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Alternating Water Sources to Minimize Contaminant Accumulation in Food Plants from Treated Wastewater Irrigation

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Abstract

The use of treated wastewater (TWW) for agricultural irrigation is a critical measure in advancing sustainable water management and agricultural production. However, TWW irrigation in agriculture serves as a conduit to introduce many contaminants of emerging concern (CECs) into the soil-plant-food continuum, posing potential environmental and human health risks. Currently, there are few practical options to mitigate the potential risk while promoting the safe reuse of TWW. In this greenhouse study, the accumulation of 11 commonly occurring CECs was evaluated in three vegetables (radish, lettuce, and tomato) subjected to two different irrigation schemes: whole-season irrigation with CEC-spiked water (FULL), and half-season irrigation with CEC-spiked water, followed by irrigation with clean water for the remaining season (HALF). Significant decreases (57.0-99.8%, $p < 0.05$) in the accumulation of meprobamate, carbamazepine, PFBS, PFBA, and PFHxA in edible tissues were found for the HALF treatment with the alternating irrigation scheme. The CEC accumulation reduction was attributed to reduced chemical input, soil degradation, plant metabolism, and plant growth dilution. The structural equation modeling showed that this mitigation strategy was particularly effective for CECs with a high bioaccumulation potential and short half-life in soil, while less effective for those that are more persistent. The study findings demonstrate the effectiveness of this simple and on-farm applicable management strategy that can be used to minimize the potential contamination of food crops from the use of TWW and other marginal water sources in agriculture, while promoting safe reuse and contributing to environmental sustainability.

Keywords: Contaminants of emerging concern; PFAS; Wastewater irrigation; Plant uptake and accumulation; Water reuse

1. Introduction

Treated municipal wastewater (TWW) is a promising alternative water resource for augmenting agricultural irrigation and conserving freshwater, especially in arid and semi-arid regions (Shi et al., 2022; Singh, 2021; Sokolow et al., 2019). However, despite the increasing need for reuse of TWW and other marginal water for agricultural irrigation, the potential risks associated with contaminants in TWW remain a significant challenge for the broader adoption of this practice (Carter et al., 2019; Natasha et al., 2023; Ruan et al., 2023). Due to industrial activities, household consumption of pharmaceuticals and personal care products (PPCPs), and other chemicals lead to the accumulation of these contaminants in municipal wastewater, and they may appear in treated wastewater due to incomplete removal (Lin et al., 2020; Rogowska et al., 2020; Tran et al., 2018). Many contaminants of emerging concern (CECs), including PPCPs, per- and polyfluoroalkyl substances (PFAS), flame retardants, and plasticizers, are known to have biological activity and may have adverse ecological and human health effects at environmentally relevant concentrations (Anderko and Pennea, 2020; Christou et al., 2017a; Sharma et al., 2019; Tang et al., 2020; Yang et al., 2022).

The ubiquitous occurrence of CECs in agricultural fields receiving TWW irrigation has been increasingly documented (Ben Mordechay et al., 2022; Biel-Maeso et al., 2018; Christou et al., 2017b; LeFevre et al., 2017; Pullagurala et al., 2018). For example, concentrations of CECs in samples of food crops, collected from 445 commercial fields, varied among plant species and organs (Ben Mordechay et al., 2021). In general, leaves exhibited the highest accumulation, ranging from <0.1 to 2,470 ng/g, while median concentrations of <10 ng/g were found in roots, fruits, or tubers (Ben Mordechay et al., 2021). Martínez-Piernas et al. (2019) analyzed 74 frequently occurring CECs in TWW and found 12 of the target compounds in lettuce and radish, at concentrations of 0.03-57.6 ng/g. Under field conditions, the total concentrations of 19 PPCPs in the edible tissues of vegetables irrigated with TWW ranged from 0.01 to 3.87 ng/g (Wu et al., 2014). Although our understanding of plant accumulation of CECs has improved greatly over the last decade, research on mitigation strategies to minimize the potential accumulation of CECs in food crops is limited. The lack of practical management strategies hinders the broader adoption of TWW irrigation in agriculture.

A potentially effective and on-farm applicable mitigation strategy is a hybrid or alternating irrigation scheme, e.g., TWW irrigation for the first part of the growing season, followed by freshwater (FW) irrigation for the remaining season. Conceptually, the use of TWW irrigation only for the first part of the growing season reduces the chemical input and allows time for the attenuation of CECs through processes such as soil degradation, plant metabolism, and plant growth dilution. In a preliminary study, we used hydroponic cultivation to demonstrate this concept, and observed reductions ranging from 52.0-96.6% for select CECs in lettuce and tomato grown in nutrient solutions (Shi et al., 2023b). However, the TWW-soil-plant continuum represents a much more complex system than hydroponic cultivation, and processes such as adsorption/desorption and rhizosphere microbial degradation likely play important roles in influencing plant accumulation of CECs (Mei et al., 2021; Sutherland and Ralph, 2019; Yu et al., 2021). To further advance this concept for eventual field implementation, we carried out greenhouse experiments, in which three common vegetables were grown in soil. Radish, lettuce, and tomato were chosen as model food plants in this study, as they represent root, leafy, and fruit vegetables. We hypothesized that when irrigation with TWW is discontinued, CECs dissipate in the soil-plant system due to rhizosphere degradation, plant metabolism, and growth dilution, leading to reductions in CEC accumulation in the edible tissue at maturity. Structural equation modeling (SEM) was further used to explore the contribution of various factors to the reduced CEC accumulation. The findings of this study are expected to solidify alternating irrigation as a feasible mitigation practice, contributing to an increased acceptance of TWW and other marginal waters to sustain agriculture and the environment.

2. Materials and Methods

Chemicals

Eleven compounds were selected in this study based on their occurrence and generally high levels in TWW. The selected test compounds included acetaminophen, caffeine, meprobamate, ibuprofen, naproxen, carbamazepine, atenolol, fluoxetine, perfluorobutanesulfonic acid (PFBS), perfluorobutanoic acid (PFBA), and perfluorohexanoic acid (PFHxA), covering a range of chemical classes and physicochemical properties (Table S1). The sources of chemical standards are provided in Text S1. Stock solutions of all target compounds were prepared in methanol and stored at -20°C prior to use. The QuEChERS extraction kit containing 6 g magnesium sulfate ($MgSO_4$) and 1.5 g sodium acetate (NaOAc) and cleanup kit containing 400 mg of primary secondary amine (PSA), 400 mg of bulk carbograph, and 1200 mg of magnesium sulfate were purchased from Agilent (Santa Clara, CA). High-purity Fisher HPLC grade solvents were used for all extractions and analyses (Fisher Scientific, Waltham, MA). Deionized (DI) water was produced in-house using a Barnstead E-Pure water purification system (Thermo Scientific, Dubuque, IA) for all analysis.

Soil properties

The soil was collected from a field at the University of California, Riverside Agricultural Operations and sieved through a 2-mm mesh after air drying. Particle size distribution was determined by the 12-h hydrometer method (Klute, 1986). The soil was classified as a sandy loam based on the texture (51.9% sand, 43.5% silt, and 4.6% clay). A soil pH of 6.5 was measured using the soil slurry method (Donohue, 1992). Total carbon and nitrogen contents were determined using a FlashEA NC Analyzer (Thermo Fisher, Waltham, MA), while the major elements were characterized by inductively coupled plasma-optical emission spectroscopy (ICP-OES) (PerkinElmer Optima 7300DV). Specific soil properties are summarized in Table S2. In addition, degradation and adsorption of CECs in the soil were measured for individual CECs using batch incubation or batch equilibration methods (Xu et al., 2009), from which half-life ($T_{1/2}$) values and adsorption coefficients (K_d) were derived and used for data interpretation and model prediction.

Greenhouse experiments

Three vegetable species, i.e., radish (*Raphanus sativus* L.), lettuce (*Lactuca sativa* L.), and tomato (*Solanum lycopersicum* L.), were selected as they represent leaf, root, and fruit vegetables, respectively. The seeds of these vegetables were first germinated on wet filter paper (Cytiva, MA) until the root had emerged. Then, 3 seedlings were transferred to polypropylene pots (17 cm height, 10 cm top diameter, 7 cm bottom diameter) containing moist soil (1.2 kg dry weight). Deionized water was periodically added to each container to maintain a water content of 75% of the soil's maximum water-holding capacity, to compensate for the water loss from evapotranspiration. This ensured that the plants received sufficient water for growth, while preventing water from leaching from the bottom of the containers. The plants were grown in a greenhouse receiving full sunlight, with a daily temperature variation of 15 to 40 °C and a relative air humidity of 30 to 60%.

When the cotyledons had developed, each container was thinned to one plant and subjected to one of the following two irrigation treatments: the FULL treatment received irrigation with

CEC-spiked water (5 μg/L of each CEC in DI water) throughout the entire growth period, while the HALF treatment received CEC-spiked water for the first half of the growth period and then received only DI water for the second half. Plant-free and CEC-free controls were included to monitor the background levels of CECs in soil and plant tissues. Since daily watering needs varied for the different plant species, the same total volume of spiked water was added to each container daily, while any additional watering needs were accounted for with DI water. In addition, the amount of water applied was increased to accommodate plant growth during the second half of the growing season. To supplement nutrients, a water-soluble fertilizer (Peters Professional 20-20-20 General Purpose Fertilizer) was applied along with the irrigation water once a week at 125 mg/L.

Triplicates from each treatment group of each plant species were sacrificed at four different time points: 1/4, 2/4 (water source switch point for HALF treatment), 3/4, and 4/4 (harvest point) of the total growth period. The total growth durations for radish, lettuce, and tomato were 37, 49 and 93 days, respectively, when they reached maturity or market-ready state. For the HALF treatment, the irrigation water was switched from CEC-spiked solution to fresh water at the middle point, or day-17 and day-25 for the radish and lettuce, respectively. For the tomato, the water source switch was at day-42, when the fruit began to develop. The control treatment groups were sampled only at the end of the growing season, i.e., harvest point. The growth period and sampling time points for each vegetable are shown in Figure S1.

For sampling, the entire plant was carefully removed from the soil and separated into roots and shoots (and fruits for tomato) after being carefully rinsed with DI water. The collected soil was thoroughly homogenized, and a small fraction was used for subsequent chemical analysis.

All plant and soil materials were stored in a −80 °C freezer prior to sample preparation and chemical analysis.

Chemical extraction and analysis

Soil samples were freeze-dried for 72 h and then ground into fine particles using a mortar and pestle. A 2.0-g aliquot of soil was weighed into a 15 mL polypropylene centrifuge tube (Sigma, St. Louis, MO). Each soil sample was spiked with 50 µL of a mixture of isotope-labeled CECs (2 mg/L stock solution in methanol) as the recovery surrogate. The soil samples were extracted and analyzed according to a modified AOAC method (Lehotay et al., 2007). Briefly, 2 mL of DI water and 5 mL of acetonitrile containing 1% acetic acid were added to the sample tube and the mixture was vortexed for 1 min, then shaken at 200 rpm for 5 min. The slurry was added with 2 g of anhydrous $MgSO_4$ and 0.5 g of NaOAc, and the sample tube was shaken at 200 rpm for another 5 min, followed by centrifugation at 3500 rpm for 20 min.

The freeze-dried plant tissues were homogenized into powder with a stainless-steel grinder, before weighing a 0.5-g aliquot into a 50 mL polypropylene centrifuge tube and spiking with 50 µL of a mixture of isotope-labeled CECs. The plant tissue extraction procedure was similar to that of the soil samples, with 4 mL of DI water, 10 mL of acetonitrile (1% acetic acid), 6 g of $MgSO_4$, and 1 g NaOAc. The supernatant was collected in a 15 mL centrifuge tube containing 1 g d-SPE cleanup sorbents (200 mg PSA, 200 mg bulk carbograph, 600 mg $MgSO_4$). The samples were vortexed for 1 min, followed by centrifugation at 3500 rpm for 20 min.

The supernatant was collected after centrifugation, dried under nitrogen, and reconstituted with 1 mL water/methanol (1/1, v/v) for both soil and plant samples. All extracts were transferred into 2 mL polypropylene microcentrifuge tubes and centrifuged at 15000 rpm for 15 min. The supernatant was then transferred to a 300-μL polypropylene vial for instrumental analysis.

Concentrations of the target CECs were determined on a Waters ACQUITY ultraperformance liquid chromatograph (UPLC) in tandem with a Micromass triple quadrupole (TQD) mass spectrometer with an electrospray ionization source (Waters, Milford, MA). Additional details on LC−MS/MS analysis can be found in Text S2 and Table S3.

Quality Assurance/Control and Statistical Analysis

Confirmation of the target CECs was achieved using the observed ion transitions and comparison against peak retention times of authentic standards in mass spectrometry and chromatography. Matrix blanks were obtained from non-spiked plants grown in CEC-free growth media for each species. Solvent blanks (1:1, v/v methanol/water), matrix blanks, and matrix spike analyses were included to monitor for method variation and background contamination. Stable isotope-labeled surrogates (deuterium or ^{13}C) were included in all samples to determine analyte recoveries, correct matrix effects, and instrument response shifts. Limits of quantification (LOQ) and recoveries were established for each analyte through preliminary experiments and are summarized in Table S4. An analytical precision measurement was performed by analyzing one sample of the calibration standard in triplicate for every 10-20 samples analyzed, and a <20% relative standard deviation was observed throughout the study.

Data analysis and post-processing were performed using GraphPad Prism (La Jolla, CA). To evaluate the difference between the FULL and HALF treatments, statistical analyses including one-way analysis of variance (ANOVA) and Student's t-test were performed, with a significance level of $p < 0.05$. The partial least square Structural Equation Modelling (SEM) analysis was used to evaluate the relationships between reduction factor (RF) in different plant compartments and various physiochemical properties, i.e., log K_{ow}, K_d, solubility, root concentration factor (RCF), and translocation factor (TF). In this study, WarpPLS 8.0 (ScriptWarp Systems, Laredo, TX) software was employed to generate the model using the robust maximum likelihood method.

3. Results and Discussion

3.1 CEC accumulation in plant tissues

In this study, the effect of irrigation alternation on the plant accumulation of CECs was characterized in three different vegetable species grown in soil under greenhouse conditions. To monitor changes in CEC concentrations in plant tissues and soil, samples of soil and plant tissues were collected for each vegetable species at four different time points, i.e., the water source switch point, harvest point, and two midway time points (Figure S1). The plants grown under the two irrigation schemes showed no significant differences in their biomass ($p > 0.05$). For the same treatment, there were significant variations among the different CECs in their levels in the plant tissues and soil, even though the same nominal concentration (5 µg/L) was used for all CECs (Figures 1 and 2, Figures S2 and S3). For example, at the time of harvest, PFBA (227.1 ± 82.8 ng/g), PFHxA (26.2 ± 7.7 ng/g) and meprobamate (10.6 ± 1.9 ng/g) were detected in the radish root (edible tissue) for the FULL treatment. A similar pattern was observed in the edible tissues of lettuce (lettuce shoot) and tomato (tomato fruit). In contrast, acetaminophen, ibuprofen, caffeine, and meprobamate were infrequently detected, or detected at much lower levels.

When detected, the CEC accumulation in plants from the HALF treatment was significantly lower ($p < 0.05$) than that from the FULL treatment, and the difference was observed in both edible and non-edible tissues (Figures 3 and S4). For example, in radish tuber at harvest, the levels of PFBA, PFBS, and carbamazepine were 227.1 ± 82.8, 28.0 ± 11.2, and 26.5 ± 0.6 ng/g, respectively, for the FULL treatment, which decreased to 67.4 ± 42.7, 10.5 ± 4.3 and 4.2 ± 3.1

ng/g, respectively, for the HALF treatment. A similar trend was observed in lettuce, with PFBA having the greatest shoot accumulation at 3926.1 ± 284.5 ng/g at harvest for the FULL treatment, while the concentration was 1189.6 ± 75.1 ng/g under the HALF irrigation scheme. Tomato fruits from the FULL treatment showed a significant accumulation of PFBA and PFHxA at 2595.7 ± 550.9 and 637.2 ± 149.9 ng/g, respectively, while the corresponding levels were 612.5 ± 196.6 and 130.3 ± 81.2 ng/g for the HALF treatment.

It can also be noted that despite being in direct contact with the soil, radish tuber accumulated significantly less CECs than lettuce shoot or tomato fruit on a dry biomass basis. The differences may be due to the upward translocation of these mobile compounds driven by plant transpiration. For example, the concentrations of PFAS in radish shoots in the FULL treatment ranged from 565.7 to 7239.5 ng/g, which were an order of magnitude higher than those in the tuber. A similar trend was observed in lettuce and tomato whole plants. For example, carbamazepine and PFBA were detected at 40.7 ± 6.4 and 282.1 ± 110.2 ng/g, respectively, in lettuce roots at harvest in the FULL treatment, which were significantly lower than those detected in the lettuce shoot (336.4 ± 26.3 and 3926.1 ± 384.5 ng/g, respectively). Likewise, the levels of PFBA and PFHxA in tomato roots at harvest were 69.2 ± 43.4 and 33.0 ± 17.6 ng/g, respectively, while the levels in tomato shoots were 1536.0 ± 137.8 and 440.5 ± 71.6 ng/g, and the respective values for tomato fruit were 2596.7 ± 551.0 and 637.2 ± 150.0 ng/g (Figure 3 and Figure S4). A high percentage of water taken up by the tomato plant is used for fruit development, as compared with the amount of water that transpires (Fitter and Hay, 2012; Yakushiji et al., 1998). Observations from this and other studies suggest that for highly mobile compounds such as short chain PFAS, upward translocation is an important process contributing to their accumulation in above-ground tissues, including the fruit.

To characterize the translocation of CECs in plants after root uptake, translocation factor (TF) was calculated as the ratio of the chemical concentration in the shoot (aboveground part) to that in the root (C_{shoot}/C_{root}). Acetaminophen, meprobamate, carbamazepine, and all three PFAS compounds showed a strong tendency for upward movement, with TF > 1, while other CECs showed limited translocation (Figure S5). Compounds with moderate log K_{ow} (1 to 3) exhibited high TFs, as observed with acetaminophen, meprobamate, and carbamazepine, which could be attributed to their ability to move through the xylem vessels (Miller et al., 2016; Roberts and Oparka, 2003; Tester and Leigh, 2001). PFAS compounds with relatively short carbon chains are hydrophilic and recalcitrant to microbial degradation and plant metabolism, and can readily penetrate roots and translocate upward, which may have contributed to their high accumulation in the above-ground parts (Jiao et al., 2020; Zhang et al., 2019). It is worth noting that even though PFBA and PFBS have the same carbon chain length, their different functional groups led to distinctly different accumulation patterns, with PFBS consistently exhibiting greater accumulation in above-ground tissues among the different plant species (Dal Ferro et al., 2021).

The uptake and translocation of CECs in plants appeared to be influenced by their physiochemical properties. Previous studies suggested a positive correlation between root uptake and pH-adjusted log K_{ow} for neutral compounds and a negative correlation with translocation due to hydrophilicity-regulated transport via xylems (Wu et al., 2013). In the soil porewater (pH = 6.5) under the experimental conditions, only acetaminophen and carbamazepine were expected to remain primarily in the neutral form, while ibuprofen, naproxen, PFBS, PFBA, and PFHxA mostly existed as anionic species. Over 90% of caffeine, meprobamate, atenolol, and fluoxetine were present as cationic species. Nonionic compounds with moderate hydrophobicity ($2 < \log K_{ow} < 5$) are known to diffuse readily across root cell membranes (Briggs et al., 1982; Trapp, 2009), while cationic chemicals can be attracted via electrostatic interaction (Inoue et al., 1998; Trapp, 2009), explaining the high accumulation of carbamazepine and atenolol in roots. Conversely, the limited uptake of anionic ibuprofen and naproxen may be attributed to their negative charge, limited lipophilic binding, and short half-life in soil and plants (Schopfer and Brennicke, 2010). The observed PFAS uptake and translocation differed from the other CECs, likely because of their amphiphilic characteristics (Gredelj et al., 2020). In addition to dislocating the negative charge due the strong electron-withdrawing effect of fluorine atoms, the relatively high accumulation of PFBA in roots may also be ascribed to its ability to bypass the Casparian strip and accumulate in vascular tissues (Felizeter et al., 2012).

3.2 CEC residues in soil

The concentrations of most CECs in soil were found to decrease over time after switching to a clean water source for the HALF treatments (Figure 2), which may be attributed to microbial degradation and phytoextraction (Clarke and Cummins, 2015; Shi et al., 2023a; Yakushiji et al., 1998). Acetaminophen and naproxen were present only at trace levels (<1 ng/g) throughout the cultivation period, suggesting rapid degradation in soil (Patel et al., 2019; Phong Vo et al., 2019). A previous study using ^{14}C labeling showed that a significant portion (73.4–93.3%) of acetaminophen formed non-extractable or bound residues in soil (Li et al., 2014). This was consistent with the estimated short half-life ($T_{1/2} = 0.95$ days) for acetaminophen in this study. Among the 11 targeted chemicals, acetaminophen, caffeine, ibuprofen, and naproxen showed short persistence ($T_{1/2} < 7$ days) in the soil, while carbamazepine ($T_{1/2} = 293$ days) and PFAS compounds ($T_{1/2} > 10$ years) were found to be persistent. Plant uptake may also have contributed to the dissipation of CECs in the soil, especially in a soil container system (Shi et al., 2023a). For instance, PFHxA and PFBA exhibited high soil concentrations for the first half of the growth period which decreased in both the FULL and HALF treatments during the second half of the growth period, along with a decrease in the total amount of chemical accumulated in the plant tissue. The observed decreases suggest the removal of persistent compounds by plants, while compounds with short half-lives were likely removed by degradation in soil.

In soil, a chemical is distributed between water and the soil solid phase, and the partition coefficient K_d regulates the level of CECs in the soil porewater that is potentially available for root uptake. As shown in Table S1, K_d varied over three orders of magnitude for the CECs considered in this study. Chemicals with high K_d values are more likely to adsorb to soil particles, resulting in lower porewater concentrations, and hence limited uptake into the root (Li et al., 2019). For instance, fluoxetine (K_d = 214.5 mL/g) exhibited the highest accumulation in roots among a select group of CECs under hydroponic conditions (Shi et al., 2023b), while negligible accumulation in the root was observed in the soil-plant systems considered in this study. In general, chemicals with large $T_{1/2}$ and small K_d values, such as carbamazepine and the three PFAS compounds (Table S1), consistently showed greater plant uptake and translocation, as well as accumulation in the edible tissues at harvest.

3.3 Reduction in CEC accumulation with irrigation alternation

At harvest, only a handful of the target CECs were found above the detection limits in the edible tissues. For the detected CECs, significant reductions in accumulation ($p < 0.05$) were consistently observed for meprobamate, carbamazepine, PFBS, PFBA and PFHxA in the edible part of the plants from the HALF treatment as compared to the FULL treatment. To quantitatively evaluate the effect of the alternating irrigation scheme on CEC accumulation, a reduction factor (RF) was calculated as follows (Table 1):

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

where C_{FULL} and C_{HALF} were the CEC concentrations in specific plant tissue with FULL and HALF treatments at the harvest time, respectively. The RF values were not derived for those CECs with levels below the limit of detection. The RF serves to demonstrate the decrease in CEC accumulation in the edible part of plants resulting from the switch from irrigation with contaminated water to clean water. While the RF does not provide a direct comparison of CEC reduction under equal exposure conditions—due to the FULL and HALF treatments receiving different amounts of CECs—it allows for an evaluation of the effectiveness of the alternating irrigation scheme in practical settings, where contaminant mass loadings are expected to differ due to the different irrigation intervals of contaminated water such as TWW.

Among the edible tissues, CEC levels were reduced by 27.5-100% for radish root, 9.3-98.9% for lettuce shoot, and 57.9-99.8% for tomato fruit in the HALF treatment. Among the different CECs with significant accumulations, the reduction for meprobamate and carbamazepine were higher, ranging from 81.0% to 99.8%, as compared to those for PFAS compounds, which varied between 57.0% and 93.3%. In non-edible tissues from the HALF treatments, high reduction rates were also observed. For example, in lettuce roots, the level of meprobamate, naproxen and fluoxetine decreased by 98.4, 94.3 and 93.6% in the HALF treatment, respectively. In tomato roots, the corresponding reductions were 99.5, 98.4, and 82.6%, while they were 97.1, 100.0, and 91.8% for tomato leaves. Likewise, in radish shoots, the reductions for these compounds were 88.2, 100.0, and 92.1%, respectively. The concurrent reductions in non-edible tissues suggest that the decreased uptake into the plant root, metabolism after uptake, and growth dilutions due to increases in biomass contributed to the decreased accumulation in the edible tissues at the end of the study. For the same CECs, quantitative differences were observed in the reduction of atenolol among plant species; the RF value was 66.9% in radish roots, compared to over 85% in both lettuce and tomato roots. This disparity may be attributed to longer growth durations and more pronounced translocation stemming from higher transpiration rates.

For the HALF treatments, the source of irrigation was changed at approximately the middle point of each plant species' growth duration. Additionally, more water was added to each plant species during the second half of the growth period to account for the larger biomasses resulting from plant growth. For radish, lettuce, and tomato plants, the quantities of irrigation water were 0.96, 1.25, and 4.25 L per plant container before the point of switch, which accounted for 31.4, 34.2, and 30.7% of the total amount of water that each plant species received for the entire season. Therefore, the total chemical input for the HALF treatment was 68.6, 65.8 and 69.3% less than that of the FULL treatment for radish, lettuce, and tomato, respectively. The reduced chemical input in the HALF treatment group played a major role in the overall reductions in CEC accumulation in the tissues at harvest. However, the changes in chemical input alone could not explain the overall reductions. For example, additional reductions in radish roots and lettuce shoots were observed for meprobamate, carbamazepine, and fluoxetine, with 81.0-98.9% less accumulation in the HALF treatment. In the tomato fruit, a significant ($p < 0.01$) difference between the HALF and FULL treatments was observed for meprobamate, carbamazepine, PFBS, PFBA and PFHxA, as the concentration decreased by 76.4-99.8% with the alternation. Therefore, other processes and factors, such as degradation in soil, adsorption/desorption, plant metabolism, and growth dilution, likely also contributed to the ultimate reductions in CEC accumulation in edible tissues at harvest. In contrast, the reductions of persistent chemicals, exemplified by PFAS accumulation in the edible part of radish (57.0-70.3%) and lettuce (65.0-69.7%), were somewhat similar to the reduction in their chemical loads between the two treatments. Therefore, the reduction due to irrigation water alternation for persistent chemicals was more effective for fruit vegetables than leafy or root vegetables. In general, greater reductions were observed for unstable CECs with a short soil half-life, such as meprobamate and fluoxetine, suggesting that their accumulation in plants would be more responsive to the change in irrigation water sources.

Soil served as a sink for CECs introduced by irrigation water. Chemical residues in the soil continued to be available for plant uptake after the chemical input was stopped at the switch point. This was evidenced by the increase in the total chemical mass accumulation after the change of water sources in the HALF treatment (Figure S6). For example, at the 3/4 time point, the total amount (the product of chemical concentration multiplied by the total biomass) of PFHxA in radish was significantly greater ($p < 0.05$) at 559.9 ± 174.0 ng, as compared to that at the switch point (225.5 ± 67.0 ng). The total accumulated amount of PFHxA continued to increase over time and reached 828.0 ± 196.5 ng at the time of harvest. It must be noted that the PFAS compounds considered in this study were short-chain PFAS with high mobility and bioavailability. As the chain length increases, plant uptake and translocation of PFAS generally decrease. More PFAS compounds, including those with different functional groups as well as PFAS precursors, should be evaluated to gain a more complete understanding of PFAS accumulation by food crops and the potential dietary intakes through human consumption.

In this study, we tested the alternating irrigation scheme by choosing the middle growth point as the water source switch point. Different degrees of reductions in contaminant accumulation may be expected when irrigation water is changed at other time points during plant growth. Future research should consider the influence of the timing of irrigation water source change on contaminant accumulation in edible tissues. In addition, to better delineate the contribution of soil degradation, plant metabolism, and growth dilution, the same chemical mass loading may be used in treatments with different irrigation schedules. Therefore, future studies examining the interplay among irrigation scheduling, mass loading, and target crops are warranted to improve our understanding and ability to optimize this mitigation strategy.

3.4 Structural equation modeling analysis

In recent years, SEM has been frequently used as an effective approach to quantify the nonlinear relationship of multiple variables (Li et al., 2020b; Neo et al., 2017). For example, Li et al. (2020b) utilized SEM to understand the contribution of environmental factors on sulfamethoxazole attenuation in natural water samples. This statistical approach was also employed to evaluate diverse climatic and soil factors on temperature sensitivity of soil respiration at global and regional scales (Li et al., 2020a). In this study, SEM was applied to better understand the factors influencing the reduction of CEC accumulation in plant tissues through the alternating irrigation scheme, including the interactions between the degree of reduction in plant tissues and a chemical's hydrophobicity, solubility, soil-water partition, and plant metabolism (Figure 4). The applicability of the model was evaluated based on 10 global model fit and quality indices, as detailed in Table S5, which yielded highly significant values within acceptable ranges, indicating a favorable fit. The β-values in Figure 4 represent the path coefficients, and the p-values indicate their level of significance. The effect sizes (*ES*) indicate the significance of the independent variable's impact on the dependent variable, calculated as the absolute value of the individual contribution to the R-squared (R^2) coefficients of the latent variable. The R^2 values, indicating the percentage of variability explained by the hypothesized independent latent variables, demonstrate the strength of the predictors’ explanatory power in the model.

The results showed that among the physiochemical properties, log K_{ow} had a significant effect on RCF ($\beta = 0.40$, $p < 0.01$), which suggests that hydrophobic compounds are more likely to have a greater root accumulation (Akenga et al., 2021; Wu et al., 2013). Conversely, the weak correlation between TF and log K_{ow} indicated that the translocation of compounds in vegetables is primarily mediated by transpiration-driven water movement (Chuang et al., 2019). This was also evident in the significant positive relation ($\beta = 0.68$, $p < 0.001$) between TF and solubility ($ES = 0.54$), which was consistent with previous studies showing that water solubility facilitates a chemical's translocation in plants (Kinney and Heuvel, 2020). As plants were grown in soil in this study, K_d was found to have a negative relation with RCF ($\beta = -0.27$, $p = 0.056$) with a marginal significance and a small effect ($ES = 0.05$), which underscored the above assumption that chemicals strongly adsorbed to soil generally exhibit a lower bioavailability for plant uptake.

The reduction of CEC accumulation in each plant compartment could be decided by the input (RCF for root, TF for shoot) and output (TF for root and metabolism for all tissues), following the mass balance principle. A significant positive effect of TF ($\beta = 0.51$, $p < 0.001$) on reduction in root and a marginally negative impact on reduction in shoot ($\beta = -0.28$, $p = 0.053$) were observed. This finding indicated that strong translocation of CECs promoted their accumulation in plant shoots as an input route while facilitating their reduction in plant roots as an output route. Additionally, RCF showed a significant positive relation with reduction in root accumulation of CECs ($\beta = 0.36$, $p < 0.05$). For instance, meprobamate (RCF > 215) and PFBA (RCF > 35) demonstrated great bioaccumulation potential across all three plant species, with large reductions in root concentrations from the alternating irrigation scheme, ranging from 88.2-99.8% and 70.3-94.2%, respectively. This was in agreement with previous studies showing that smaller reductions were seen for those CECs with limited plant accumulation, while reductions were greater for CECs with significant accumulation (Shi et al., 2023b). The analysis further showed a significant positive correlation between the percentage of reduction in CEC accumulation between root and shoot ($\beta = 0.55$, $p < 0.001$), likely due to the intrinsically similar metabolism potential for the same chemical in different plant tissues. Soil half-life was found to have a significant negative effect on the reduction of CECs in the root ($\beta = -0.46$, $p < 0.001$). Chemicals with shorter half-lives in the soil underwent rapid degradation, which decreased the uptake of the CECs by plants when irrigation with TWW was stopped, resulting in a more pronounced reduction in their accumulation in plant roots. For example, the relatively short half-lives of meprobamate, naproxen, and fluoxetine in soil (29.7, 2.7, and 55.6 d, respectively), combined with their relatively high plant metabolism potential (Wu et al., 2016, 2013), likely resulted in greater reductions for the plants considered in this study. Among the three factors, soil half-life showed a slightly greater contribution (*ES* = 0.21) than RCF (*ES* = 0.17) or TF (*ES* = 0.19) to the CEC reduction in roots, underlying the importance of the persistence of CECs in soil in governing their overall fate in the TWW-soil-plant continuum.

The SEM model explained up to 57% of the variability in the reduction of CEC accumulation caused by the alternating irrigation treatment in the root, and 52% in the shoot. However, log K_{ow} and K_d explained a relatively small percentage of the variability (19%), suggesting that the influence of physicochemical properties such as K_{ow} was indirect and likely complex (Akenga et al., 2021). The reduction in CEC accumulation in plants due to the alternating irrigation scheme appeared to be better related to the plant's uptake and translocation potential of the chemical, as well as the chemical’s plant metabolism potential. For example, the relatively small reduction in PFAS levels could primarily be ascribed to their long half-lives in soil ($T_{1/2} > 10$ years) and high translocation potential. In contrast, the relatively short half-lives of meprobamate, naproxen, and fluoxetine in soil, combined with their relatively high plant metabolism potential (Wu et al., 2016, 2013) resulted in more effective reductions in plant accumulation in response to the alternating irrigation strategy. Taken together, our findings demonstrated that the alternating irrigation scheme was generally effective for a wide range of CECs but was particularly effective for CECs with a higher bioaccumulation potential and shorter half-life in soil. Contaminants with a greater mobility and persistence (e.g., short chain PFAS) pose a more pressing concern for accumulation in food crops, and additional mitigation strategies need to be explored for such CECs.

4. Conclusions

This greenhouse study demonstrated that a simple change in irrigation scheme may be effective at reducing the accumulation of many CECs in food crops from TWW irrigation. The reduction in CEC accumulation as the result of the alternating irrigation scheme may be attributed to reduced chemical input in the soil-plant system, as well as attenuation caused by soil degradation, plant metabolism, and growth dilution. The alternating irrigation scheme was particularly effective for CECs with a high bioaccumulation potential and short half-life in soil. For persistent compounds such as PFAS with a high accumulation potential, a substantial decrease in their accumulation in the edible tissue at maturity was also observed due to the reduced chemical input, adsorption in soil, and plant growth dilution. Among the different plant species considered in this study, fruit vegetables (tomato) appeared to respond to the alternating irrigation scheme more effectively than leafy or root vegetables.

This study marks a significant stride in understanding the impact of an alternating irrigation scheme on the accumulation of CECs in food plants under environmentally relevant conditions. This advancement is valuable for ensuring the safety and sustainability of agricultural practices using recycled water. Although only a small set of CECs were considered in this study, the same strategy could be adapted for other non-traditional water sources and a wider range of contaminants. The systematic assessment of potential human exposure risk to CECs aims to enhance public awareness and promote the safe use of marginal waters, providing a foundation for future research and policy development. However, it must be noted that the current study was conducted under controlled conditions with relatively high CEC concentrations (5 μg/L) and limited growth space. In agricultural fields, additional factors may influence the accumulation and reduction of CECs in soil and plants, such as more abundant microbial activity, earthworm function, leaching to deeper soil layers, and surface runoff, among others. Therefore, studies conducted under realistic field conditions using treated wastewater are necessary to further demonstrate the feasibility and efficacy of this strategy for reducing plant accumulation of CECs. Modifications to existing infrastructure to create flexible irrigation systems that can accommodate alternation between TWW and conventional water sources are also necessary for the broad implementation of this management strategy.

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References

Akenga, P., Gachanja, A., Fitzsimons, M.F., Tappin, A., Comber, S., 2021. Uptake, accumulation and impact of antiretroviral and antiviral pharmaceutical compounds in lettuce. Sci. Total Environ. 766, 144499. https://doi.org/10.1016/j.scitotenv.2020.144499

Anderko, L., Pennea, E., 2020. Exposures to per-and polyfluoroalkyl substances (PFAS): Potential risks to reproductive and children's health. Curr. Probl. Pediatr. Adolesc. Health Care 50, 100760. https://doi.org/10.1016/j.cppeds.2020.100760

Ben Mordechay, E., Mordehay, V., Tarchitzky, J., Chefetz, B., 2021. Pharmaceuticals in edible crops irrigated with reclaimed wastewater: Evidence from a large survey in Israel. J. Hazard. Mater. 416, 126184. https://doi.org/10.1016/j.jhazmat.2021.126184

Ben Mordechay, E., Sinai, T., Berman, T., Dichtiar, R., Keinan-Boker, L., Tarchitzky, J., Maor, Y., Mordehay, V., Manor, O., Chefetz, B., 2022. Wastewater-derived organic contaminants in fresh produce: Dietary exposure and human health concerns. Water Res. 223, 118986. https://doi.org/10.1016/j.watres.2022.118986

Biel-Maeso, M., Corada-Fernández, C., Lara-Martín, P.A., 2018. Monitoring the occurrence of pharmaceuticals in soils irrigated with reclaimed wastewater. Environ. Pollut. 235, 312–321. https://doi.org/10.1016/j.envpol.2017.12.085

Briggs, G.G., Bromilow, R.H., Evans, A.A., 1982. Relationships between lipophilicity and root uptake and translocation of non-ionised chemicals by barley. Pestic. Sci. 13, 495–504. https://doi.org/10.1002/ps.2780130506

Carter, L.J., Chefetz, B., Abdeen, Z., Boxall, A.B.A.A., 2019. Emerging investigator series: towards a framework for establishing the impacts of pharmaceuticals in wastewater irrigation systems on agro-ecosystems and human health. Environ. Sci. Process. Impacts 21, 605–622. https://doi.org/10.1039/c9em00020h

Christou, A., Agüera, A., Bayona, J.M., Cytryn, E., Fotopoulos, V., Lambropoulou, D., Manaia, C.M., Michael, C., Revitt, M., Schröder, P., Fatta-Kassinos, D., 2017a. The potential implications of reclaimed wastewater reuse for irrigation on the agricultural environment: the knowns and unknowns of the fate of antibiotics and antibiotic resistant bacteria and resistance genes–a review. Water Res. 123, 448–467. https://doi.org/10.1016/j.watres.2017.07.004

Christou, A., Karaolia, P., Hapeshi, E., Michael, C., Fatta-Kassinos, D., 2017b. Long-term wastewater irrigation of vegetables in real agricultural systems: Concentration of pharmaceuticals in soil, uptake and bioaccumulation in tomato fruits and human health risk assessment. Water Res. 109, 24–34. https://doi.org/10.1016/j.watres.2016.11.033

Chuang, Y.-H., Liu, C.-H., Sallach, J.B., Hammerschmidt, R., Zhang, W., Boyd, S.A., Li, H., 2019. Mechanistic study on uptake and transport of pharmaceuticals in lettuce from water. Environ. Int. 131, 104976. https://doi.org/10.1016/j.envint.2019.104976

Clarke, R.M., Cummins, E., 2015. Evaluation of "Classic" and Emerging Contaminants Resulting from the Application of Biosolids to Agricultural Lands: A Review. Hum. Ecol. Risk Assess. 21, 492–513. https://doi.org/10.1080/10807039.2014.930295

Dal Ferro, N., Pellizzaro, A., Fant, M., Zerlottin, M., Borin, M., 2021. Uptake and translocation of perfluoroalkyl acids by hydroponically grown lettuce and spinach exposed to spiked solution and treated wastewaters. Sci. Total Environ. 772, 145523. https://doi.org/10.1016/j.scitotenv.2021.145523

Donohue, S.J., 1992. Reference soil and media diagnostic procedures for the southern region of the United States.

Felizeter, S., McLachlan, M.S., de Voogt, P., 2012. Uptake of Perfluorinated Alkyl Acids by Hydroponically Grown Lettuce (Lactuca sativa). Environ. Sci. Technol. 46, 11735–11743. https://doi.org/10.1021/es302398u

Fitter, A.H., Hay, R.K.M., 2012. Environmental physiology of plants. Academic press.

Gredelj, A., Polesel, F., Trapp, S., 2020. Model-based analysis of the uptake of perfluoroalkyl acids (PFAAs) from soil into plants. Chemosphere 244, 125534. https://doi.org/10.1016/j.chemosphere.2019.125534

Inoue, J., Chamberlain, K., Bromilow, R.H., 1998. Physicochemical factors affecting the uptake by roots and translocation to shoots of amine bases in barley. Pestic. Sci. 54, 8–21. https://doi.org/10.1002/(SICI)1096-9063(199809)54:1<8::AID-PS793>3.0.CO;2-E

Jiao, X., Shi, Q., Gan, J., 2020. Uptake, accumulation and metabolism of PFASs in plants and health perspectives: A critical review. Crit. Rev. Environ. Sci. Technol. 1–32. https://doi.org/10.1080/10643389.2020.1809219

Kinney, C.A., Heuvel, B. Vanden, 2020. Translocation of pharmaceuticals and personal care products after land application of biosolids. Curr. Opin. Environ. Sci. Heal. 14, 23–30. https://doi.org/10.1016/j.coesh.2019.11.004

Klute, A., 1986. Water retention: laboratory methods. Methods soil Anal. part 1 Phys. Mineral. methods 5, 635–662.

LeFevre, G.H., Lipsky, A., Hyland, K.C., Blaine, A.C., Higgins, C.P., Luthy, R.G., 2017. Benzotriazole (BT) and BT plant metabolites in crops irrigated with recycled water. Environ. Sci. Water Res. Technol. 3, 213–223. https://doi.org/10.1039/c6ew00270f

Lehotay, S.J., O'Neil, M., Tully, J., García, A.V., Contreras, M., Mol, H., Heinke, V., Anspach, T., Lach, G., Fussell, R., Mastovska, K., Poulsen, M.E., Brown, A., Hammack, W., Cook, J.M., Alder, L., Lindtner, K., Vila, M.G., Hopper, M., de Kok, A., Hiemstra, M., Schenck, F., Williams, A., Parker, A., 2007. Determination of Pesticide Residues in Foods by Acetonitrile Extraction and Partitioning with Magnesium Sulfate: Collaborative Study. J. AOAC Int. 90, 485–520. https://doi.org/10.1093/jaoac/90.2.485

Li, J., Pei, J., Pendall, E., Fang, C., Nie, M., 2020a. Spatial heterogeneity of temperature sensitivity of soil respiration: A global analysis of field observations. Soil Biol. Biochem. 141, 107675. https://doi.org/10.1016/j.soilbio.2019.107675

Li, J., Ye, Q., Gan, J., 2014. Degradation and transformation products of acetaminophen in soil. Water Res. 49, 44–52. https://doi.org/10.1016/j.watres.2013.11.008

Li, Y., Sallach, J.B., Zhang, W., Boyd, S.A., Li, H., 2019. Insight into the distribution of pharmaceuticals in soil-water-plant systems. Water Res. 152, 38–46. https://doi.org/10.1016/j.watres.2018.12.039

Li, Y., Zhang, H., Rashid, A., Hu, A., Xin, K., Li, H., Adyari, B., Wang, Y., Yu, C.-P., Sun, Q., 2020b. Bisphenol A attenuation in natural microcosm: Contribution of ecological components and identification of transformation pathways through stable isotope tracing. J. Hazard. Mater. 385, 121584. https://doi.org/10.1016/j.jhazmat.2019.121584

Lin, X., Xu, J., Keller, A.A., He, L., Gu, Y., Zheng, W., Sun, D., Lu, Z., Huang, J., Huang, X., Li, G., 2020. Occurrence and risk assessment of emerging contaminants in a water reclamation and ecological reuse project. Sci. Total Environ. 744, 140977. https://doi.org/10.1016/j.scitotenv.2020.140977

Martínez-Piernas, A.B., Plaza-Bolaños, P., Fernández-Ibáñez, P., Agüera, A., 2019. Organic Microcontaminants in Tomato Crops Irrigated with Reclaimed Water Grown under Field Conditions: Occurrence, Uptake, and Health Risk Assessment. J. Agric. Food Chem. https://doi.org/10.1021/acs.jafc.9b01656

Mei, W., Sun, H., Song, M., Jiang, L., Li, Y., Lu, W., Ying, G.-G., Luo, C., Zhang, G., 2021. Per- and polyfluoroalkyl substances (PFASs) in the soil–plant system: Sorption, root uptake, and translocation. Environ. Int. 156, 106642. https://doi.org/10.1016/j.envint.2021.106642

Miller, E.L., Nason, S.L., Karthikeyan, K.G., Pedersen, J.A., 2016. Root uptake of parmaceuticals and personal care product ingredients. Environ. Sci. Technol. 50, 525–541. https://doi.org/10.1021/acs.est.5b01546

Natasha, Shahid, M., Khalid, S., Murtaza, B., Anwar, H., Shah, A.H., Sardar, A., Shabbir, Z., Niazi, N.K., 2023. A critical analysis of wastewater use in agriculture and associated health risks in Pakistan. Environ. Geochem. Health 45, 5599–5618.

https://doi.org/10.1007/s10653-020-00702-3

Neo, S.M., Choong, W.W., Ahamad, R. Bin, 2017. Differential environmental psychological factors in determining low carbon behaviour among urban and suburban residents through responsible environmental behaviour model. Sustain. Cities Soc. 31, 225–233. https://doi.org/10.1016/j.scs.2017.03.003

Patel, M., Kumar, R., Kishor, K., Mlsna, T., Pittman, C.U., Mohan, D., 2019. Pharmaceuticals of Emerging Concern in Aquatic Systems: Chemistry, Occurrence, Effects, and Removal Methods. Chem. Rev. 119, 3510–3673. https://doi.org/10.1021/acs.chemrev.8b00299

Phong Vo, H.N., Le, G.K., Hong Nguyen, T.M., Bui, X.-T., Nguyen, K.H., Rene, E.R., Vo, T.D.H., Thanh Cao, N.-D., Mohan, R., 2019. Acetaminophen micropollutant: Historical and current occurrences, toxicity, removal strategies and transformation pathways in different environments. Chemosphere 236, 124391. https://doi.org/10.1016/j.chemosphere.2019.124391

Pullagurala, V.L.R.R., Rawat, S., Adisa, I.O., Hernandez-Viezcas, J.A., Peralta-Videa, J.R., Gardea-Torresdey, J.L., 2018. Plant uptake and translocation of contaminants of emerging concern in soil. Sci. Total Environ. 636, 1585–1596. https://doi.org/10.1016/j.scitotenv.2018.04.375

ROBERTS, A.G., OPARKA, K.J., 2003. Plasmodesmata and the control of symplastic transport. Plant. Cell Environ. 26, 103–124. https://doi.org/10.1046/j.1365-3040.2003.00950.x

Rogowska, J., Cieszynska-Semenowicz, M., Ratajczyk, W., Wolska, L., 2020. Micropollutants in treated wastewater. Ambio 49, 487–503. https://doi.org/10.1007/s13280-019-01219-5

Ruan, X., Ge, S., Jiao, Z., Zhan, W., Wang, Y., 2023. Bioaccumulation and risk assessment of potential toxic elements in the soil-vegetable system as influenced by historical wastewater irrigation. Agric. Water Manag. 279, 108197. https://doi.org/10.1016/j.agwat.2023.108197

Schopfer, P., Brennicke, A., 2010. Physiologie der Regeneration und Transplantation, in: Pflanzenphysiologie. Springer Berlin Heidelberg, Berlin, Heidelberg, pp. 535–547. https://doi.org/10.1007/978-3-662-49880-4_24

Sharma, B.M., Bečanová, J., Scheringer, M., Sharma, A., Bharat, G.K., Whitehead, P.G., Klánová, J., Nizzetto, L., 2019. Health and ecological risk assessment of emerging contaminants (pharmaceuticals, personal care products, and artificial sweeteners) in surface and groundwater (drinking water) in the Ganges River Basin, India. Sci. Total Environ. 646, 1459–1467. https://doi.org/10.1016/j.scitotenv.2018.07.235

Shi, Q., Kaur, P., Gan, J., 2023a. Harnessing the potential of phytoremediation for mitigating the risk of emerging contaminants. Curr. Opin. Environ. Sci. Heal. 32, 100448. https://doi.org/10.1016/j.coesh.2023.100448

Shi, Q., Xiong, Y., Kaur, P., Dennis, N.M., Schlenk, D., Gan, J., 2023b. Strategy to Minimize Plant Accumulation of Contaminants of Emerging Concern: Alternation between Treated Wastewater and Freshwater Irrigation. Environ. Sci. Technol. Lett. 10, 302–307. https://doi.org/10.1021/acs.estlett.3c00058

Shi, Q., Xiong, Y., Kaur, P., Sy, N.D., Gan, J., 2022. Contaminants of emerging concerns in recycled water: Fate and risks in agroecosystems. Sci. Total Environ. 814, 152527. https://doi.org/10.1016/j.scitotenv.2021.152527

Singh, A., 2021. A review of wastewater irrigation: Environmental implications. Resour. Conserv. Recycl. 168, 105454. https://doi.org/10.1016/j.resconrec.2021.105454

Sokolow, S., Godwin, H., Cole, B.L., 2019. Perspectives on the future of recycled water in California: results from interviews with water management professionals. J. Environ. Plan. Manag. 62, 1908–1928. https://doi.org/10.1080/09640568.2018.1523051

Sutherland, D.L., Ralph, P.J., 2019. Microalgal bioremediation of emerging contaminants - Opportunities and challenges. Water Res. 164, 114921. https://doi.org/10.1016/j.watres.2019.114921

Tang, Y., Zhong, Y., Li, H., Huang, Y., Guo, X., Yang, F., Wu, Y., 2020. Contaminants of emerging concern in aquatic environment: Occurrence, monitoring, fate, and risk assessment. Water Environ. Res. 92, 1811–1817. https://doi.org/10.1002/wer.1438

Tester, M., Leigh, R.A., 2001. Partitioning of nutrient transport processes in roots. J. Exp. Bot. 52, 445–457. https://doi.org/10.1093/jxb/52.suppl_1.445

Tran, N.H., Reinhard, M., Gin, K.Y.-H., 2018. Occurrence and fate of emerging contaminants in municipal wastewater treatment plants from different geographical regions-a review. Water Res. 133, 182–207. https://doi.org/https://doi.org/10.1016/j.watres.2017.12.029

Trapp, S., 2009. Bioaccumulation of Polar and Ionizable Compounds in Plants, in: Ecotoxicology Modeling. Springer, pp. 299–353. https://doi.org/10.1007/978-1-4419-0197-2_11

Wu, X., Conkle, J.L., Ernst, F., Gan, J., 2014. Treated wastewater irrigation: Uptake of pharmaceutical and personal care products by common vegetables under field conditions. Environ. Sci. Technol. 48, 11286–11293. https://doi.org/10.1021/es502868k

Wu, X., Ernst, F., Conkle, J.L., Gan, J., 2013. Comparative uptake and translocation of pharmaceutical and personal care products (PPCPs) by common vegetables. Environ. Int. 60, 15–22. https://doi.org/10.1016/j.envint.2013.07.015

Wu, X., Fu, Q., Gan, J., 2016. Metabolism of pharmaceutical and personal care products by carrot cell cultures. Environ. Pollut. 211, 141–147.

https://doi.org/https://doi.org/10.1016/j.envpol.2015.12.050

Xu, J., Wu, L., Chang, A.C., 2009. Degradation and adsorption of selected pharmaceuticals and personal care products (PPCPs) in agricultural soils. Chemosphere 77, 1299–1305. https://doi.org/https://doi.org/10.1016/j.chemosphere.2009.09.063

Yakushiji, H., Morinaga, K., Nonami, H., 1998. Sugar Accumulation and Partitioning in Satsuma Mandarin Tree Tissues and Fruit in Response to Drought Stress. J. Am. Soc. Hortic. Sci. 123, 719–726. https://doi.org/10.21273/JASHS.123.4.719

Yang, Y., Chen, P., Ma, S., Lu, S., Yu, Y., An, T., 2022. A critical review of human internal exposure and the health risks of organophosphate ester flame retardants and their metabolites. Crit. Rev. Environ. Sci. Technol. 52, 1528–1560. https://doi.org/10.1080/10643389.2020.1859307

Yu, P.-F., Li, Y.-W., Zou, L.-J., Liu, B.-L., Xiang, L., Zhao, H.-M., Li, H., Cai, Q.-Y., Hou, X.-W., Mo, C.-H., Wong, M.H., Li, Q.X., 2021. Variety-Selective Rhizospheric Activation, Uptake, and Subcellular Distribution of Perfluorooctanesulfonate (PFOS) in Lettuce (Lactuca sativa L.). Environ. Sci. Technol. 55, 8730–8741. https://doi.org/10.1021/acs.est.1c01175

Zhang, L., Sun, H., Wang, Q., Chen, H., Yao, Y., Zhao, Z., Alder, A.C., 2019. Uptake mechanisms of perfluoroalkyl acids with different carbon chain lengths (C2-C8) by wheat (Triticum acstivnm L.). Sci. Total Environ. 654, 19–27. https://doi.org/10.1016/j.scitotenv.2018.10.443

Tables and Figures

Table 1. Reduction Factors (RF) for Target CECs in Different Compartments of Radish, Lettuce and Tomato

Chemical	**Radish**		**Lettuce**		**Tomato**		
	root (%)	**shoot (%)**	**root (%)**	**shoot (%)**	**root (%)**	**shoot (%)**	**fruit (%)**
Acetaminophen	27.5	27.5	64.0	22.9	61.0	-12.6	ND
Caffeine	48.4	69.5	77.8	48.0	74.6	21.1	ND
Meprobamate	94.3	88.2	98.4	98.9	99.5	97.1	99.8
Ibuprofen	ND	41.8	ND	9.3	56.0	ND	57.9
Naproxen	100.0	100.0	94.3	ND	98.4	100.0	ND
Carbamazepine	84.2	47.2	96.7	81.0	99.2	88.1	95.5
Atenolol	66.9	55.7	85.0	10.9	85.6	76.9	ND
Fluoxetine	92.3	92.1	93.6	94.1	82.6	91.8	66.8
Perfluorobutanesulfonic acid	62.5	63.9	52.4	65.0	93.5	43.5	93.3
Perfluorobutanoic acid	70.3	59.1	94.2	69.7	91.7	22.8	76.4
Perfluorohexanoic acid	57.0	66.0	69.9	65.8	93.7	42.4	79.6

ND: The RF values were not derived for those CECs with levels below the limit of detection

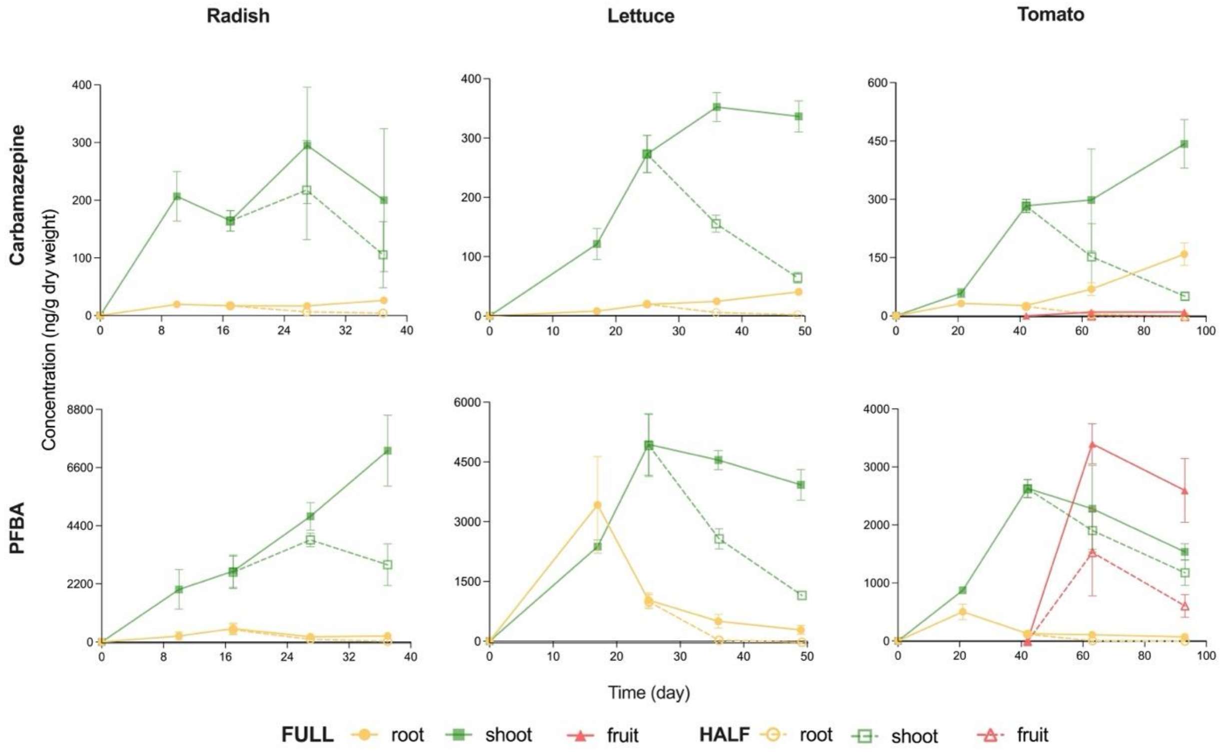

Figure 1. Temporal variations in carbamazepine and perfluorobutanoic acid (PFBA) concentrations in various plant tissues under FULL and HALF treatments. Each data point represents the arithmetic mean concentration of triplicate samples (n = 3). The error bar represents the standard deviation.

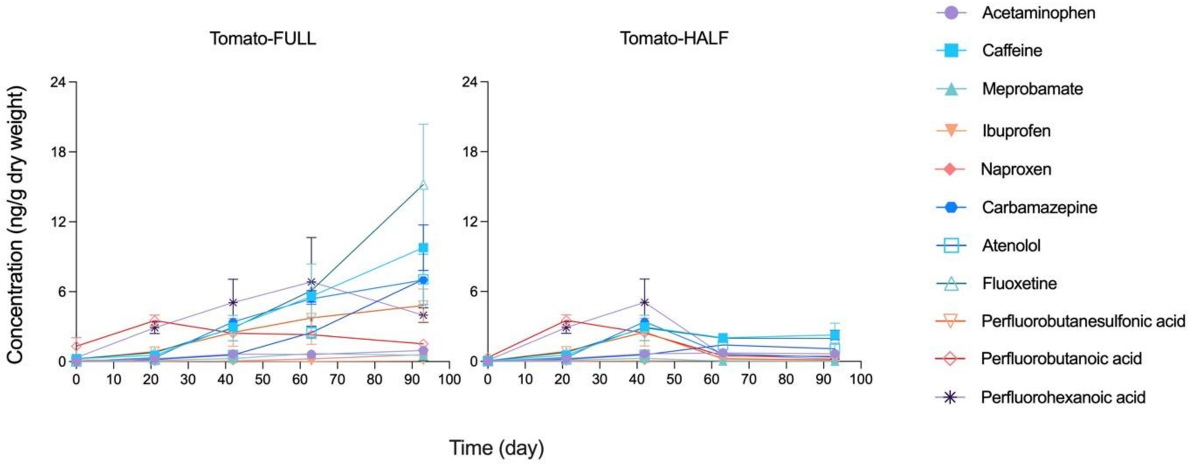

Figure 2. Temporal variations of target CEC concentrations in the soil during tomato growth under FULL and HALF treatments. Each data point represents the arithmetic mean concentration of triplicate samples (n = 3). The error bar represents the standard error.

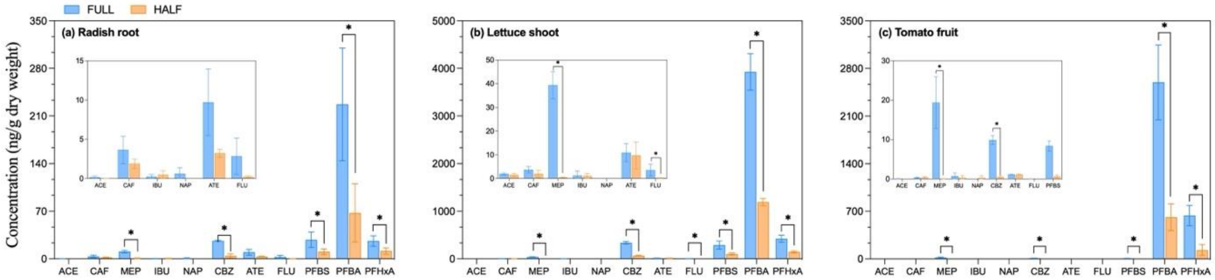

Figure 3. Accumulation of target CECs in edible parts of radish (a), lettuce (b), and tomato (c) at harvest point under FULL and HALF irrigation schemes. Radish, lettuce, and tomato were harvested 37, 49 and 93 days after planting. ACE, acetaminophen; CAF, caffeine; MBP, meprobamate; IBU, ibuprofen; NAP, naproxen; CBZ, carbamazepine; ATE, atenolol; FLU, fluoxetine; PFBS, perfluorobutanesulfonic acid; PFBA, perfluorobutanoic acid; PFHxA, perfluorohexanoic acid.

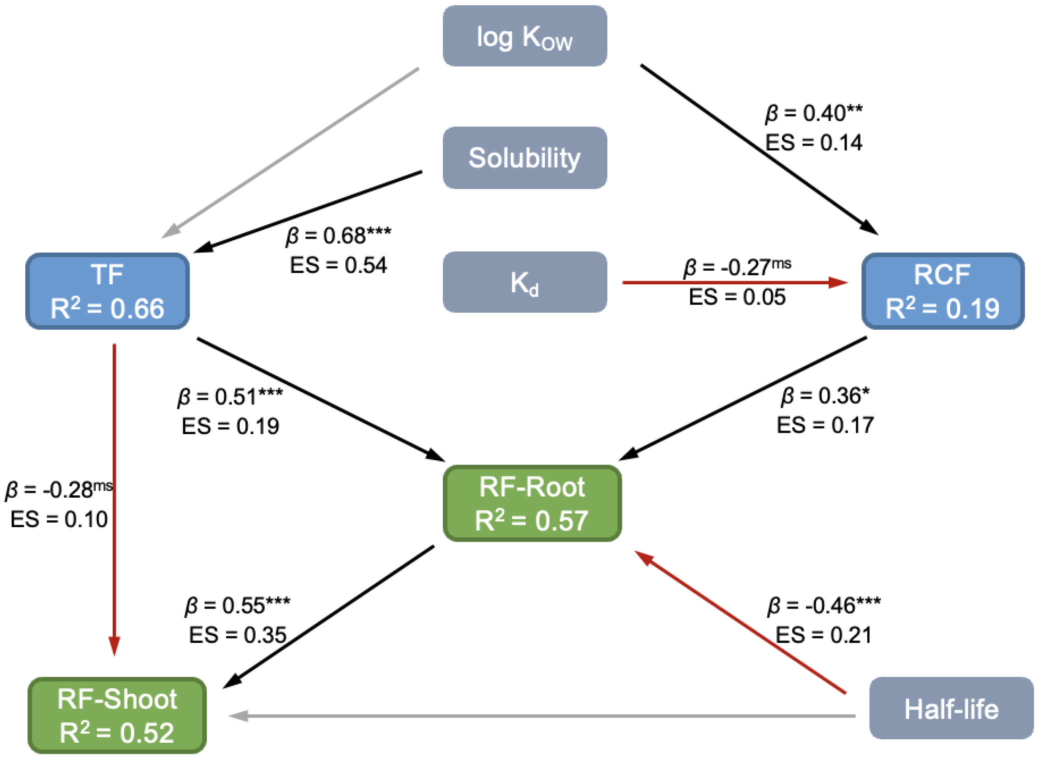

Figure 4. Structural equation models showing the relationship between compound physiochemical properties and reduction factors of plant tissue. Black lines indicate positive relationships, while red lines indicate negative relationships. R^2 is the coefficient of determination indicating the variability explained for each dependent variable. β-values indicate the path coefficients. The level of significance is indicated by ^{ms} (marginal significance) ($p \approx 0.05$), * ($p < 0.05$), ** ($p < 0.01$), and *** ($p < 0.001$). The effect size (ES) categorizes the influence of an independent variable on a dependent variable: <0.02 (weak), 0.02 (small), 0.15 (medium), and 0.35 (large). TF, translocation factor; RCF, root concentration factor, log K_{ow}, water partition coefficient; K_d, adsorption coefficient.