + HCO_3^- \rightarrow CO_3^{\bullet-} + SO_4^{2-} + H^+$ $k_4 = 1.6\times10^6\ M^{-1}s^{-1}$

${}^{\bullet}OH + HCO_3^- \rightarrow CO_3^{\bullet-} + H_2O$ $k_{11} = 8.5\times10^6\ M^{-1}s^{-1}$

$Cl_2^{\bullet-} + HCO_3^- \rightarrow 2Cl^- + H^+ + CO_3^{\bullet-}$ $k_{21} = 8.0\times10^7\ M^{-1}s^{-1}$

$CO_3^{\bullet-}$ reacted with chemical constituents via the following reactions:

$CO_3^{\bullet-} + NO_2^- \rightarrow CO_3^{2-} + {}^{\bullet}NO_2$ $k_{24} = 6.6\times10^5\ M^{-1}s^{-1}$

$CO_3^{\bullet-} + CBZ \rightarrow Product$ $k_{25} = 2.51\times10^6\ M^{-1}s^{-1}$

$CO_3^{\bullet-} + S_2O_8^{2-} \rightarrow Product$ $k_{26} = 10^6\ M^{-1}s^{-1}$

$CO_3^{\bullet-} + Cl^- \rightarrow Product$ $k_{27} = 10^6\ M^{-1}s^{-1}$

Because $CO_3^{\bullet-}$ reacts slowly with water quality parameters, the second order reaction rate constant of $CO_3^{\bullet-}$ reacting with $S_2O_8^{2-}$ and Cl^- were conservatively assumed to be 10^6 $M^{-1}s^{-1}$.

Accordingly, the theoretical $[CO_3^{\bullet-}]_{SS}$ can be expressed as:

$$[CO_3^{\bullet-}]_{SS} = \frac{(k_4[SO_4^{\bullet-}]_{SS} + k_{11}[OH^{\cdot}]_{SS} + k_{21}[Cl_2^{\bullet-}]_{SS})[HCO_3^-]}{k_{24}[NO_2^-] + k_{25}[CBZ] + k_{26}[S_2O_8^{2-}] + k_{27}[Cl^-]} \quad \text{(Equation S13)}$$

Under the experimental condition in this study, the ratio of steady-state concentrations of $CO_3^{\bullet-}$ to $SO_4^{\bullet-}$ based on Equation S8 was calculated by substituting equations S2 and S7:

$$\frac{[CO_3^{\bullet-}]_{SS}}{[SO_4^{\bullet-}]_{SS}} = 3.02 \times 10^2 \quad \text{(Equation S14)}$$

Determination of the steady-state concentration of radicals

The carbamazepine degradation rate in recycled water with UV/PS can be expressed as,

$$r_{CBZ} = r_d^{norm} + k_{\bullet OH,CBZ}[\bullet OH]_{SS} + k_{SO_4^{\bullet-},CBZ}[SO_4^{\bullet-}]_{SS} + k_{Cl^{\bullet},CBZ}[Cl^{\bullet}]_{SS} + k_{Cl_2^{\bullet-},CBZ}[Cl_2^{\bullet-}]_{SS} + k_{CO_3^{\bullet-},CBZ}[CO_3^{\bullet-}]_{SS} \quad \text{(Equation S15)}$$

where, r_d^{norm} is the normalized direct photolysis rate, and r_{CBZ} is the observed pseudo-first order degradation rate of carbamazepine in recycled water with UV/PS that was measured experimentally as 2.18×10^{-3} s^{-1}. $k_{\bullet OH,CBZ}$, $k_{SO_4^{\bullet-},CBZ}$, $k_{Cl^{\bullet},CBZ}$, $k_{Cl_2^{\bullet-},CBZ}$, and $k_{CO_3^{\bullet-},CBZ}$ are the second-order rate constants between $^{\bullet}OH$, $SO_4^{\bullet-}$, $Cl^{\bullet}$, $Cl_2^{\bullet-}$, and $CO_3^{\bullet-}$ and CBZ respectively, which are known as $k_{\bullet OH,CBZ} = 8.80 \times 10^9$ $M^{-1}s^{-1}$, $k_{SO_4^{\bullet-},CBZ} = 1.90 \times 10^9$ $M^{-1}s^{-1}$, $k_{Cl^{\bullet},CBZ} = 2.70 \times 10^9$ $M^{-1}s^{-1}$, $k_{Cl_2^{\bullet-},CBZ} = 2.20 \times 10^6$ $M^{-1}s^{-1}$, and $k_{CO_3^{\bullet-},CBZ} = 2.51 \times 10^6$ $M^{-1}s^{-1}$.[7,14,18,19] By substituting equation S2, S4, S7, and S9 into equation S10 the steady-state concentration of $^{\bullet}OH$, $SO_4^{\bullet-}$, $Cl^{\bullet}$, $Cl_2^{\bullet-}$, and $CO_3^{\bullet-}$ radicals

was calculated as 1.32×10^{-14} M, 7.40×10^{-13} M, 2.69×10^{-14} M, 4.79×10^{-12} M, and 2.23×10^{-10} M respectively.

Text S5. Calculation of normalized direct photolysis rate, k_d

Normalized direct photolysis of CBZ with low pressure UV lamp at 254 nm was calculated as,

$$r_d^{norm} = (f_{CBZ} \times r_d) \quad \text{(Equation S16)}$$

where, r_d^{norm} is the normalized direct photolysis rate, f_{CBZ} is the fraction of UV light absorbed by CBZ in the UV/PS system, and r_d is the experimentally observed apparent pseudo-first order direct UV photolysis rate of carbamazepine in recycled water without persulfate. This rate was measured experimentally as 7.74×10^{-4} s^{-1} (Figure S6A).

f_{CBZ} is calculated as:

$$f_{CBZ} = \frac{\varepsilon_{CBZ} c_{CBZ}}{\sum \varepsilon_i c_i} = \frac{\varepsilon_{CBZ} c_{CBZ}}{\varepsilon_{CBZ} c_{CBZ} + \varepsilon_{PS} c_{PS}} \quad \text{(Equation S17)}$$

where, ε_{CBZ} and c_{CBZ} are the molar absorption coefficient ($M^{-1}cm^{-1}$) and concentration (M) of CBZ. ε_i and c_i are the molar absorption coefficient and concentration of solution constituents (CBZ and persulfate). The molar absorption coefficients of CBZ and persulfate are 6.07×10^3 $M^{-1}cm^{-1}$ and 21.1 $M^{-1}cm^{-1}$, respectively.[20,21] Under the experimental condition of 7.39×10^{-2} mM of $S_2O_8^{2-}$ and 6.35×10^{-6} mM of CBZ, f_{CBZ} was calculated to be 2%.

By substituting f_{CBZ} into equation S11,

$r_d^{norm} = 1.55 \times 10^{-5}$ s^{-1}

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Appendix C

Supporting information for Chapter 4

Previously published on Journal of Hazardous Materials Letters

Azad A., Farooq H., Verdi A., Liu H., Integrating UV/Persulfate and Deficit Irrigation of Recycled Water: Strategy to Minimize Crop Accumulation of Trace Organic Contaminants and Enhance Crop Yield, *Journal of Hazardous Materials Letters*, 2024, DOI: https://doi.org/10.1016/j.hazl.2024.100115

Table S1 Properties of PPCPs in this study; chemical structure, class information, $\log_{10}$ transformation of the octanol-water partition coefficient (log K_{ow}), $\log_{10}$ transformation of the acid dissociation constant (pK_a).

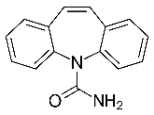
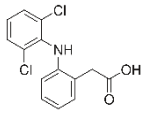
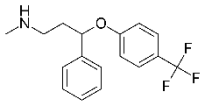
PPCPs	**Chemical Structure**	**Class**	**log K_{ow}** [1]	**pK_a** [1,2]
Carbamazepine (CBZ)		Anticonvulsant	2.45	2.30; 13.90
Diclofenac (DCF)		Anti-inflammatory	4.51	4.15
Fluoxetine (FLX)		Antidepressant	4.05	10.09

Table S2 Chemical composition of the recycled water used in this study.

Chemical constituents	**Concentration**	**Unit**
pH	7.5	--
Cl^-	144 ± 2.7	mg/L
NO_3^-	4.0 ± 0.01	mg/L as N
NO_2^-	0.06 ± 0.01	mg/L as N
SO_4^{2-}	195 ± 1.2	mg/L
Alkalinity	112 ± 1.2	mg/L as $CaCO_3$
NH_3	0.91 ± 0.02	mg/L as N

Table S3 Reactions and rate constants of radicals in recycled water for carbamazepine degradation.

No.	Reaction	Rate constant	Ref.
1	$SO_4^{\bullet-} + S_2O_8^{2-} \rightarrow S_2O_8^{-\bullet} + SO_4^{2-}$	$6.6\times10^5\ M^{-1}s^{-1}$	[3]
2	$SO_4^{\bullet-} + H_2O \rightarrow {}^{\bullet}OH + HSO_4^{2-}$	$6.6\times10^2\ s^{-1}$	[4]
3	$SO_4^{\bullet-} + Cl^- \leftrightarrow Cl^{\bullet} + SO_4^{2-}$	$k_+ = 3.2\times10^8\ M^{-1}s^{-1}$ $k_- = 2.1\times10^8\ M^{-1}s^{-1}$	[5]
4	$SO_4^{\bullet-} + HCO_3^- \rightarrow CO_3^{\bullet-} + SO_4^{2-} + H^+$	$1.6\times10^6\ M^{-1}s^{-1}$	[5]
5	$SO_4^{\bullet-} + NO_3^- \rightarrow NO_3\bullet + SO_4^{2-}$	$2.1\times10^6\ M^{-1}s^{-1}$	[6]
6	$SO_4^{\bullet-} + NO_2^- \rightarrow {}^{\bullet}NO_2 + SO_4^{2-}$	$9.8\times10^8\ M^{-1}s^{-1}$	[7]
7	$SO_4^{\bullet-}$ + CBZ → product	$1.9\times10^9\ M^{-1}s^{-1}$	[8]
8	${}^{\bullet}OH + S_2O_8^{2-} \rightarrow S_2O_8^{-\bullet} + OH^-$	$1.4\times10^7\ M^{-1}s^{-1}$	[9]
9	${}^{\bullet}OH + NO_2^- \rightarrow {}^{\bullet}NO_2 + HO^-$	$1.2\times10^{10}\ M^{-1}s^{-1}$	[7]
10	${}^{\bullet}OH + Cl^- \leftrightarrow ClOH^{\bullet-}$	$k_+ = 4.3\times10^9\ M^{-1}s^{-1}$ $k_- = 6.1\times10^9\ s^{-1}$	[6]
11	${}^{\bullet}OH + HCO_3^- \rightarrow CO_3^{\bullet-} + H_2O$	$8.5\times10^6\ M^{-1}s^{-1}$	[6]
12	${}^{\bullet}OH$ + CBZ → product	$8.8\times10^9\ M^{-1}s^{-1}$	[10]
13	$Cl^{\bullet} + S_2O_8^{2-} \rightarrow S_2O_8^{-\bullet} + Cl^-$	$8.8\times10^6\ M^{-1}s^{-1}$	[11]
14	$Cl^{\bullet} + Cl^- \rightarrow Cl_2^{\bullet-}$	$8.5\times10^9\ M^{-1}s^{-1}$	[12]

15	$Cl^{\bullet} + H_2O \leftrightarrow ClOH^{\bullet -} + H^+$	$k_+ = 2.5\times10^5\ s^{-1}$ $k_- = 2.1\times10^{10}\ M^{-1}s^{-1}$	[13]
16	$Cl^{\bullet} + HCO_3^- \rightarrow Cl^- + CO_3^{\bullet -}$	$2.2\times10^8\ M^{-1}s^{-1}$	[14]
17	$Cl^{\bullet} + NO_2^- \rightarrow Cl^- + {}^{\bullet}NO_2$	$8.8\times10^9\ M^{-1}s^{-1}$	[6]
18	$Cl^{\bullet} + CBZ \rightarrow$ Product	$2.7\times10^9\ M^{-1}s^{-1}$	[15]
19	$Cl_2^{\bullet -} + S_2O_8^{2-} \rightarrow S_2O_8^{\bullet -} + 2Cl^-$	$6.0\times10^5\ M^{-1}s^{-1}$	[16]
20	$Cl_2^{\bullet -} + H_2O \rightarrow HClOH^{\bullet} + Cl^-$	$1.3\times10^3\ s^{-1}$	[17]
21	$Cl_2^{\bullet -} + HCO_3^- \rightarrow 2Cl^- + H^+ + CO_3^{\bullet -}$	$8.0\times10^7\ M^{-1}s^{-1}$	[18]
22	$Cl_2^{\bullet -} + NO_2^- \rightarrow Cl^- + Cl^- + {}^{\bullet}NO_2$	$2.5\times10^8\ M^{-1}s^{-1}$	[6]
23	$Cl_2^{\bullet -} + CBZ \rightarrow$ Product	$2.2\times10^6\ M^{-1}s^{-1}$	[15]
24	$CO_3^{\bullet -} + NO_2^- \rightarrow CO_3^{2-} + {}^{\bullet}NO_2$	$6.6\times10^5\ M^{-1}s^{-1}$	[6]
25	$CO_3^{\bullet -} + CBZ \rightarrow$ Product	$2.51\times10^6\ M^{-1}s^{-1}$	[8]
26	${}^{\bullet}OH + NOM \rightarrow$ product	$3.3 \times 10^8\ M^{-1}s^{-1}$	[19]

Table S4 Recoveries of deuterated compounds in biomass and water.

Compounds	Recovery (%)				
	Lettuce	**Carrot**	**Tomato**	**Spiked recycled water**	**Treated recycled water**
Carbamazepine-d_{10}	89 ± 15	96 ± 14	65 ± 15	121 ± 42	80 ± 33
Diclofenac-d_4 sodium	96 ± 14	145 ± 35	91 ± 30	134 ± 46	99 ± 43
Fluoxetine-d_5 hydrochloride	35 ± 15	29 ± 15	49 ± 16	45 ± 21	42 ± 18

Table S5 The crop coefficient (K_c) values of edible crops in the early, middle and end of their growth cycles.

Crop	**$K_{c\ ini}$**	**$K_{c\ mid}$**	**$K_{c\ end}$**
Carrot	0.70	1.05	0.95
Lettuce	0.70	1.00	0.95
Tomato	0.70	1.15	0.90

Table S6 Effect of NOM on radical steady state concentration in recycled water system.

$[^{\bullet}R]_{ss}$ (M)	0 mg C/L NOM	0.4 mg C/L NOM	5.8 mg C/L NOM
$^{\bullet}OH$	3.13×10^{-14}	3.12×10^{-14}	2.99×10^{-14}
$SO_4^{\bullet-}$	1.83×10^{-12}	1.83×10^{-12}	1.83×10^{-12}
$Cl^{\bullet}$	6.65×10^{-14}	6.65×10^{-14}	6.65×10^{-14}
$Cl_2^{\bullet-}$	1.18×10^{-11}	1.18×10^{-11}	1.18×10^{-11}
$CO_3^{\bullet-}$	5.52×10^{-10}	5.52×10^{-10}	5.52×10^{-10}

Figure S1 Crop irrigation trial in the greenhouse setup.

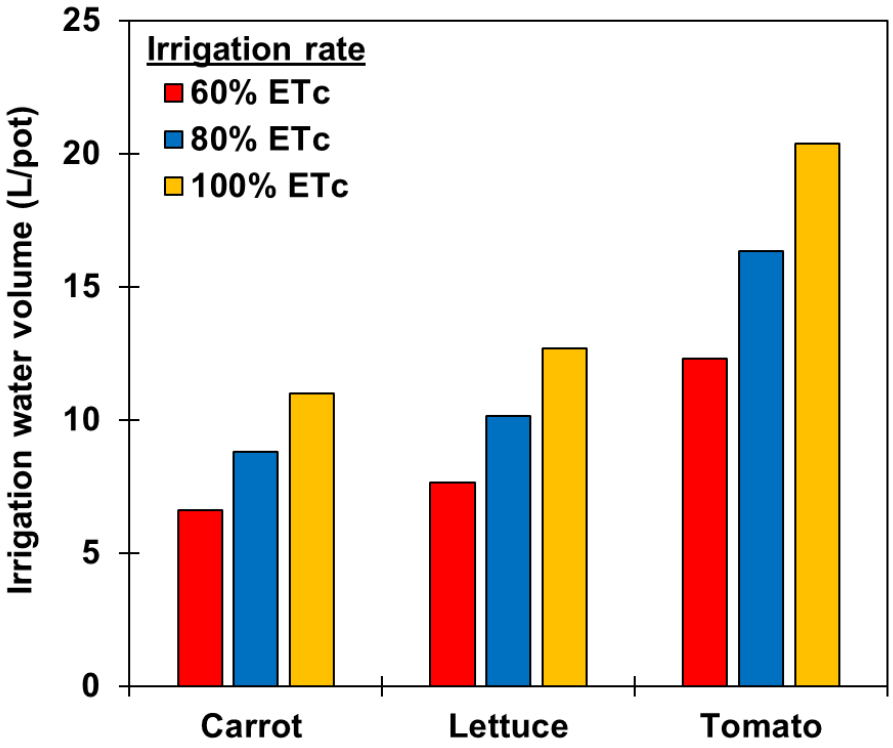


Figure S2 The volume of irrigation water for edible crops when irrigated at three different irrigation rates.

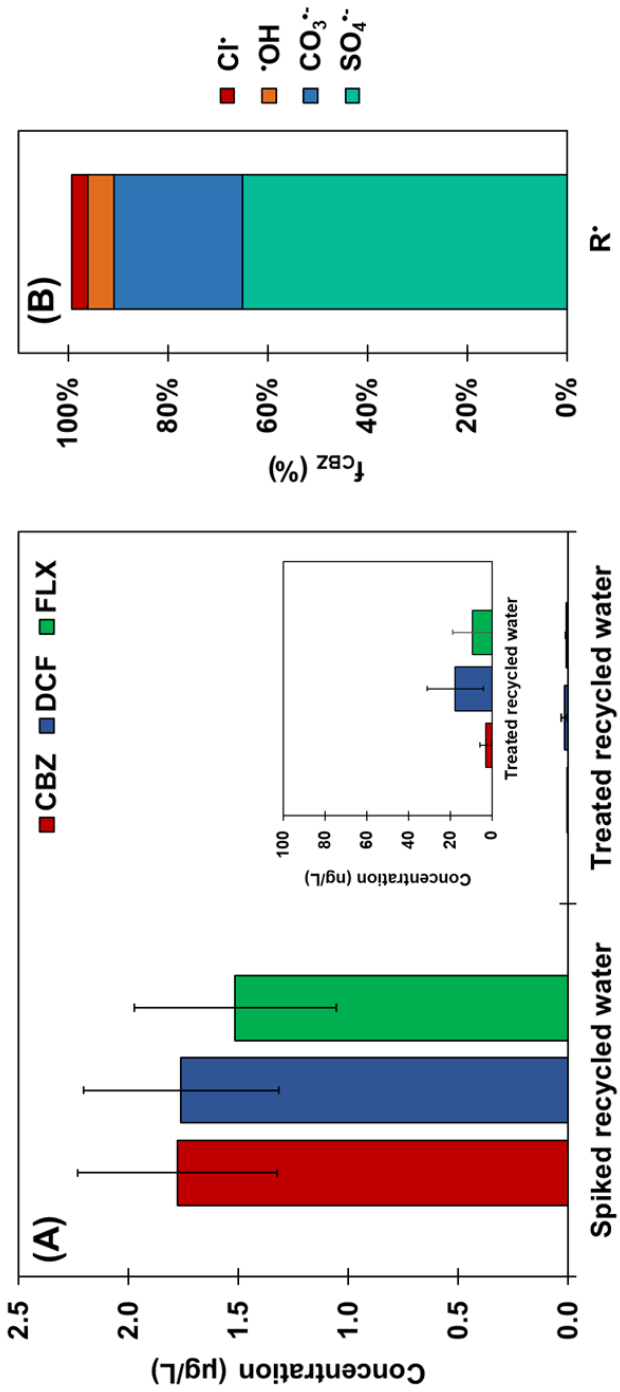


Figure S3 (A) Initial concentration of PPCPs in different kinds of irrigation water, and (B) radical distribution of carbamazepine degradation by UV/PS. No residual PPCP was detected in tap water control. Carbamazepine (CBZ), diclofenac (DCF) , and fluoxetine (FLX). f_{CBZ} is the contribution of radical species towards CBZ degradation in the UV/PS system.

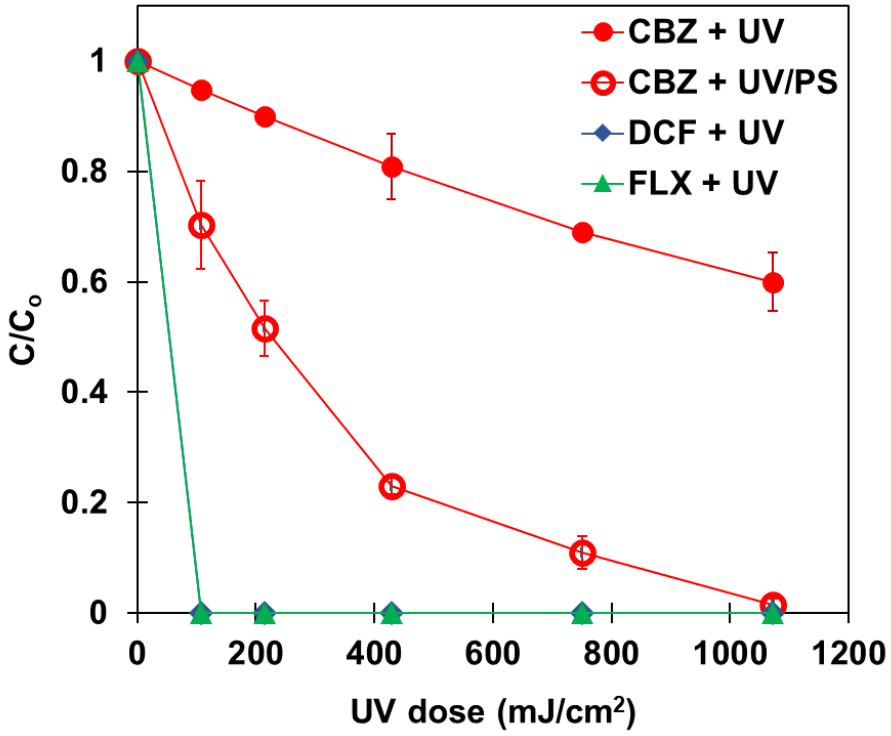


Figure S4 UV and UV/PS photolysis of PPCPs in recycled water. Carbamazepine (CBZ), diclofenac (DCF), and fluoxetine (FLX). $[S_2O_8^{2-}]_o$ = 35 mg/L.

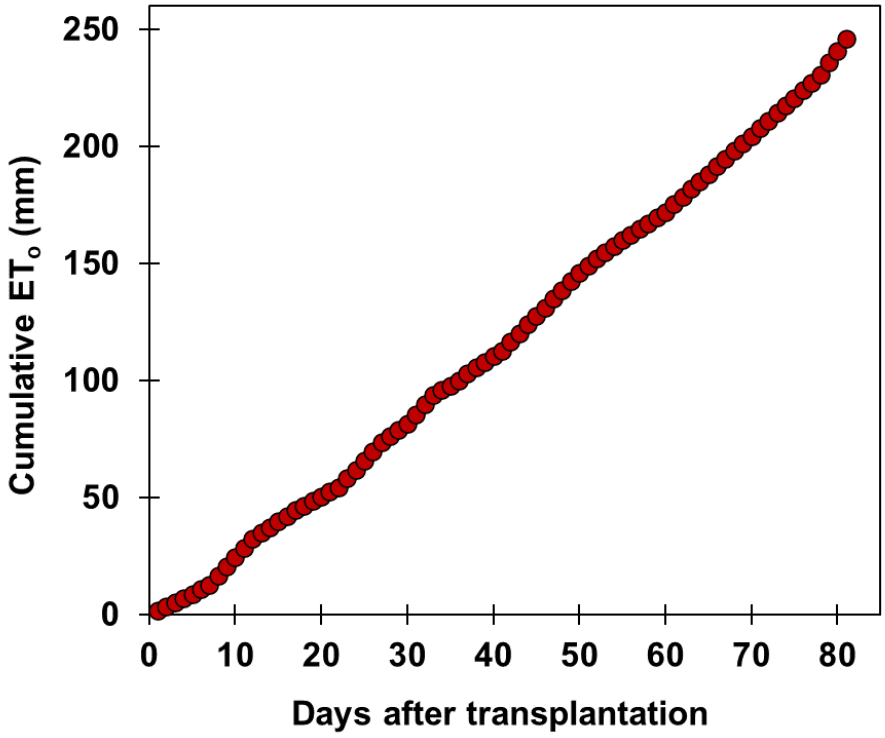


Figure S5 Cumulative reference evapotranspiration (ET_o) for the duration of the greenhouse trial.

Text S1. Chemicals and materials

Recycled water at the South Coast Research and Extension Center was sourced from Irvine Ranch Water District, where, it received tertiary treatment involving particle removal and chlorine or UV disinfection [20]. The water was stored at 4°C within 2 hours of collection for further treatment. Carbamazepine was purchased from Acros Organics, Diclofenac-Na salt and fluoxetine-HCl were purchased from Alfa Aesar. Carbamazepine-d_{10}, diclofenac-d_4 sodium, and fluoxetine-d_5 hydrochloride were purchased from TRC (Toronto Research Chemicals). Potassium Persulfate was purchased from J.T.Baker. Deionized water (DI) (resistivity of 18.2 MΩ) was prepared using a Millipore system. Individual stock solution of PPCP and their deuterated compound was prepared in methanol and stored in an amber glass vial at -20°C.

Text S2. Greenhouse experiment

Seeds of lettuce, carrot, and tomato were obtained from a local nursery in Riverside, CA. A standard potting soil mix (UC Soil Mix 3) was used as a potting medium, maintaining a bulk density of 1.34 g/cm^3. Plants were acclimated for two weeks after transplanting before the trial, during which tap water was used for irrigation.

The experiment utilized 5-gallon pots with holes at the bottom to allow leached water to escape. A total of 81 plastic pots were arranged on wooden planks 20 cm above the greenhouse floor. Two different pot sizes were used to grow the plants. Black plastic pots (15 cm top diameter, 30 cm height) were used to grow lettuce, while white plastic pots (13.5 cm top diameter, 33 cm height) were used to grow carrot and tomato.

Carrot seeds were planted in small plastic pots (3 cm top diameter, 6 cm height) with three holes at the bottom in early February. The pots were filled with UC Soil Mix 3 and irrigated through the holes at the bottom via capillary action. Seedlings were thinned regularly to get a single healthy seedling in each pot. Lettuce seeds were planted into the multi-celled germination trays for approximately 4 weeks to produce transplant seedlings for the subsequent experiments. Tomato seeds were planted in the six-celled trays to grow transplant seedlings for the subsequent experiments.

After a month, one tomato seedling at the fourth leaf stage was transplanted into all experimental pots. On February 24, three lettuce seedlings at 4–5 true leaf stage were transplanted to each pot. Three carrot seedlings from small pots were transferred to larger experimental pots by creating three holes with an auger.

Text S3. Analysis of water and plant tissue samples

2 mL water sample was spiked with deuterated surrogates to reach a predetermined concentration of 1 µg/L. The water samples were then loaded onto the HLB cartridges (150 mg, Waters) that were preconditioned with 7 mL methanol and 7 mL DI water. After the extract passed through the cartridge, 15 mL methanol was used to elute the analytes. The methanol extract was further dried under nitrogen gas and reconstituted in 0.5 mL methanol. The final samples were centrifuged at 16,000g for 30 minutes and injected into HPLC-HRMS/MS for analysis.

The freeze-dried samples were then cut into small pieces, ground to a fine powder using a pestle and mortar while adding liquid nitrogen and stored at -20°C for PPCP extraction.

0.2 grams of powdered lettuce, carrot, and tomato biomass samples were placed in a 50 mL centrifuge tube and spiked with 50 µL of 400 µg/L of deuterated surrogates before the extraction. PPCPs in plant tissue samples were extracted using 20 mL of acetonitrile in an ultrasonic water bath for 30 minutes, followed by centrifugation at 10,000 rpm for 10 min. The supernatant was pooled after centrifugation. The plan tissue samples were extracted once more with 20 mL of acetonitrile and then centrifuged. The combined extracts were dried under nitrogen gas using a nitrogen evaporator (N-EVAP 111, Organomation) and redissolved in 1 mL methanol followed by mixing with 20 mL DI water. The aqueous solution was loaded onto HLB cartridges (150 mg, Waters) that were preconditioned with 7 mL methanol and 7 mL DI water. After the extract passed through the cartridge, 15 mL methanol was used to elute the analytes. The methanol extract was further dried under nitrogen gas and reconstituted in 1 mL methanol. The final samples were centrifuged at 16,000g for 30 min and filtered through 0.22 µm polytetrafluoroethylene (PTFE) membrane filters to remove solids. Final samples were injected into HPLC-HRMS/MS for analysis. The spiked deuterated surrogates were used to determine the overall analyte recovery for the entire extraction and clean up procedure. The samples after SPE cleanup were analyzed on a high-resolution liquid chromatography from ThermoFisher Q Extractive Hybrid Quadrupole Orbitrap (HPLC-HRMS/MS) with a HESI-II and ESI source. The separation of analytes was performed at 30°C using a Waters XBridge C18 column (2.1 mm × 50 mm × 3.5 µm). The mobile phase A was LC-MS grade water and B was pure methanol, both amended with 1% formic acid. The flow rate was 0.35 mL/min with the following gradient: 5% A: 0-1 min,

5-95% A: 1-16 min, 95% A: 16-21 min, and 5% A: 21-26 min. Data acquisition was performed in both positive and negative ESI mode.

Text S4. Calculation of the fate of each reactive radical species

All the reactions and citations of rate constants for this calculation are listed in Table S3.

Fate of $^{\bullet}OH$ in UV/$S_2O_8^{2-}$

$^{\bullet}OH$ was generated via the following reaction:

$SO_4^{\bullet-} + H_2O \rightarrow {}^{\bullet}OH + HSO_4^{2-}$ $k_2 = 6.6\times10^2\ s^{-1}$

Once $^{\bullet}OH$ was generated, it participated in the following reactions:

$^{\bullet}OH + S_2O_8^{2-} \rightarrow S_2O_8^{\bullet-} + OH^-$ $k_8 = 1.4\times10^7\ M^{-1}s^{-1}$

$^{\bullet}OH + NO_2^- \rightarrow {}^{\bullet}NO_2 + HO^-$ $k_9 = 1.2\times10^{10}\ M^{-1}s^{-1}$

$^{\bullet}OH + HCO_3^- \rightarrow CO_3^{\bullet-} + H_2O$ $k_{11} = 8.5\times10^6\ M^{-1}s^{-1}$

$^{\bullet}OH$ + CBZ → product $k_{12} = 8.8\times10^9\ M^{-1}s^{-1}$

$^{\bullet}OH$ + NOM → product $k_{26} = 3.3\times10^8\ M^{-1}s^{-1}$

Therefore, the theoretical $[^{\bullet}OH]_{SS}$ can be expressed as:

$$[OH^{\cdot}]_{SS} = \frac{k_2\,[SO_4^{\cdot-}]_{SS}}{k_8[S_2O_8^{2-}]+k_9[NO_2^-]+k_{11}[HCO_3^-]+k_{12}[CBZ]+k_{26}[NOM]} \quad \text{(Equation S18)}$$

Under the experimental condition of 1.82×10^{-1} mM of $S_2O_8^{2-}$, 1.30×10^{-3} mM of NO_2^-, 2.40 mM of HCO_3^-, 6.35×10^{-6} mM of CBZ, and 0 mg C/L NOM the ratio of steady-state concentrations of $^{\bullet}OH$ to $SO_4^{\bullet-}$ based on Equation S1 was calculated as:

$$\frac{[OH^{\cdot}]_{SS}}{[SO_4^{\cdot-}]_{SS}} = 1.71\times10^{-2} \quad \text{(Equation S19)}$$

Fate of $Cl^{\bullet}$ in UV/$S_2O_8^{2-}$

$Cl^{\bullet}$ was generated via the following reaction:

$SO_4^{\bullet-} + Cl^- \leftrightarrow Cl^{\bullet} + SO_4^{2-}$ $k_{+3} = 3.2\times10^8\ M^{-1}s^{-1}$, $k_{-3} = 2.1\times10^8\ M^{-1}s^{-1}$

$Cl^{\bullet}$ reacted with chemical constituents via the following reactions:

$Cl^{\bullet} + S_2O_8^{2-} \rightarrow S_2O_8^{-\bullet} + Cl^-$ $k_{13} = 8.8\times10^6\ M^{-1}s^{-1}$

$Cl^{\bullet} + Cl^- \rightarrow Cl_2^{\bullet-}$ $k_{14} = 8.5\times10^9\ M^{-1}s^{-1}$

$Cl^{\bullet} + H_2O \leftrightarrow ClOH^{\bullet-} + H^+$ $k_{+15} = 2.5\times10^5\ s^{-1}$, $k_{-15} = 2.1\times10^{10}\ M^{-1}s^{-1}$

$Cl^{\bullet} + HCO_3^- \rightarrow Cl^- + CO_3^{\bullet-}$ $k_{16} = 2.2\times10^8\ M^{-1}s^{-1}$

$Cl^{\bullet} + NO_2^- \rightarrow Cl^- + {}^{\bullet}NO_2$ $k_{17} = 8.8\times10^9\ M^{-1}s^{-1}$

$Cl^{\bullet} + CBZ \rightarrow$ Product $k_{18} = 2.7\times10^9\ M^{-1}s^{-1}$

For $Cl^{\bullet}$ reactions with water (Reaction 9 above), the pseudo first-order rate constant for the reverse reaction at pH 7.5 was calculated to be $6.64\times10^2\ s^{-1}$, significantly lower (by three orders of magnitude) than the forward rate constant ($2.5\times10^5\ s^{-1}$). Consequently, for this calculation, the reverse reaction was considered negligible.

Therefore. the theoretical $[Cl^{\bullet}]_{SS}$ can be expressed as:

$$[Cl^{\cdot}]_{SS} = \frac{k_{+3}[SO_4^{\cdot-}]_{SS}\,[Cl^-]}{k_{13}[S_2O_8^{2-}]+k_{14}[Cl^-]+k_{+15}+k_{16}[HCO_3^-]+k_{17}[NO_2^-]+k_{18}[CBZ]+k_{-3}[SO_4^{2-}]}$$

(Equation S20)

Under the experimental condition of 1.82×10^{-1} mM of $S_2O_8^{2-}$, 1.30×10^{-3} mM of NO_2^-, 2.40 mM of HCO_3^-, 4.06 mM of Cl^-, 2.03 mM of SO_4^{2-}, and 6.35×10^{-6} mM of CBZ, the ratio of steady-state concentrations of $Cl^{\bullet}$ to $SO_4^{\bullet-}$ based on Equation S3 was calculated as:

$$\frac{[Cl^{\cdot}]_{SS}}{[SO_4^{\cdot-}]_{SS}} = 3.64\times10^{-2}$$ (Equation S21)

Fate of $Cl_2^{\bullet-}$ in UV/$S_2O_8^{2-}$

$Cl_2^{\bullet-}$ was generated via the following reaction:

$Cl^{\bullet} + Cl^- \rightarrow Cl_2^{\bullet-}$ $k_{14} = 8.5\times10^9\ M^{-1}s^{-1}$

$Cl_2^{\bullet-}$ participated in the following reactions:

$Cl_2^{\bullet-} + S_2O_8^{2-} \rightarrow S_2O_8^{\bullet-} + 2Cl^-$ $k_{19} = 6.0\times10^5\ M^{-1}s^{-1}$

$Cl_2^{\bullet-} + H_2O \rightarrow HClOH^{\bullet} + Cl^-$ $k_{20} = 1.3\times10^3\ s^{-1}$

$Cl_2^{\bullet-} + HCO_3^- \rightarrow 2Cl^- + H^+ + CO_3^{\bullet-}$ $k_{21} = 8.0\times10^7\ M^{-1}s^{-1}$

$Cl_2^{\bullet-} + NO_2^- \rightarrow Cl^- + Cl^- + {}^{\bullet}NO_2$ $k_{22} = 2.5\times10^8\ M^{-1}s^{-1}$

$Cl_2^{\bullet-} + CBZ \rightarrow$ Product $k_{23} = 2.2\times10^6\ M^{-1}s^{-1}$

Therefore, the theoretical $[Cl_2^{\bullet-}]_{SS}$ can be expressed as:

$$[Cl_2^{\bullet-}]_{SS} = \frac{k_{14}\,[Cl^-]\,[Cl^{\cdot}]_{SS}}{k_{19}[S_2O_8^{2-}]+k_{20}+k_{21}[HCO_3^-]+k_{22}[NO_2^-]+k_{23}[CBZ]} \qquad \text{(Equation S22)}$$

Under the experimental condition in this study, the ratio of steady-state concentrations of $Cl_2^{\bullet-}$ to $Cl^{\bullet}$ based on Equation S5 was calculated as:

$$\frac{[Cl_2^{\bullet-}]_{SS}}{[Cl^{\cdot}]_{SS}} = 1.78\times10^{-2} \qquad \text{(Equation S23)}$$

Substituting equation S4 in equation S6, the following relationship is generated:

$$\frac{[Cl_2^{\bullet-}]_{SS}}{[SO_4^{\cdot-}]_{SS}} = 6.48 \qquad \text{(Equation S24)}$$

Fate of $CO_3^{\bullet-}$ in UV/$S_2O_8^{2-}$

$CO_3^{\bullet-}$ was generated via the following reactions:

$SO_4^{\bullet-} + HCO_3^- \rightarrow CO_3^{\bullet-} + SO_4^{2-} + H^+$ $k_4 = 1.6\times10^6\ M^{-1}s^{-1}$

${}^{\bullet}OH + HCO_3^- \rightarrow CO_3^{\bullet-} + H_2O$ $k_{11} = 8.5\times10^6\ M^{-1}s^{-1}$

$Cl_2^{\bullet-} + HCO_3^- \rightarrow 2Cl^- + H^+ + CO_3^{\bullet-}$ $k_{21} = 8.0\times10^7\ M^{-1}s^{-1}$

$CO_3^{\bullet-}$ reacted with chemical constituents via the following reactions:

$CO_3^{\bullet-} + NO_2^- \rightarrow CO_3^{2-} + {}^{\bullet}NO_2$ $k_{24} = 6.6\times10^5\ M^{-1}s^{-1}$

$CO_3^{\bullet-} + CBZ \rightarrow Product$ $k_{25} = 2.51\times10^6\ M^{-1}s^{-1}$

$CO_3^{\bullet-} + S_2O_8^{2-} \rightarrow Product$ $k_{26} = 10^6\ M^{-1}s^{-1}$

$CO_3^{\bullet-} + Cl^- \rightarrow Product$ $k_{27} = 10^6\ M^{-1}s^{-1}$

Because $CO_3^{\bullet-}$ reacts slowly with water quality parameters, the second order reaction rate constant of $CO_3^{\bullet-}$ reacting with $S_2O_8^{2-}$ and Cl^- were conservatively assumed to be $10^6\ M^{-1}s^{-1}$.

Accordingly, the theoretical $[CO_3^{\bullet-}]_{SS}$ can be expressed as:

$$[CO_3^{\bullet-}]_{SS} = \frac{(k_4[SO_4^{\bullet-}]_{SS} + k_{11}[OH^{\cdot}]_{SS} + k_{21}[Cl_2^{\bullet-}]_{SS})[HCO_3^-]}{k_{24}[NO_2^-] + k_{25}[CBZ] + k_{26}[S_2O_8^{2-}] + k_{27}[Cl^-]} \quad \text{(Equation S25)}$$

Under the experimental condition in this study, the ratio of steady-state concentrations of $CO_3^{\bullet-}$ to $SO_4^{\bullet-}$ based on Equation S8 was calculated by substituting equations S2 and S7:

$$\frac{[CO_3^{\bullet-}]_{SS}}{[SO_4^{\bullet-}]_{SS}} = 3.02 \times 10^2 \quad \text{(Equation S26)}$$

<u>Determination of the steady-state concentration of radicals</u>

The carbamazepine degradation rate in recycled water with UV/PS can be expressed as,

$$r_{CBZ} = r_d^{norm} + k_{\bullet OH,CBZ}[\bullet OH]_{SS} + k_{SO_4^{\bullet-},CBZ}[SO_4^{\bullet-}]_{SS} + k_{Cl^{\bullet},CBZ}[Cl^{\bullet}]_{SS} + k_{Cl_2^{\bullet-},CBZ}[Cl_2^{\bullet-}]_{SS} + k_{CO_3^{\bullet-},CBZ}[CO_3^{\bullet-}]_{SS} \quad \text{(Equation S27)}$$

where, r_d^{norm} is the normalized direct photolysis rate, and r_{CBZ} is the observed pseudo-first order degradation rate of carbamazepine in recycled water with UV/PS that was measured experimentally as $5.35 \times 10^{-3}\ s^{-1}$. $k_{\bullet OH,CBZ}$, $k_{SO_4^{\bullet-},CBZ}$, $k_{Cl^{\bullet},CBZ}$, $k_{Cl_2^{\bullet-},CBZ}$, and $k_{CO_3^{\bullet-},CBZ}$ are the second-order rate constants between $^{\bullet}OH$, $SO_4^{\bullet-}$, $Cl^{\bullet}$, $Cl_2^{\bullet-}$, and $CO_3^{\bullet-}$ and

CBZ respectively, which are known as $k_{\bullet OH,CBZ} = 8.80 \times 10^9$ $M^{-1}s^{-1}$, $k_{SO_4^{\bullet-},CBZ} = 1.90 \times 10^9$ $M^{-1}s^{-1}$, $k_{Cl^{\bullet},CBZ} = 2.70 \times 10^9$ $M^{-1}s^{-1}$, $k_{Cl_2^{\bullet-},CBZ} = 2.20 \times 10^6$ $M^{-1}s^{-1}$, and $k_{CO_3^{\bullet-},CBZ} = 2.51 \times 10^6$ $M^{-1}s^{-1}$.[8,15,21,22] By substituting equation S2, S4, S7, and S9 into equation S10 the steady-state concentration of $^{\bullet}OH$, $SO_4^{\bullet-}$, $Cl^{\bullet}$, $Cl_2^{\bullet-}$, and $CO_3^{\bullet-}$ radicals was calculated as 3.13×10^{-14} M, 1.83×10^{-12} M, 6.65×10^{-14} M, 1.18×10^{-11} M, and 5.52×10^{-10} M respectively.

<u>Percentage contributions of different reactive radicals to CBZ degradation</u>

The percent contribution of different radicals to degrade CBZ via UV/persulfate in the recycled water system was calculated by,

$$f_{R^{\cdot}} = \frac{k_{R^{\cdot},CBZ}[R^{\cdot}]_{SS}}{r_{CBZ}} \times 100\% \qquad \text{(Equation S28)}$$

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.

Text S5. Calculation of normalized direct photolysis rate, kd

Normalized direct photolysis of CBZ with low pressure UV lamp at 254 nm was calculated as,

$$r_d^{norm} = (f_{CBZ} \times r_d) \quad \text{(Equation S29)}$$

where, r_d^{norm} is the normalized direct photolysis rate, f_{CBZ} is the fraction of UV light absorbed by CBZ in the UV/PS system, and r_d is the experimentally observed apparent pseudo-first order direct UV photolysis rate of carbamazepine in recycled water without persulfate. This rate was measured experimentally as 8.63×10^{-4} s^{-1} (Figure S3).

f_{CBZ} is calculated as:

$$f_{CBZ} = \frac{\varepsilon_{CBZ} c_{CBZ}}{\sum \varepsilon_i c_i} = \frac{\varepsilon_{CBZ} c_{CBZ}}{\varepsilon_{CBZ} c_{CBZ} + \varepsilon_{PS} c_{PS}} \quad \text{(Equation S30)}$$

where, ε_{CBZ} and c_{CBZ} are the molar absorption coefficient ($M^{-1}cm^{-1}$) and concentration (M) of CBZ. ε_i and c_i are the molar absorption coefficient and concentration of solution constituents (CBZ and persulfate). The molar absorption coefficients of CBZ and persulfate are 6.07×10^3 $M^{-1}cm^{-1}$ and 21.1 $M^{-1}cm^{-1}$, respectively [23,24]. Under the experimental condition of 1.82×10^{-1} mM of $S_2O_8^{2-}$ and 6.35×10^{-6} mM of CBZ, f_{CBZ} was calculated to be 1%.

By substituting f_{CBZ} into equation S11,

$r_d^{norm} = 8.63 \times 10^{-6}$ s^{-1}

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