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Authors

Shi, Qingyang
Shen, Dahang
Yates, Rebecca
et al.

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Qingyang Shi, Dahang Shen, Rebecca Yates, Catherine Chou, Andrea Barajas, Jingjing Zhang, Daniel Schlenk, and Jay Gan*

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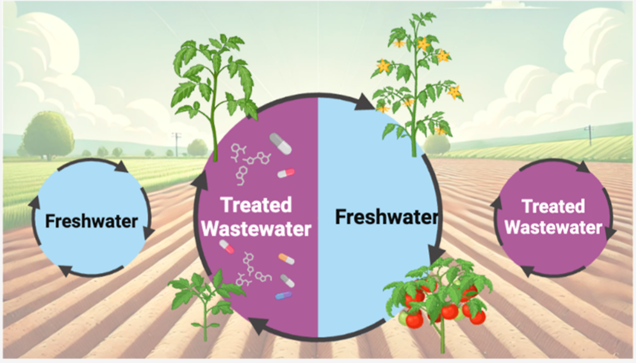

ABSTRACT: The reuse of treated wastewater (TWW) for irrigation alleviates freshwater (FW) scarcity while supporting a circular economy. However, the potential human exposure to contaminants of emerging concern (CECs) through plant accumulation is a significant barrier. Currently, knowledge on CEC contamination of edible produce and effective mitigation strategies for the safe reuse of TWW is limited, particularly under field conditions. This study examined the accumulation of a representative set of CECs, including perfluoroalkyl and polyfluoroalkyl substances (PFAS), pharmaceuticals and personal care products, and tire wear particle (TWP) chemicals, in radish, lettuce, and tomato under three irrigation practices: FULL (continuous TWW irrigation), HALF (midseason switch from TWW to FW), and FW-only. Despite low PFAS concentrations (8.1−25.7 ng/L) in TWW, the plant uptake was consistently observed, including in tomato fruits. Alternating TWW with FW significantly reduced CEC accumulation in edible tissues, particularly for compounds with short half-lives, with reductions up to 82.4% even for persistent PFAS. For most CECs and plant species, edible tissue concentrations were similar between the HALF and FW treatments. These findings demonstrate the on-farm applicability of simple irrigation modifications to reduce food contamination and contribute to the promotion of safe reuse of nonconventional waters.

KEYWORDS: *contaminants of emerging concern, PFAS, wastewater reuse, plant uptake, accumulation*

INTRODUCTION

Population increases, coupled with regionally varying changes in aridity and drought characteristics, intensify the demand for freshwater (FW) in many arid and semiarid regions around the world.[1,2] According to the 2023 U.N. World Water Development Report, two billion people currently lack access to safe drinking water.[3] From 2010 to 2018, there was a notable 5% increase in agricultural water withdrawals, now accounting for 72% of the total global FW use. Against this backdrop, the use of treated wastewater (TWW) for agricultural irrigation is increasingly regarded as a highly valuable practice, offering dual benefits of a circular economy and enhanced resiliency in water resource management.[4,5] The practice of water reuse is well established in some arid regions globally. For instance, Israel leads in water recycling innovation, redirecting approximately 90% of its TWW for irrigation.[6] Conversely, in the European Union, only 2.5% of urban TWW is reused.[7] Despite the adoption of water reuse in California for park irrigation as early as 1912, <10% of TWW is recycled nationwide in the United States, highlighting a significant untapped potential for beneficial reuse.[6,8]

Although existing regulations regarding water reuse have comprehensively addressed risks associated with nutrients, salinity, pathogens, and metals, human exposure to organic microcontaminants has received comparatively little attention.[8−12] Contaminants of emerging concern (CECs), including an ever-expanding list of pharmaceuticals and personal care products (PPCPs), per- and polyfluoroalkyl substances (PFAS), flame retardants, and tire-wear particle (TWP) chemicals, and their metabolites, among others, are ubiquitous in the environment.[13] Many studies have documented the presence of CECs in TWW and the introduction of CECs into agricultural fields through TWW irrigation.[14−19] For instance, Nguyen et al. reported pharmaceutical residues in agricultural soils at concentrations

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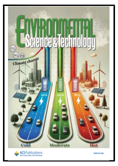

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ranging from 0.048 ng/g to 1420.76 μg/g.[20] In another study, 12 PPCPs were detected in TWW at 0.67−22.92 ng/L, with the same compounds found at 0.029−28.13 ng/g in soil and <0.01−28.01 ng/g in cucumber, eggplant, long bean, and wheat.[21] Moreover, an increasing number of greenhouse studies show that common food crops are capable of taking up and accumulating CECs, and that the accumulation varies among different CECs, plant species, and even different organs of the same plant.[22−24] These findings have contributed to the perception that consumption of TWW-irrigated food crops may pose unintended human health risks due to CEC contamination.[14,25] Such concerns, if not adequately addressed, hinder the broader adoption of TWW for agricultural irrigation.

Our current understanding of human exposure to CECs from the consumption of food crops irrigated with TWW is constrained by limited field observations. In hydroponic or soil containers under greenhouse conditions, many processes are omitted or altered compared to the field. In addition, controlled experiments often use unrealistically high chemical concentrations. Another challenge in addressing the concerns of CECs in TWW is the continual inclusion of new substances. For instance, PFAS and TWPs have recently gained widespread recognition for their ubiquitous occurrence and potential adverse human health or ecotoxicological effects.[26−31] In addition, little effort to date has been devoted to the development of practical mitigation strategies. The availability of effective mitigation strategies in the face of an ever-expanding pool of CECs is crucial for the promotion of beneficial and safe TWW reuse.

In this study, field experiments were carried out to evaluate the accumulation of CECs in TWW-irrigated vegetables in an area that had received TWW irrigation since 2011. The list of CECs considered in this study included multiple PFASs, TWPs, and PPCPs. The effectiveness of a newly developed mitigation strategy, previously demonstrated to be effective in hydroponic and soil container systems,[32,33] was further tested under field conditions. The mitigation strategy uses an alternating irrigation scheme, i.e., TWW irrigation for the first half of the growing season, followed by FW irrigation for the second half of the season. The findings provide helpful insights into CEC accumulation in food crops under realistic conditions and facilitate safe and sustainable TWW reuse on the farm scale.

■ MATERIALS AND METHODS

Chemicals. A representative set of 32 CECs was selected on the basis of their occurrence in TWW, detection frequency in previous studies, and the feasibility of accurate quantification using our analytical methods. The list included 10 PFAS compounds, i.e., pentafluoropropionic acid (PFPrA), perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluorooctanoic acid (PFOA), perfluorobutanesulfonic acid (PFBS), perfluorohexanesulfonic acid (PFHxA), perfluorooctanesulfonic acid (PFOS), 2H,2H,3H,3H-perfluorooctanoic acid (5:3 FTCA), 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoic acid (GenX), four TWPs, i.e., benzothiazole, diphenylguanidine (DPG), hexa(methoxymethyl)melamine (HMMM), *N*-(1,3-dimethylbutyl)-*N*′-phenyl-*p*-phenylenediamine quinone (6PPD-Q), and 18 PPCPs, i.e., bezafibrate, ibuprofen, bisphenol A, naproxen, acetaminophen, gabapentin, diethyltoluamide (DEET), caffeine, benzotriazole, primidone, meprobamate, carbamazepine, phenytoin, sulfamethoxazole, lamotrigine, atenolol, fluoxetine and venlafaxine. The diverse set of selected CECs offered a unique opportunity to understand the effects of long-term TWW irrigation on the accumulation of CECs in soil and their transfer potential into food plants. The inclusion of PFASs and TWPs in this study was justified by their importance as priority CECs and the general lack of field observations to date. Specific details about the sources of chemical standards and isotopically labeled internal standards are provided in Text S1. All organic solvents used in this study were of HPLC- and MS-grade (Fisher Scientific, Fair Lawn, NJ). Ultrapure water was generated in-house using a Milli-Q water purification system (Millipore, Carrigtwohill, Cork, Ireland).

Field-Plot Experiments. The field experiments were carried out at the University of California South Coast Research and Extension Center (SCREC), located in Irvine, Southern California. This area, representative of the agricultural and horticultural environments within California's south coastal plain temperate climate zone, experiences a Mediterranean climate with minimal rainfall during summer, necessitating irrigation as the principal water source for agriculture. For this study, potable water and TWW were supplied by the Irvine Ranch Water District. The TWW, compliant with the California Department of Public Health's wastewater reclamation standards for agricultural irrigation, was subjected to chlorination and tertiary treatment (filtration and reverse osmosis) prior to use.[34] Most of the SCREC fields were switched to TWW irrigation in 2011, and therefore, the TWW treatment plots had received TWW irrigation for more than 10 years at the time of this study.

A detailed map of the field plots outlining four primary treatments is provided in Figure S1. For the FULL treatment, TWW was used for irrigation for the entire growth period (from sowing to harvest: 45, 68, and 105 days for radish, lettuce, and tomato, respectively), while in the HALF treatment, TWW irrigation was used for the first half of the growing season and was then transitioned to irrigation with FW for the second half of the growth period (17, 26, and 42 days for radish, lettuce, and tomato, respectively). An additional treatment using FW for irrigation throughout the growing season was used as the background control due to the site's historical TWW use. Each treatment consisted of three sections of raised beds as replicates, each measuring 18 × 1 m (length, furrow to furrow). The plots were used for growing radish (*Raphanus sativus* L.), lettuce (*Lactuca sativa* L.), and tomato (*Solanum lycopersicum* L.), representing root, leafy, and fruit vegetables, respectively. These crops, typically consumed raw without cooking, provide a worst-case exposure scenario for human exposure. To prevent cross-contamination, a bed without plants was included as the buffer between treatments. The soil texture was characterized as a loamy sand soil, with a clay content of 12.3% and an organic carbon content of 0.91%. Details on the physicochemical characteristics of the soil at the field site are given in Table S1. Furthermore, the degradation and adsorption of target CECs in soil were analyzed for each compound using batch incubation/equilibration techniques.[35] Soil samples were collected from the SCREC field site and incubated under controlled conditions that closely mimic the ambient temperature and humidity during the field experiments. A detailed description of the degradation and adsorption experiments is provided in Text S2. The calculated half-life ($T_{1/2}$) values and adsorption coefficients (K_d), along with other physicochemical properties of the chemicals, are summarized in Table S2. The $T_{1/2}$ values presented in Table S2 are derived from the dissipation of the extractable fraction of the parent compounds, without the consideration of nonextractable residues.

Following sowing, a drip tube (16 mm tape buried 10 cm below the surface at the center of each bed) was used to apply TWW or FW for about 4 h to maintain the surface soil moisture. As the seeds emerged, irrigation was adjusted every 3−4 days based on soil moisture and plant growth conditions. For the HALF treatment, the irrigation water was switched from TWW to FW on days 20, 35, and 53 from seed emergence for radish, lettuce, and tomato, respectively. The different times were used to accommodate their different growth durations, so the water source change occurred in the middle of their growing season. For the FULL or control treatment, TWW or FW was used throughout the growing season. Irrigation was suspended during rain events and resumed only after the soil dried, following standard agricultural practices. While trace amounts of target chemicals may be introduced by rain and agronomic practices (e.g., fertilization and pest control), these inputs were not quantified and would be reflected via blank control treatment (FW irrigation only).

Sample Collection and Extraction. *Irrigation Water.* Prior to use for sample collection, 1 L polypropylene bottles were rinsed with ultrapure water and methanol. Samples of the FW and TWW were collected at the inlet of the irrigation system. After collection, samples were stored in a cooler during transportation and analyzed within 48 h using the method given in a study by Wu et al.[36] Briefly, 50 ng of isotope-labeled standards was added as surrogates to each water sample. The samples were then extracted using HLB/WAX cartridges (150 mg, Waters, Milford, MA) following the standard protocols outlined in Text S3. The eluates were concentrated to near dryness under a stream of nitrogen and reconstituted in a 1:1 water/methanol mixture for analysis.

Soil Porewater. Soil samples were collected 3 days after the latest irrigation event and just before the next irrigation event, when water redistribution in the soil was assumed to be at equilibrium. A bulk soil sample was collected to 8 cm depth from the rhizosphere around the vegetable roots and was pooled to form a composite sample. A 20 g (dry weight) aliquot of soil was mixed with 40 mL of ultrapure water containing 0.2% NaN_3 in a 50 mL centrifuge tube. The mixture was shaken at 120 rpm on a mechanical shaker for 24 h followed by centrifugation at 3500 rpm for 30 min. The resulting supernatant (30 mL) was then transferred to a new 50 mL centrifuge tube for the solid-phase extraction, as described above.

Soil. Soil samples were collected with a soil auger (40 cm in diameter) and were vertically segmented into three layers (top: 0−5 cm; middle: 10−15 cm; and bottom: 35−40 cm) to assess the mobility of CECs. Extraction of soil samples followed the methods detailed in a previous study with a QuEChERS extraction and cleanup kit (Agilent, Santa Clara, CA).[33] Briefly, 2.0 g of freeze-dried and ground soil was spiked with 50 μL of the isotope-labeled CEC mixture. Then, 2 mL of water and 5 mL of acetonitrile containing 1% acetic acid were added. The mixture was vigorously vortexed and shaken, followed by the addition of 2 g of anhydrous magnesium sulfate ($MgSO_4$) and 0.5 g of sodium acetate (NaOAc). The sample tube was manually shaken to ensure thorough mixing, followed by centrifugation at 3500 rpm for 20 min to generate the supernatant.

Plant Tissues. At the time of harvest, triplicate samples of the vegetables were collected from each bed. The plant samples were washed with ultrapure water to remove any soil residue. The edible portions were carefully separated using a knife cleaned with ethanol, and the samples were subsequently frozen at −80 °C. After freeze-drying to remove water, the plant tissues were ground into a fine powder, from which a 0.5 g aliquot was used for extraction. The extraction procedure for the target CECs in plant tissues followed a method similar to that used for soil samples, with the solvent mixture consisting of 4 mL of water, 10 mL of acetonitrile (containing 1% acetic acid), 6 g of $MgSO_4$, and 1 g of NaOAc. The resulting mixture was centrifuged, and the liquid phase was transferred to a 15 mL centrifuge tube containing 1 g of cleanup sorbent (cleanup kit containing 200 mg of primary secondary amine, 200 mg of bulk Carbograph, and 600 mg of $MgSO_4$). Following vortexing and centrifugation, the upper layer of the supernatant was collected.

All extracted samples were dried under nitrogen and reconstituted in 1.0 mL of a 1:1 (v/v) water−methanol solution. To avoid loss through filtration, samples were centrifuged at 14,000 rpm for 15 min, and 200 μL of the supernatant was transferred to a 300 μL polypropylene vial for instrumental analysis.

Instrumental Analysis, Quality Assurance/Control, and Statistical Analysis. The samples were analyzed using Waters ACQUITY ultraperformance liquid chromatography connected to a Xevo triple quadrupole mass spectrometer (Waters, Milford, MA). Additional information on LC−MS/MS analysis and quality assurance/control is provided in Text S4 and Table S3. Limits of quantification and recoveries were established for each analyte through preliminary experiments and are summarized in Table S4.

Data analysis and postprocessing were conducted using GraphPad Prism (La Jolla, CA). To discern significant differences between the FULL and HALF treatments, statistical tests including one-way ANOVA and Student's *t*-test were employed, with significance established at $p < 0.05$.

RESULTS AND DISCUSSION

CECs in Irrigation Water. Concentrations of the target CECs in TWW and FW were measured periodically throughout the field study (Table 1). Compared to FW [nondetectable (ND) to 16.5 ng/L], TWW generally showed higher concentrations of CECs (1.8−12274.3 ng/L). These findings were consistent with previous studies that reported similar CEC concentrations in TWW/reclaimed wastewater.[36−40] Naproxen, bezafibrate, and lamotrigine were not detected in any of the FW samples. In contrast, all target CECs were detected in at least one of the TWW samples collected at different times. Relatively high concentrations of TWPs were present in TWW. For instance, DPG and HMMM were detected at 300.2 ± 235.4 and 553.5 ± 312.6 ng/L, respectively. In contrast, TWP concentrations in FW were much lower, ranging from 0.4 to 16.5 ng/L. The presence of DPG in TWW has been infrequently reported, although it was found to be up to 520 ng/L after rain events and as high as 58.8 μg/L in urban surface runoff.[41,42] High concentrations of HMMM were observed by Alhelou et al. in a wastewater treatment plant influenced by industrial water, with the total concentration of HMMM and its transformation products

Table 1. CEC Concentrations (ng/L) in FW and TWW Used in the Study

chemical	freshwater	treated wastewater
PFPrA	5.1 ± 4.8	32 ± 28.8
PFBA	3.9 ± 2	9 ± 11.5
PFPeA	7.7 ± 3.6	20.1 ± 26.3
PFHxA	4.9 ± 4.5	25.7 ± 22
PFOA	3.3 ± 1.6	23.3 ± 7.1
PFBS	1.2 ± 0	7.9 ± 3.4
PFHxS	1.2 ± 0.2	9 ± 5.9
PFOS	1.3 ± 0.3	8.1 ± 4
53FTCA	2.5 ± 1.3	14.7 ± 6.2
GenX	3.4 ± 1	17.6 ± 8.5
benzothiazole	16.5 ± 3.6	28.9 ± 0
DPG	9.5 ± 8.4	300.2 ± 235.4
HMMM	0.4 ± 0.2	553.5 ± 312.6
6PPD-Q	0.5 ± 0	1.8 ± 2.2
bezafibrate	ND	31.3 ± 54.9
ibuprofen	3.8 ± 1.5	147.9 ± 62.0
bisphenol A	30.7 ± 50.4	32.3 ± 13.4
naproxen	ND	51.1 ± 41.2
acetaminophen	8.5 ± 5.6	4.8 ± 3.7
gabapentin	10.1 ± 0	2.2 ± 1.9
DEET	1.1 ± 0.4	81.4 ± 55.4
caffeine	3.2 ± 1.3	47.4 ± 32.4
benzotriazole	8.1 ± 5.3	12274.3 ± 3224.4
primidone	3.9 ± 3.4	91.4 ± 27.5
meprobamate	2 ± 1.1	140.6 ± 21.7
carbamazepine	1 ± 0.6	51.2 ± 21.7
phenytoin	1.7 ± 1.3	22.5 ± 7.6
sulfamethoxazole	1.7 ± 1.4	23.9 ± 18.3
lamotrigine	ND	509.3 ± 190.9
atenolol	4.4 ± 0.9	28.6 ± 20.1
fluoxetine	0.4 ± 0.3	4.4 ± 2.1
venlafaxine	0.7 ± 0.2	9.4 ± 6.8

reaching 4 μg/L in the effluent.[43] The presence of TWP chemicals in TWW was likely due to their widespread use and relatively high water solubility.

For PPCPs detected in this study, most compounds exhibited concentrations at <200 ng/L in TWW, with notable exceptions for benzotriazole (12274.3 ± 3224.4 ng/L) and lamotrigine (509.3 ± 190.9 ng/L). Previous studies showed that in conventional activated sludge WWTPs, benzotriazole concentrations reached 7.7 μg/L in Germany, 4.1 μg/L in various Western European samples, and 10 μg/L in Switzerland.[44−46] The prevalence of benzotriazole in WWTPs was likely due to its widespread use as a corrosion inhibitor and an UV stabilizer. Compared with the other chemical groups, PFAS was found at relatively low concentrations in TWW, ranging from 8.1 to 25.7 ng/L, consistent with previously reported levels where the total concentrations of 24 PFAS were 30−198 ng/L in the effluent of six WWTPs throughout the year.[47] All target PFASs were also detected at trace levels (1.2−7.7 ng/L) in FW, likely due to their environmental ubiquity and persistence.

More than 10 years ago, TWW from the same source as the present study, i.e., Irvine Ranch Water District, was analyzed for 19 PPCPs, and DEET (181 ± 160 ng/L), meprobamate (87 ± 54 ng/L), and primidone (35 ± 28 ng/L) were found at relatively high concentrations.[36] The current study showed comparable concentrations for these chemicals in TWW: 81.4 ± 55.4 ng/L for DEET, 140.6 ± 21.7 ng/L for meprobamate, and 91.4 ± 27.5 ng/L for primidone. Other frequently detected PPCPs such as acetaminophen, carbamazepine, ibuprofen, naproxen, atenolol, sulfamethoxazole, and fluoxetine were present at lower concentrations (0.43−27 ng/L) in the earlier study than the current study (4.4−147.9 ng/L). The consistent detection of some CECs in TWW justifies the continuing environmental and public health concerns, emphasizing the need to understand the fate and risks of CECs introduced through TWW irrigation under field conditions and the consideration of mitigation practices.

CECs in Soil and Soil Porewater. The concentrations of CEC were measured in soil at three depths (0, 5, 10−15, and 35−40 cm) and in soil porewater during the study. In TWW-irrigated soil, the highest concentrations were found for DPG in the surface soil, at 56.6, 25.2, and 11.7 ng/g from the radish, lettuce, and tomato plots, respectively (Figure 1). Relatively high concentrations of DPG were also found in the lower-depth soil samples. In addition, benzothiazole, DEET, and benzotriazole were found at relatively high concentrations in

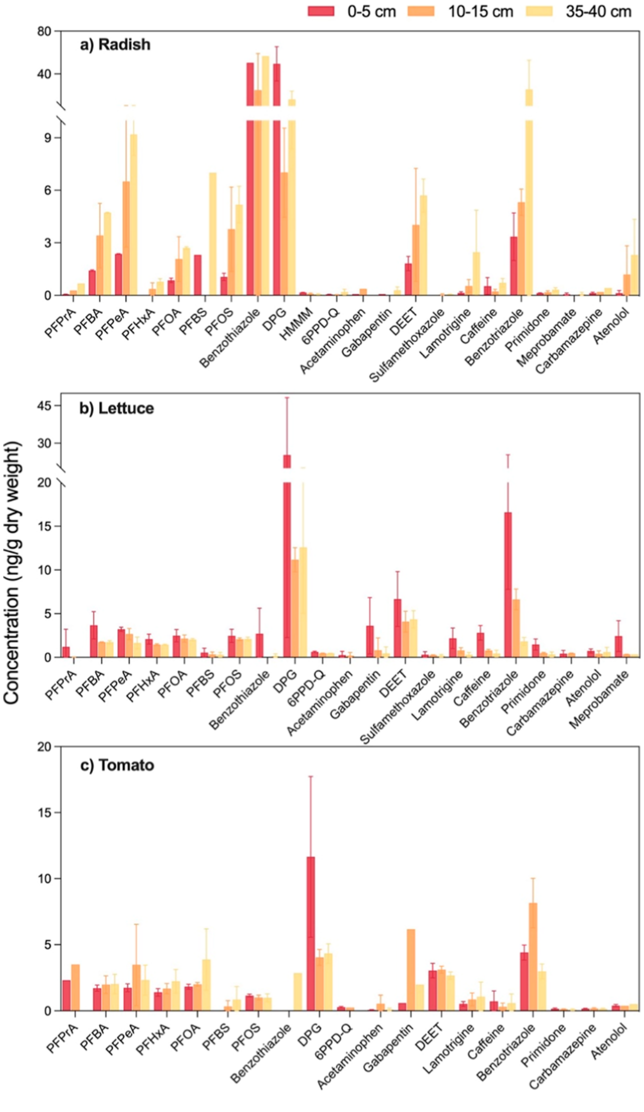

Figure 1. Concentrations (ng/g dry weight) of CECs at different soil depths receiving TWW cultivated with (a) radish, (b) lettuce, and (c) tomato.

the soil. It is also worth noting that perfluoroalkyl acids were consistently detected at low nanogram per gram levels in the soils, often displaying a uniform distribution pattern throughout the depths. For example, PFOA levels in soil from the lettuce treatment remained relatively similar at 2.5 ± 0.7, 2.2 ± 0.4, and 2.0 ± 0.1 ng/g for soil layers of 0−5, 10−15, and 35−40 cm, respectively. For those CECs detected in the soil, there was not a clear decreasing trend with the soil depth. This may be attributed to the fact that the soil had been mixed through plowing and digging over time and that the lowest sampling depth in this study was only 40 cm. It is also likely that many of the CECs considered in this study are mobile and move downward with water after irrigation and precipitation.

At this site, TWW irrigation had been practiced since 2011, and therefore, the field plots had been exposed to the associated CECs for more than 10 years. The target CECs did not show a significant accumulation trend in the soil, and the concentrations were generally in the low ng/g range for individual CECs. Although present at high levels (>90 ng/L) in TWW, HMMM, ibuprofen, primidone, lamotrigine, and meprobamate were found at low concentrations (<5 ng/g) in soil across the different depths. This observation suggested that these substances did not persist in soil.[37,48,49] The generally limited accumulation of CECs in soil over time may be attributed to soil microbial degradation, phytoextraction, and the fact that many CECs in TWW were present at very low concentrations. Although not evaluated directly in this study, the long-term reuse of TWW for irrigation in this region (groundwater table >20 m) should pose limited risk to contaminate groundwater through leaching.

Soil porewater samples from the rhizospheres of the three vegetables showed considerable variations in concentrations among different CECs (Figure 2). Benzotriazole showed the highest levels at 671.4 ± 483.0, 494.3 ± 184.9, and 2065.7 ± 684.9 ng/L in the radish, lettuce, and tomato soil porewater, respectively, likely due to its high concentration in TWW and weak soil adsorption (K_d = 0.82 mL/g). Conversely, some CECs like PFAS, though present at low concentrations in TWW and soil, reached relatively high levels in the soil porewater, up to 199.9 ng/L in the radish soil, 375.1 ng/L in the lettuce soil, and 1257.5 ng/L in the tomato soil for individual PFAS. Previous studies showed that chemicals in soil porewater constitute the dominant fraction available for plant uptake.[50] Despite low concentrations of PFAS in TWW and the bulk soil, their persistence, owing to minimal biotic or abiotic degradation, leads to accumulation in rhizosphere porewater. Combined with the continuous transport of PFAS via transpiration and the absence of loss processes within the plant, this likely contributed to the accumulation of the selected PFAS in plant tissues.[51]

CECs in Edible Vegetable Tissues. The vegetables were harvested at market-ready sizes to determine the CEC accumulation in the edible tissues. The edible parts, i.e., root (tuber) of radish, leaves/stems of lettuce, and fruits of tomato, were extracted and analyzed for the target CECs (Figure 3). In vegetables irrigated with TWW for the entire season (i.e., FULL treatment), CEC concentrations in the edible tissues varied greatly from ND to 264.9 ng/g, with plant- and organ-specific distributions. The legacy PFAS (eight perfluoroalkyl substances) were frequently detected in all three vegetable types, whereas the two emerging PFAS (5:3 FTCA and GenX) were not detected, despite their presence in TWW. The legacy PFAS exhibited consistent accumulation in all vegetables, with

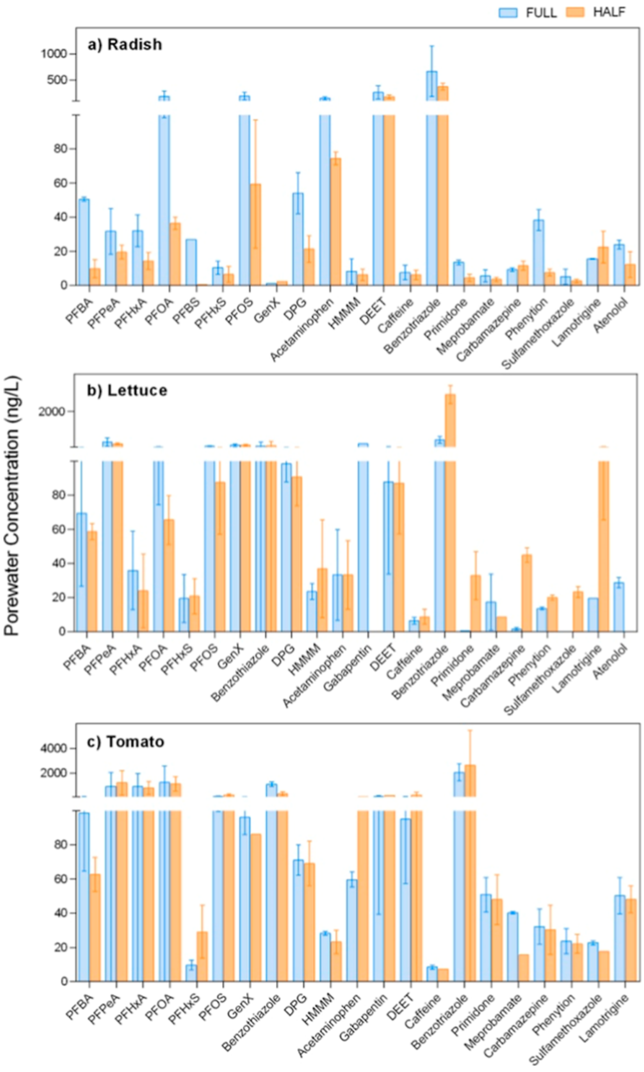

Figure 2. Concentrations (ng/L) of CECs in soil porewater in the root zone of (a) radish, (b) lettuce, and (c) tomato at harvest under the FULL and HALF treatment irrigation schemes.

accumulation apparently influenced by the carbon chain length and functional groups. For example, PFPrA (C3) showed a greater accumulation in plant tissues, with concentrations ranging from 30.8 to 53.8 ng/g, whereas PFOA (C8) levels were considerably lower (3.1−4.7 ng/g). This could be attributed to the higher water solubility and smaller molecular size of short-chain PFAS, which likely facilitated their uptake by plant roots and translocation through the vascular cylinder, whereas long-chain PFASs tend to sorb more readily to root surfaces.[52,53] Additionally, functional groups appeared to affect the PFAS accumulation. For instance, although having the same carbon chain length, PFBS was found to accumulate in tomato fruits at levels much lower (0.7 ± 0.5 ng/g) than PFBA (24.3 ± 11.4 ng/g). A similar pattern was also observed with radish and lettuce. These field observations corroborated trends from previous controlled experiments, demonstrating that when PFASs have equal carbon chain lengths, PFCAs consistently exhibited a higher uptake potential than PFSAs.[52] For example, Knight et al. reported that the average log BAF for PFOS was about 3.5−4.5 times lower than that of PFOA in a soil-plant system, where beans were exposed to a nominal PFAS concentration of 500 μg/kg.[54] This discrepancy

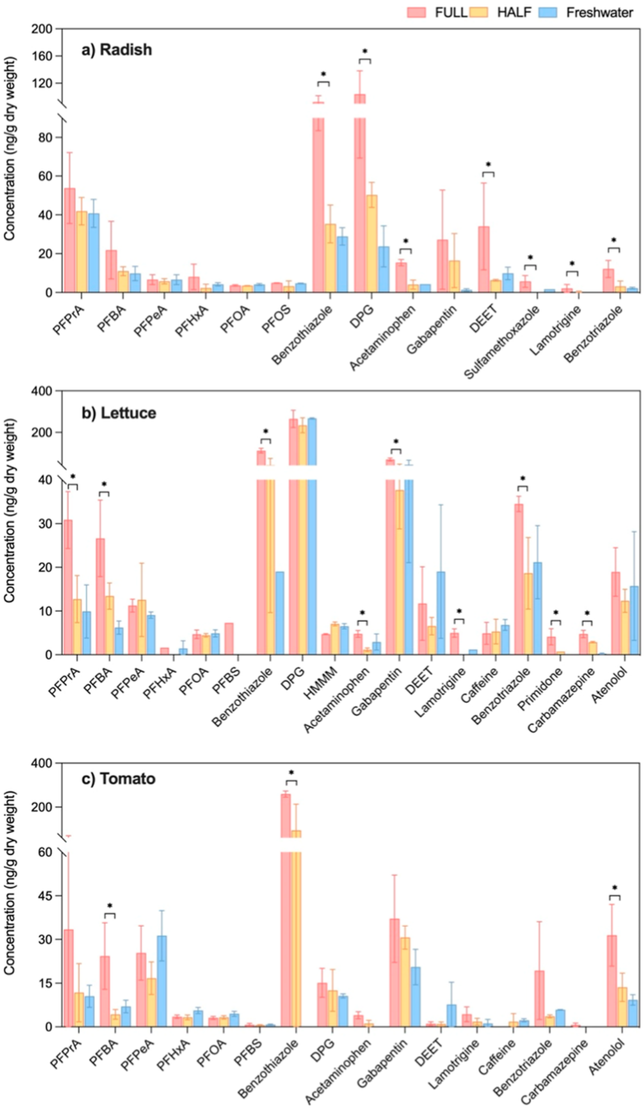

Figure 3. Concentrations (ng/g dry weight) of CECs in the edible part of (a) radish, (b) lettuce, and (c) tomato irrigated with the FULL or HALF TWW, or FW only.

suggested that the type of functional groups in PFAS played an important role in their uptake and translocation by plants and should be considered when assessing the overall risk of PFAS in agro-food systems.[52]

Two TWPs, DPG and benzothiazole, were found at the highest concentrations in the radish and lettuce tissues. Specifically, DPG accumulated to levels of 103.7 ± 34.5 ng/g in radish and 264.9 ± 41.5 ng/g in lettuce, while benzothiazole was detected at 92.6 ± 9.1 and 111.2 ± 11.7 ng/g, respectively. Benzothiazole, a neutral compound (log K_{ow} = 2.01), was also found to accumulate to high concentrations in tomato fruits (259.1 ± 13.8 ng/g). This finding aligned with the bell-shaped relationship between log K_{ow} and transpiration stream concentration factor values, which peaks at log K_{ow} of around 2.[53,55] The transporter-mediated uptake is influenced by functional group attributes, such as size, position, and charge distribution.[56] Active transporter proteins may also facilitate the uptake of benzothiazole in lettuce, as well as benzotriazole, which is structurally related to benzothiazole.[57,58] In contrast, lower concentrations of DPG (15.1 ± 5.0 ng/g) were observed in tomato fruits despite its high levels in TWW. Its cationic form likely contributed to its association with negatively charged root cell walls, limiting its translocation to fruits as compared to lettuce leaves.[57] Lower accumulation in tomato fruits was also observed for some other CECs (Figure 3c). Despite its presence in TWW, HMMM showed limited accumulation in the edible parts of radish (0.9 ± 0.2 ng/g) and lettuce (4.7 ± 0.1 ng/g) and was not detected in tomato fruits. This contrasts with its previously high uptake in hydroponically grown lettuce.[57] The difference likely stems from HMMM's strong soil adsorption (K_d = 6.40 mL/g), limiting its availability in a soil-plant system. This explanation was further supported by the low porewater concentration of HMMM (8.3−28.3 ng/L) (Figure 2). In comparison, benzothiazole showed significantly higher concentrations in porewater, ranging from 161.0 to 1121.2 ng/L, which was consistent with its elevated levels detected in plant tissues.

Significant variations in the CEC concentrations were observed across the three different vegetables. Among the 32 target CECs, more CECs were detected in lettuce (19) than that in tomato (13) or radish (14). The relatively higher number of compounds found in lettuce leaves compared to fruits or roots was consistent with previous studies.[33,36] Lettuce exhibited the highest CEC accumulation; for example, gabapentin, benzotriazole, atenolol, and DEET were detected at concentrations of 68.7 ± 7.5, 34.5 ± 1.8, 19.0 ± 5.6, and 11.8 ± 8.4 ng/g, respectively. In comparison, these compounds were detected at levels of up to 34.0 ng/g in radish and up to 37.1 ng/g in tomato fruits. The uptake and translocation of nonionic CECs in plants are thought to be driven by the transpiration stream, leading to their greater occurrence in leaves than that in fruits or tuber roots.[59−61] The variation in CEC accumulation may also result from differences in xenobiotic metabolism across different plant compartments and species. For instance, benzotriazole metabolism has been shown to differ by organs, with metabolites such as glycosylated benzotriazole and benzotriazole-acetyl-alanine detected in roots and shoots but not in fruits.[62]

In a study conducted under similar conditions with a focus on PPCPs,[36] DEET was found at 2.8 ng/g in root vegetables, while primidone and carbamazepine were found at up to 0.3 and 0.04 ng/g in leafy vegetables, respectively. In the current study, these compounds were found at higher levels, with DEET reaching 34.0 ± 22.4 ng/g in radish and primidone and carbamazepine at 4.1 ± 1.9 and 4.7 ± 0.8 ng/g, respectively, in lettuce irrigated with TWW. However, it must be noted that despite over a decade of TWW irrigation, CEC accumulation in edible plant tissues and soil remained generally low under field conditions, suggesting limited long-term accumulation and associated risks. Effective and farm-scale implementable mitigation strategies can further minimize the likelihood of CEC accumulation in food crops grown with TWW irrigation.

Reduction of CEC Accumulation by Alternating Irrigation. In this field study, we further evaluated the effectiveness of an irrigation alternation scheme as a practical option to minimize CEC accumulation in edible plant tissues. This approach was shown, under controlled experimental conditions, to be effective in reducing plant accumulation of CECs, especially for compounds with a high bioaccumulation potential and/or short soil half-life.[32,33] Under the field conditions, the FULL treatment plots were irrigated with TWW throughout the growing season, while the HALF plots received TWW for irrigation initially, followed by FW irrigation for the remainder of the growing season. A FW irrigation control, where plants were irrigated with FW for the entire duration of the study, was included to monitor background CECs and served as a negative control.

At harvest, the detected CECs consistently showed higher accumulation under the FULL treatment compared to the HALF treatment for the same chemicals. For example, in lettuce leaves, the levels of PFPrA, PFBA, benzothiazole, gabapentin, and benzotriazole ranged from 26.6 to 111.2 ng/g for the FULL treatment, while they were detected at 12.7–41.7 ng/g for the HALF treatment. In addition, many of the CECs from the HALF treatment showed accumulation levels similar to those from the FW control treatment (Figure 3). For instance, benzothiazole concentrations in radish tubers were 92.6 ± 9.1 ng/g in the FULL treatment, while the concentrations in the HALF treatment (35.3 ± 9.8 ng/g) were considerably lower ($p = 0.0018$) and similar ($p = 0.38$) to that from the FW control treatment (28.9 ± 4.4 ng/g). The similarity in CEC accumulation levels between the HALF and FW treatments suggested that if TWW irrigation is used only for the first half of the growing season, then there would be an added level of safety for most CECs.

A reduction factor (RF) was calculated to characterize the effectiveness of irrigation alternation in reducing CEC accumulation in edible plant tissues

$$\mathrm{RF} = \frac{C_{\mathrm{FULL}} - C_{\mathrm{HALF}}}{C_{\mathrm{FULL}}} \times 100\%$$

where C_{FULL} and C_{HALF} represent the concentrations of CECs in the edible tissue under the FULL and HALF treatments, respectively, at harvest. The calculation of RF was not carried out for CECs with concentrations below the detection limits or CECs with tissue concentrations below 10 ng/g in the FULL treatment due to significant variability and noise in the low-concentration data. The derived RF values for some of the CECs are shown in Table 2. In edible tissues, the reduction of CEC accumulation attributable to irrigation alternation ranged from 22.2 to 81.4% for radish, from −11.9 to 62.5% for lettuce, and from 17.0 to 82.4% for tomato fruits (Table 2). Among the CECs with relatively high accumulation in the edible plant tissue, a great degree of reduction was observed for PFPrA, PFBA, and benzotriazole in the tomato fruit, ranging from 64.8 to 82.4%, while in all three vegetables, benzothiazole showed >60% reductions. The significant reduction in benzothiazole accumulation with irrigation alternation across all plant tissues could be due to its susceptibility to degradation in soil and/or metabolism in plants.[63] Similar patterns of reduction were also observed for other CECs that share comparable characteristics. For example, in the radish edible tissue, the levels of acetaminophen, gabapentin, and benzotriazole ranged from 12.1 to 27.2 ng/g in the FULL treatment, while they were detected at 3.1 to 16.5 ng/g in the HALF treatment, representing 39.5–74.1% reductions. In lettuce and tomato, these chemicals exhibited RF values of 45.2–45.9% and 17.4–81.4%, respectively. These chemicals are characterized by a short half-life in soil, high solubility, and limited adsorption to soil, which likely contributed to their rapid dissipation in soil and significant translocation to the above-ground part, leading to relatively higher reductions in the radish tuber. Following uptake by plant roots, rapid metabolism may further explain the losses observed in the system. For example, *Arabidopsis* has been shown to quickly take up and assimilate benzotriazole via glycosylation, enabling conjugation without the need for additional functional group modification during phase I activation.[58] Some RF values were negative, i.e., −11.9% of PFPeA in lettuce, which could be attributed to the continuous uptake and translocation after the switch to FW irrigation and/or high variability in the analysis of field samples, particularly for contaminants at trace levels.

Table 2. RF for Target CECs in the Edible Tissues of Radish, Lettuce, and Tomato with the Alternating Irrigation Scheme[a]

chemical	radish (%)	lettuce (%)	tomato (%)
PFPrA	22.2	58.7	64.8
PFBA	49.7	49.5	82.4
PFPeA	ND	−11.9	34.1
benzothiazole	61.9	62.5	63.7
diphenylguanidine	51.6	11.6	17.0
acetaminophen	73.7	ND	ND
gabapentin	39.5	45.2	17.4
diethyltoluamide	81.4	44.1	10.3
benzotriazole	74.1	45.9	81.4
atenolol	ND	34.9	56.8

[a] ND: The RF values were not derived.

The relative reduction in plant accumulation also varied among different plant species for the same CECs. For example, DPG was accumulated at similarly high levels in radish and lettuce, detected at 103.7 and 264.9 ng/g in the FULL treatment, but was present only at 15.1 ng/g in the tomato fruit. DPG concentration decreased to 50.2 ± 6.5 ng/g in the HALF treatment, representing a 51.6% reduction in radish. However, concentrations of DPG in lettuce and tomato showed little change between the two treatments. For the CECs that showed a significant reduction in all three vegetables, lettuce appeared to exhibit a relatively low reduction, while radish seemed to be more responsive to the irrigation change. The relatively more sensitive response for radish may be due to the fact that the edible portion of radish was in direct contact with soil, where variations in soil porewater concentrations resulting from irrigation source changes directly affected uptake into the tuber root. Tomato fruits, with additional biological barriers and requiring long-distance translocation, exhibited high variability in RF across different CECs. Although fruits are generally less metabolically active than shoots or roots, the accumulation of parent compounds largely depends on metabolic transformations before translocation and on their susceptibility to soil degradation, which affects uptake into roots.[62] Consequently, short soil half-life chemicals, such as benzothiazole, benzotriazole, and atenolol, exhibited higher RF values in tomato fruits.

Significant reductions were observed for PFBA in lettuce ($p = 0.049$) and tomato ($p = 0.037$). Specifically, in lettuce at harvest, PFBA levels decreased from 26.6 ± 8.7 ng/g in the FULL treatment to 13.4 ± 3.0 ng/g in the HALF treatment. A similar trend was observed in tomato, with PFBA having an RF value of 82.4% for the HALF treatment. For the other PFAS, the RF values were smaller. The differences in accumulation between the FULL and HALF treatments for PFAS largely coincided with their different soil porewater concentrations. For instance, the porewater concentrations of PFPeA were 31.8 ± 13.5 and 19.6 ± 3.9 ng/L in the radish root zone for the FULL and HALF treatments, respectively, suggesting somewhat similar bioavailability ($p = 0.25$). In contrast, PFBA porewater levels in the radish FULL and HALF treatments were 50.6 ± 1.1 and 9.9 ± 5.3 ng/L, respectively, and a greater RF (49.7%) was consequently observed for PFBA in the radish tuber. The PFAS targeted in this study are recalcitrant to degradation or metabolism, and changes in accumulation in plant tissues under different irrigation conditions may be primarily influenced by the available fraction in the soil root zone. Therefore, soil porewater concentrations may serve as useful indicators of the bioavailability of contaminants for plant uptake. Simple biomimetic methods, such as passive samplers made of thin films,[64] may be used in situ to monitor bioavailable levels of CECs in the plant root zone; this approach should be explored in the evaluation of plant accumulation of CECs under different management conditions.

Limitations and Environmental Implications. This field study, carried out with irrigation with actual tertiary TWW, offered a realistic survey of the potential for accumulation of CECs in edible plant tissues when TWW is used for irrigation as well as the demonstration of a practical strategy for further reducing CEC transfer into plants. It is important to note that even though the field site had been retrofitted for TWW use for over 10 years, most target CECs were found at trace levels in the soil, likely due to the relatively low chemical loadings and/or natural attenuation, such as microbial degradation in soil. However, although typically detected at low levels in irrigation water, legacy PFASs were found in both soil and plant tissues, with short-chain PFAS being notably taken up and translocated to various plant organs, including tomato fruits. Given the newly introduced US EPA limits for PFAS in drinking water (e.g., 4 ng/L for PFOA and PFOS),[65] dietary intakes from TWW-irrigated crops may be one of the primary sources of PFAS exposure to humans and should be further addressed. In addition, TWPs like benzothiazole and DPG, under-reported in previous studies, were found at relatively high concentrations in TWW. Of the few TWPs considered in this study, DPG was further found to accumulate appreciably in plant tissues. However, the potential toxicological effects of tire additives on humans are currently largely unknown, and the implication of their contamination of food produced with TWW irrigation should be further evaluated. Furthermore, CEC metabolism by plants, such as conjugation with biomolecules in plant, may mask the accumulation of CECs in plants.[58] The biological activity of plant metabolites, including conjugates, merits further research.

Field studies, although inherently susceptible to uncertainties due to diverse interacting factors, such as soil heterogeneity, differences among individual plants, and temporal fluctuations in CEC concentrations in TWW, provide invaluable insights into the real-world accumulation of CECs through TWW irrigation and the effectiveness of irrigation scheme modifications. These factors led to significant variations in the derived field observations compared to studies under controlled conditions. In addition, potential contributions from other PFAS sources (e.g., rainfall and atmospheric deposition) were not specifically quantified in this study. Nevertheless, our findings clearly demonstrated that the alternation between TWW and FW for irrigation significantly minimized the accumulation of many CECs in edible plant tissues, with most CECs showing concentrations near the background levels found for plants grown solely with FW irrigation. Therefore, using TWW only for the first part of the growing season represents an effective and feasible option, on the farm-scale, to minimize the transfer of CECs into plant-based foods. The reduction is the result of combined effects due to degradation in soil, in-plant metabolism, growth dilution, and other factors. Although not considered in this study, the hybrid irrigation scheme may be similarly applied to other marginal waters, such as produced water and captured storm runoff water, in their reuse practices. The diverse modes of water reuse can greatly enhance environmental protection and sustainability and increase public awareness of the expanded use of marginal water sources in the face of FW scarcity induced by climate change and population growth.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.4c13666.

> Chemical information, degradation and adsorption study, detailed information on instrument analysis and quality control, water sample extraction procedure, physicochemical characteristics of the studied soil, physicochemical properties of targeted CECs in this study, optimized multiple reaction monitoring parameters for the analysis of CECs and their isotopically labeled compounds by UPLC-MS/MS, detection limits and recoveries of target analyte, environmental conditions during the study period, concentrations of CECs at different soil depths receiving TWW cultivated with radish/lettuce/tomato, concentrations of CECs in soil porewater in the root zone of radish/lettuce/tomato at harvest under the FULL and HALF treatment irrigation schemes, concentrations of CECs in the edible part of radish/lettuce/tomato irrigated with the FULL or HALF TWW, or FW only, and plant growth period and sampling schedule for radish, lettuce, and tomato (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Jay Gan − *Department of Environmental Sciences, University of California, Riverside, California 92521, United States;* orcid.org/0000-0002-7137-4988; Phone: 951-827-2712; Email: jgan@ucr.edu; Fax: 951-827-3993

Authors

Qingyang Shi − *Department of Environmental Sciences, University of California, Riverside, California 92521, United States*

Dahang Shen − *Department of Environmental Sciences, University of California, Riverside, California 92521, United States; Institute of Nuclear Agricultural Sciences, Key Laboratory of Nuclear Agricultural Sciences of Ministry of Agriculture of PRC and Zhejiang Province, Zhejiang University, Hangzhou 310058, China*

Rebecca Yates − *Department of Environmental Sciences, University of California, Riverside, California 92521, United States*

Catherine Chou − *Department of Environmental Sciences, University of California, Riverside, California 92521, United States*

Andrea Barajas − *Department of Environmental Sciences, University of California, Riverside, California 92521, United States*

Jingjing Zhang − *Department of Environmental Sciences, University of California, Riverside, California 92521, United States; Department of Pesticides, College of Plant Protection, Henan Agricultural University, Zhengzhou 450046, China;* orcid.org/0000-0002-5293-1267

Daniel Schlenk − *Department of Environmental Sciences, University of California, Riverside, California 92521, United States;* orcid.org/0000-0001-5519-2298

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.est.4c13666

Notes

The authors declare no competing financial interest.

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