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The Fate of Pharmaceuticals and Personal Care Products in Reclaimed Water Used for Irrigation of Agricultural Crops in Nevada

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Reclaiming Water for Urban Foodsheds *integrates basic scientific research with Extension outreach to examine the feasibility of using reclaimed water for irrigated agriculture in urban environments. Funded by a grant [2017-69007-26309] from the USDA National Institute of Food and Agriculture, research is being conducted in University of Nevada, Reno campus laboratories and the University of Nevada, Reno Experiment Station's Main Station Farm Laboratory and Greenhouse Complex. This publication, which is part of a series, reports on experimental research to quantify the fate of Pharmaceuticals and Personal care Products in alfalfa and green wheatgrass irrigated with reclaimed water in a greenhouse setting.*

Introduction

Growing populations and associated higher food demands are rapidly straining freshwater availability throughout the world (Elliot et al., 2014), as the need for irrigation water increases. With irrigated agriculture accounting for roughly 70% of global freshwater use, using reclaimed water, or highly treated wastewater, to irrigate agricultural lands has the potential to meet the increased demands on freshwater resources (Schlosser et al., 2014). Reclaimed water typically has been treated to: a) remove large objects, and particles; b) remove organic matter to reduce oxygen demand; c) remove excess nutrients to prevent eutrophication; and d) disinfect the water (Sharma et al., 2020). The United States used approximately 8.5 million m^3/day of reclaimed water in 2015 for irrigated agriculture, golf courses and landscapes (Tran et al., 2017). The use of reclaimed water as an alternative irrigation water source has more than doubled since 1995 and has coincided with an overall reduction in the United States' freshwater use per capita (UNESCO, 2017).

Reclaimed water has been found to contain trace levels of pharmaceuticals, such as antibiotics; anticonvulsants; analgesic pain relievers; and personal care products, including soaps, shampoos, cosmetics and insect repellents. These pharmaceuticals and personal care products (PPCPs) can persist in the treated wastewater effluent and reclaimed waters released into freshwater bodies (i.e., streams, rivers and lakes) in concentrations of up to µg/L (micrograms per liter or, 1 gram per million grams of water) levels (Watkinson et al., 2007; Hirsch et al., 1999; Clara et al., 2005). The PPCPs can have detrimental effects on living organisms, including phytotoxicity and endocrine disruption, and may lead to potential human health risk (Fu et al., 2019; Li et al., 2015; Poustie et al., 2020). Due to the persistence and potential harmful effects of some of these compounds, concerns exist about the potential for application of reclaimed water for irrigation to introduce contaminants into food crops. Uptake of these compounds by plants could unintentionally transport compounds into human or animal food chains (Poustie et al., 2020). For instance, Wu et al. (2014) showed plant uptake of compounds including primidone (anticonvulsant), sulfamethoxazole (antibiotic) and trimethoprim (antibiotic). With the increased constraints on freshwater availability and the increased application of reclaimed waters on agricultural lands, it is important to assess how PPCPs in reclaimed water may affect plants, soils, surface and groundwater, and the overall environment (Chang et al., 2002; Bixio et al., 2005; Faruqui et al., 2004).

One potential means to reduce exposure of plants to PPCPs is by adding biochar to the soil. Biochar is a carbonaceous material formed from the combustion/pyrolysis of biomass, a process of thermally decomposing organic material in the absence of oxygen. The resulting biochar can potentially remove or sequester antibiotics (Teixidó et al., 2011). Most biochars have a high surface area and aromatic components (Ahmad et al., 2012) and, as a result, may remove PPCPs from the soil solution by sorbing them onto their surface. For example, Ye et al. (2016) demonstrated that biochar significantly reduced the transport of sulfonamide into lettuce, contributing to greater lettuce biomass production in soil amended with biochar. Yanala and Pagilla (2020) showed that biochar can be used to effectively remove PPCPs from reclaimed water. Biochar has the potential to improve soil fertility due to its ability to increase enzymatic activity (Awad et al., 2012), cation exchange capacity (Belachew and Abera, 2010), microbial activity (Li et al., 2016), and available water content in soil (Abel et al., 2013).

To date, few studies have addressed the effects of reclaimed water contaminants on alfalfa (*Medicago sativa*) and green wheatgrass (*Elymus hoffmannii*), despite their importance as forage crops in (semi)arid environments. In 2013, alfalfa was the fourth largest crop in the United States in terms of production value (Wechsler & Milkove, 2017). Green wheatgrass is a commonly used forage crop in (semi)arid regions because it has salt-tolerant properties (Steppuhn & Asay, 2005).

The objectives of this study were to evaluate the effects of using reclaimed water on the growth of and uptake of PPCPs by alfalfa and green wheatgrass. In addition, we assessed if biochar, when used as a soil amendment, has the potential to minimize the uptake of contaminants by crops. To address our objectives, we conducted our experiments in a greenhouse to allow us to control the amount and composition of irrigation the plants received. We varied the quality of reclaimed water used for irrigation and added biochar to a subset of alfalfa and green wheatgrass plants.

Research Methods

Sixty 7.6 L pots were each filled with 6 kg of soil collected from the University of Nevada, Reno Main Station Farm Laboratory. Soil belonged to the Truckee series (i.e., fine-loamy, mixed, super active, mesic Fluvaquentic Haploxerolls) and had been irrigated annually with reclaimed water for at least a decade. The soil had a high organic matter content (5.2%), a neutral pH (7.4) and low salinity (<1dS m^{-1}). We added biochar (3% by soil volume; equivalent to 4.1 tons/acre) to 30 pots (treatment group) while the remaining 30 pots (control group) did not receive biochar. The biochar used was produced by combustion of pinyon and juniper wood in a kiln, and we sifted the biochar through a 1 cm sieve before adding it to the soil. Within the treatment group of 30 pots, 15 pots were seeded with alfalfa and 15 with green wheatgrass.

The pots were irrigated with one of three water sources: 1) tap water (used as control); 2) tap water spiked with a high level of several PPCPs (i.e., spiked tap water used for comparison with reclaimed water to study the effects of wastewater compositions); or 3) reclaimed water (treated but not to levels suitable for drinking water). After analyzing reclaimed water from the Truckee Meadows Water Reclamation Facility, the following three contaminants with the highest measured concentrations were selected for the spiked tap water solution: primidone, sulfamethoxazole and trimethoprim. Primidone is an anticonvulsant, while sulfamethoxazole and trimethoprim are antibiotics. Based on the results of prior research identifying the prevalence of these selected compounds in reclaimed water, we spiked the tap water with 10 times the average concentrations observed in treated water from a variety of studies (Table 1). The 10 times higher concentrations ensured that we had a very strong signal while ensuring that PPCPs remained dissolved.

Table 1. Compound concentrations (ng/L[1]) in the three water sources used for the greenhouse irrigation treatments. Contaminant concentrations in spiked tap water were not measured directly but calculated (in bold). Standard deviations of reclaimed water concentrations are in parentheses.

	Tap Water (n=1)	Spiked Tap Water (n=1)	Reclaimed Water (n=4)
Atrazine	0.006	0.006	Not analyzed
Caffeine	BDL[1]	BDL	306 (148)
Carbamazepine	BDL	BDL	270 (175)
Diethyltoluamide (DEET)	0.573	0.573	26 (19)
Diphenhydramine	BDL	BDL	219 (128)
Fluoxetine	BDL	BDL	49 (7)
Meprobamate	BDL	BDL	125 (77)
Primidone	BDL	**5,000**	469 (215)
Sulfamethoxazole	BDL	**200,000**	717 (204)
Trimethoprim	BDL	**50,000**	2898 (1613)

[1] BDL = Below Detection Limit.

Within each crop and biochar treatment, five pots were irrigated with tap water, five pots with spiked tap water, and five pots with reclaimed water collected from the lab. Pots were moved around the greenhouse every two weeks to account for possible variability in light levels inside the greenhouse. Each pot was given the same amount of water two or three times a week and received a total of 18 liters of water over the course of the study. Pots were allowed to drain, but no drainage was produced during the study. After approximately seven months, crops were harvested. Crops were removed from their pots, and roots and shoots were separated. Alfalfa shoots were separated into leaves and stems. We also collected soil samples from each pot. All soils, roots, shoots and leaves were oven-dried for two days at 60 C and measured for dry weight. Biochar was included in soil analysis because it was not possible to remove it from the soil.

The plant and soil materials were extracted using various solvents and an accelerated solvent extraction system (soil), centrifugation, sonication and decanting (vegetation), and solid phase extraction (soil and vegetation). Extracted samples were stored at minus 20 C until analyzed. All samples were analyzed with liquid chromatography tandem mass spectrometry in positive electrospray ionization mode.

Results

PPCPs measured in this study were atrazine (herbicide), caffeine (stimulant), carbamazepine and primidone (anticonvulsants), DEET (insect repellent), diphenhydramine (antihistamine), fluoxetine (antidepressant), meprobamate (anti-anxiety) and sulfamethoxazole and trimethoprim (antibiotics). For this publication, we primarily focused on aboveground biomass plant responses as well as their accumulation of PPCPs, since these reflect the plant parts that are used for (animal) consumption.

Water quality did not affect alfalfa or green wheatgrass biomass weight. The presence of biochar in the soil tended to increase the alfalfa shoot weight and significantly increased green wheatgrass by 18%. The presence of biochar, however, did not affect root weight.

For most compounds, water quality did not affect compound concentration in aboveground biomass. While overall, plant PPCP concentrations were very low, surprisingly sulfamethoxazole concentrations were highest in alfalfa leaves and stems, and primidone concentrations were highest in wheatgrass shoots irrigated with tap water even though concentrations of these compounds were lowest in the tap water (Figure 1 and 2; Table 1).

It is unclear why plant uptake of sulfamethoxazole and primidone was higher when irrigated with tap water. Further studies are needed to determine what soil and/or plant processes could explain this response. We did not find any effects of biochar on plant PPCP concentrations possibly because of the low, albeit realistic, amounts of biochar used and weak sorption of the ionic compounds (Figure 2).

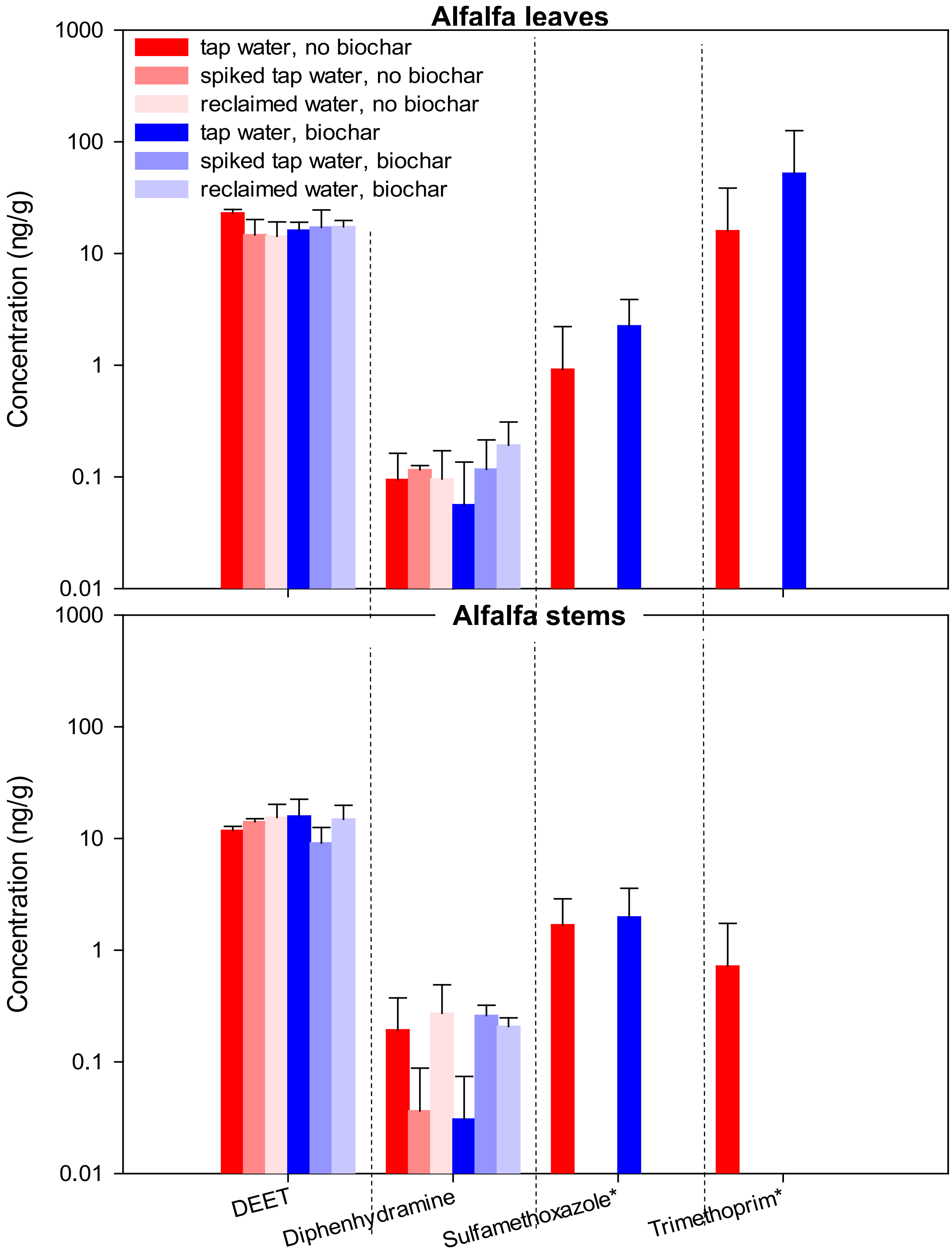

Figure 1. Contaminant concentration in alfalfa leaves (upper panel) and stems (lower panel) using three irrigation and two biochar treatments. Missing bars indicate that PPCP concentrations were below the detection limit. Water quality only had a significant overall effect on sulfamethoxazole leaf and stem concentrations. PPCPs indicated with an asterisk were added to the spiked tap water.

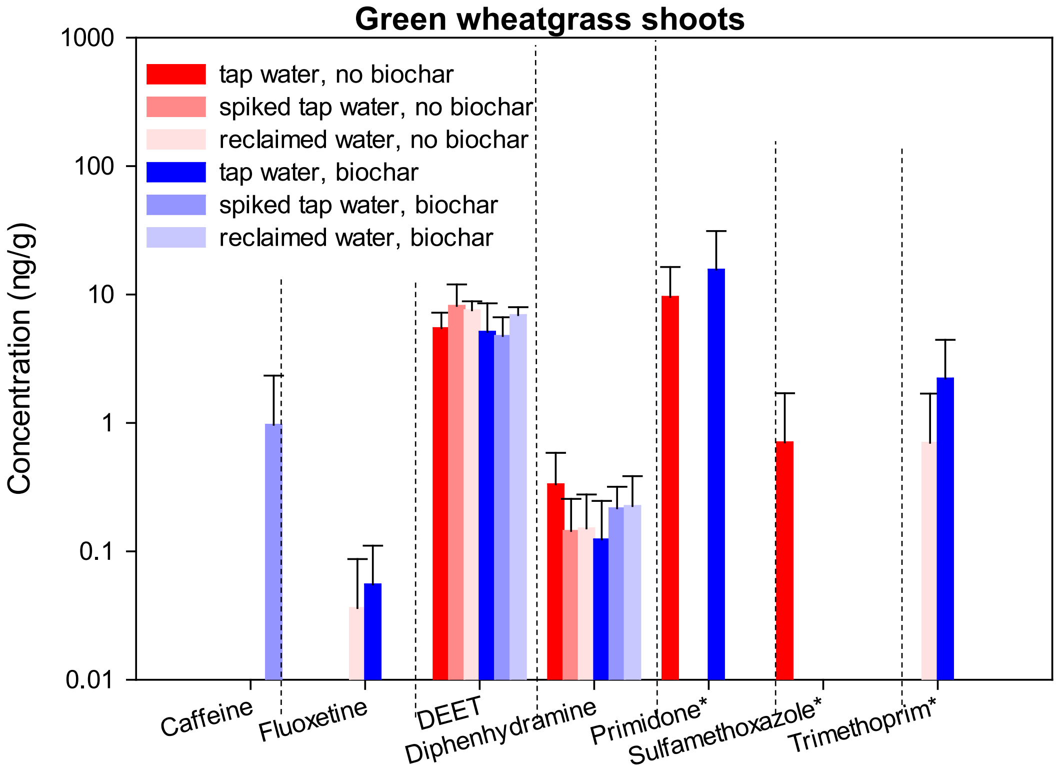

Figure 2. Contaminant concentration of green wheatgrass shoots using three irrigation and two biochar treatments. Missing bars indicate that PPCP concentrations were below the detection limit. Water quality only had a significant overall effect on primidone shoot concentrations. PPCPs indicated with an asterisk were added to the spiked tap water.

The concentrations of PPCPs in alfalfa and green wheatgrass soils were much higher for the spiked compounds (primidone and trimethoprim) when irrigated with the spiked water (Figure 3) despite these soils having been irrigated with reclaimed water for decades, but these higher soil concentrations did not result in increased plant uptake of these compounds (Figure 1 and 2). Presence of biochar caused a higher retention of caffeine in alfalfa and green wheatgrass soils, but we did not find any effect of biochar on concentrations of the remaining PPCPs.

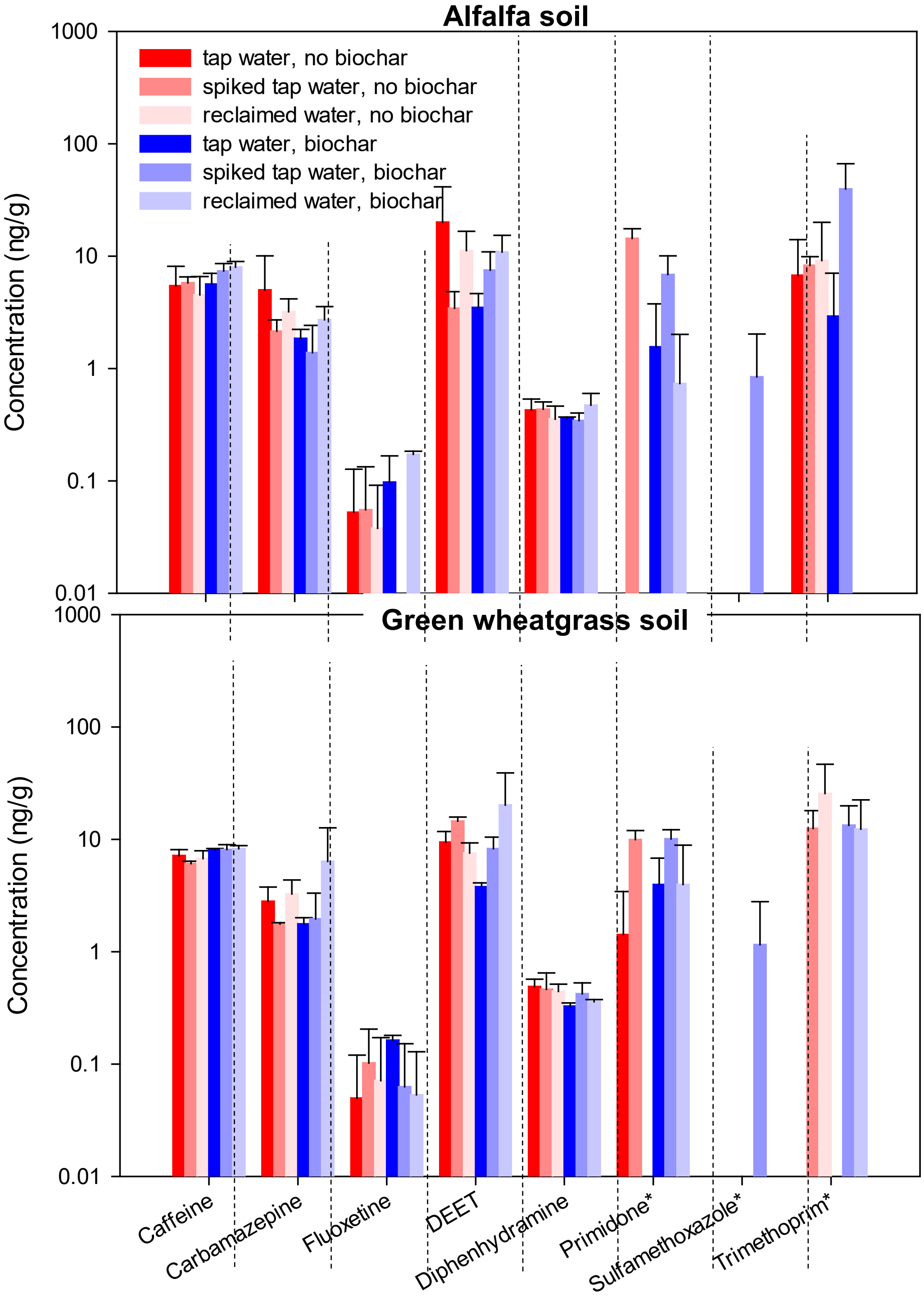

Figure 3. Contaminant concentration of soils planted with alfalfa (upper panel) or wheatgrass (lower panel) using three irrigation sources treatments. Missing bars indicate that PPCP concentrations were below the detection limit. Water quality significantly affected caffeine, primidone and trimethoprim concentrations in both alfalfa and wheatgrass soils. PPCPs indicated with an asterisk were added to the spiked tap water.

Summary and Conclusion

This greenhouse study was conducted to evaluate the impact of reclaimed water quality on plant uptake of PPCPs. We also investigated if amending soils with biochar could potentially reduce exposure of plants to PPCPs. Overall, we found very little evidence that PPCPs present in reclaimed water had any effect on plant production or PPCP uptake by plants. In fact, the only time we observed an effect of water quality was an increased uptake of sulfamethoxazole (in alfalfa) and primidone (in green wheatgrass) when irrigated with tap water, despite compound concentrations being the lowest in the tap water. It is not clear why uptake increased despite lower irrigation water concentrations, and further studies need to be conducted to determine if these results were due to changes in plant or soil behavior. While plants took up PPCPs, their concentrations were very low. Preliminary calculations suggest that the PPCP concentrations found in alfalfa are unlikely to present a human health hazard (Shahriar et al., 2021). However, additional studies are needed to determine the effects of long-term consumption of alfalfa on both animal and subsequent human health, especially as PPCP accumulation may increase over multiple growing cycles in perennial crops such as alfalfa.

Prior to the start of our greenhouse study, PPCPs were already present in the soil, as the area from which the soils were collected had been irrigated with reclaimed wastewater. Still, irrigation with spiked tapwater caused a significant increase in soil PPCP concentrations, indicating that soil PPCP concentrations are sensitive to changes in PPCP loading over time. If PPCP additions in irrigation water increase, accumulation of PPCPs is likely to increase as well. However, if PPCP loading were to decrease, plant uptake of PPCPs may continue, as PPCPs that accumulated in the soil as a result of prior irrigation with reclaimed water may continue to be released into the soil solution.

Our results point to the complexities involved in predicting the behavior and fate of chemical compounds in the environment. Despite these uncertainties, irrigating with reclaimed water did not result in increased plant uptake of PPCPs, even in cases where we spiked certain compounds at concentrations that are unlikely to occur in real-world situations.

We also did not find clear evidence that adding biochar to soils would alter plant uptake of PPCPs. While biochar may have benefits to soil fertility, it does not appear to have a major impact on the behavior of PPCPs in the soil or plant uptake from the soils when used in quantities that are commonly used for soil amendments.

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