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Composted biosolids and treated wastewater as sources of pharmaceuticals and personal care products for plant uptake: A case study with carbamazepine☆

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ABSTRACT

Irrigation with treated wastewater (TWW) and application of biosolids to arable land expose the agro-environment to pharmaceuticals and personal care products (PPCPs) which can be taken up by crops. In this project, we studied the effect of a carrier medium (e.g., biosolids and TWW) on plant (tomato, wheat and lettuce) uptake, translocation and metabolism of carbamazepine as a model for non-ionic PPCPs. Plant uptake and bioconcentration factors were significantly lower in soils amended with biosolids compared to soils irrigated with TWW. In soils amended with biosolids and irrigated with TWW, the bioavailability of carbamazepine for plant uptake was moderately decreased as compared to plants grown in soils irrigated with TWW alone. While TWW acts as a continuous source of PPCPs, biosolids act both as a source and a sink for these compounds. Moreover, it appears that decomposition of the biosolids in the soil after amendment enhances their adsorptive properties, which in turn reduces the bioavailability of PPCPs in the soil environment. In-plant metabolism of carbamazepine was found to be independent of environmental factors, such as soil type, carrier medium, and absolute amount implemented to the soil, but was controlled by the total amount taken up by the plant.

1. Introduction

Treated wastewater (TWW) and sewage sludge (biosolids), two main products of wastewater-treatment plants, are frequently applied to the agro-ecosystem. About 5.6 billion m^3 $year^{-1}$ of TWW is used for irrigation purposes globally. Although this accounts for less than 1% of the global irrigation volume (Jimenez and Asano, 2008; Puma and Cook, 2010), in some countries TWW is an essential source for irrigation. In Israel more than 85% of the produced TWW is used for irrigation (Goldstein et al., 2014), whereas in Jordan approximately 38% of the TWW is used for irrigation (Alfarra et al., 2011). In California about 46% of the used TWW is applied to agricultural land (Sato et al., 2013). On a global scale, irrigation with TWW is expected to increase due to prolonged droughts and depletion of freshwater sources. Biosolids production in the US and Europe is about 7.2 and 4.7 million tons of dry materials per year, respectively. Of that amount, approximately 50% is applied as organic amendment to agricultural lands (Beecher et al., 2007; Eurostat, 2017). Application of biosolids to arable soils increases their organic matter content, water-holding capacity, porosity and nutrient level, which in turn contributes to plant growth and yield (Singh and Agrawal, 2008).

Pharmaceuticals and personal care products (PPCPs) are essential components of modern life. Once utilized by humans or animals, PPCPs and their metabolites are excreted or washed out of the body, collected in the sewage systems and treated in wastewater-treatment plants. Incomplete removal and/or degradation of PPCPs in wastewater-treatment plants is well documented (Brooks and Huggett, 2012; Onesios et al., 2009; Wang and Wang, 2016). Thus, PPCPs are ubiquitous in TWW (ranging from ng to μg L^{-1}) and in biosolids (μg to mg kg^{-1}) (McClellan and Halden,

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2010; Miao et al., 2005; Miège et al., 2009; Xia et al., 2005). Once in the agro-ecosystem, PPCPs may undergo several fate-determining processes: adsorption/desorption (Xu et al., 2009), transport (Borgman and Chefetz, 2013), degradation/transformation (Grossberger et al., 2014; Lin and Gan, 2011), and uptake by plants (Wu et al., 2015) which may introduce PPCPs into the food chain and lead to potential human exposure (Paltiel et al., 2016).

TWW irrigation and biosolids application introduce PPCPs into the soil environment via different pathways. Irrigation with TWW continuously introduces PPCPs to the soil solution; in contrast, PPCPs originating from biosolids are added to the soil only periodically—every few growing seasons. Moreover, while TWW acts only as a source for PPCPs, biosolids can act both as a source and a sink due to their adsorptive capacity (Fu et al., 2016; Wu et al., 2010). Thus, the application practice (biosolids amendment and/or TWW irrigation) may affect the fate and bioavailability of the PPCPs introduced into the soil environment. We hypothesize that the bioavailability of PPCPs introduced via biosolids application will be lower than that introduced via TWW irrigation. In soils amended with biosolids and irrigated with TWW, biosolids will most likely reduce PPCPs bioavailability for plant uptake. These trends are expected to be influenced by the physiochemical nature (i.e., log *K*ow, charge and p*K*a) of the PPCP (Briggs et al., 1982; Trapp, 2000) and the properties of the soil (i.e., organic matter, clay content and pH).

This study focuses on carbamazepine, an anticonvulsant drug that is frequently detected in TWW and biosolids (Jelic et al., 2011; McClellan and Halden, 2010; Miège et al., 2009). Carbamazepine is also known as a relatively persistent compound in the environment (Clara et al., 2004; Grossberger et al., 2014), which is taken up by plants (Malchi et al., 2014; Riemenschneider et al., 2016; Wu et al., 2014). Using carbamazepine, we studied the effect of an application medium (biosolids, TWW, or a combined application) on plant uptake, translocation and metabolism of relatively polar non-ionic PPCPs.

2. Materials and methods

Chemicals. Carbamazepine (>97% purity) was purchased from Sigma-Aldrich Israel Ltd. (Rehovot, Israel). The carbamazepine metabolites 10,11-epoxide-carbamazepine (epoxide-CBZ) and *trans*-10,11-dihydro-10,11-dihydroxy-carbamazepine (dihydroxy-CBZ), and the labeled standards carbamazepine-13C,D2, 10,11-dihydro-10-hydroxy-carbamazepine-D3 and 10,11-epoxide-carbamazepine-D8 were purchased from Toronto Research Chemicals Inc. (Toronto, Canada). Detailed information about the physicochemical properties of the analyzed pharmaceuticals is listed in the Supporting Information Section (Table S1).

Experimental Setup. Determinate tomato (*Solanum lycopersicum*), Romaine lettuce (*Lactuca sativa*) and wheat (*Triticum aestivum*) were grown in 0.5 m^3 lysimeters (0.5 m^2 surface area) containing arable soils from three locations in the northwest Negev of Israel: Sa'ad (31.470185, 34.534356), Ein Hashlosha (31.351722, 34.403471) and Nir Oz (31.309697, 34.402075). Tomato and lettuce were irrigated with fresh water or TWW. Wheat was only rain-fed and was grown in the same soils previously irrigated with TWW or fresh water. The experimental design is presented in Fig. S1. Composted biosolids were added only once to the lysimeters previously irrigated with TWW, prior to the tomato planting at levels of 0 and 60 m^3 ha^{-1} (common agronomic practice). Each treatment (i.e., soil type, biosolids level and type of irrigation water) was performed in 3 replicates (i.e., lysimeters). The effects of the combined application of TWW and biosolids were tested on one soil type (Ein Hashlosha). Tomato (2 plants per lysimeter) and lettuce (4 plants per lysimeter) were planted in the summers of 2014 and 2015, and grown for 98 and 42 days, respectively. Plants were drip-irrigated; the total irrigation volume was 640 and 220 L per lysimeter for tomato and lettuce crops, respectively. Wheat was rain-fed during the winter of 2014–2015 for 155 days (~335 mm rain).

Composted biosolids and TWW were both provided by a conventional activated-sludge wastewater-treatment plant located in Kiryat Gat, Israel, receiving its influent from domestic and industrial sources. Properties of the soils, irrigation water and the composted biosolids are presented in Tables S2, S3 and S4, respectively. Concentrations of carbamazepine and its metabolites epoxide-CBZ and dihydroxy-CBZ were measured in the biosolids prior to application and in the TWW during the growing seasons (Table 1). TWW and biosolids were not spiked with PPCPs during the experiment.

Sample Preparation. At the end of the growing season, fruit and leaves of tomato, leaves of lettuce, and ears and leaves of wheat were collected and weighed. Soil samples (0–20 cm) were also collected during harvest. All plant subsamples were rinsed with deionized water, frozen at −20 °C, freeze-dried, and kept at −20 °C until analysis. Lettuce plants grown in Ein Hashlosha soil and irrigated with TWW were further analyzed as follows: (1) whole lettuce plants were separated into 3 sections: external, central and core (Fig. S2; top), (2) several external leaves from 3 different lettuce plants were divided into outer, middle and inner leaf parts (Fig. S2; bottom). Each section or leaf part was analyzed separately.

Freeze-dried plant material was ground to a fine powder with a planetary micro mill (Fritsch, Pulverisette 7) and extracted using an accelerated solvent extractor (ASE 350, Dionex, Sunnyvale, CA) in two static 5-min cycles with 100% methanol at 80 °C under constant pressure of 10.34 MPa. Soil samples were sieved (<2 mm), ground with a mortar and pestle and extracted using the same method. Extracts were evaporated and reconstituted with 1 mL of double-deionized water: acetonitrile: acetic acid (4:1:0.005 v/v). After reconstitution, solutions were spiked with 10 μL of a mixture of isotopically labeled internal standards, centrifuged at 24000*g* for 20 min and filtered (0.22 μm PTFE) prior to LC–MS analysis (Goldstein et al., 2014; Malchi et al., 2014).

Analytical Conditions. A quantitative analysis was conducted using a LC–MS/MS system which consisted of a 1200 Rapid Resolution LC system coupled to a 6410 triple quadrupole mass selective detector (Agilent Technologies Inc., Santa Clara, CA). Compounds were separated on an Acclaim C18 RSLC column (2.1 × 150 mm, particle size 2.2 μm, Thermo, Torrance, CA), using 1.5% acetic acid in water (A) and acetonitrile (B) as mobile phases at a flow rate of 0.3 mL min^{-1}. The gradient program was: 0–1.5 min at 90% A; 1.5–17 min, 90–4% A; 21–21.1 min, 4–90% A; 21.1–26 min at 90% A. The injection volume was 5 μL and column temperature was 40 °C. The mass spectrometer was equipped with an ESI source and operated in a positive ionization mode with the following ion source parameters: 3500 V capillary voltage, drying gas (nitrogen) temperature and flow of 350 °C and 10 L min^{-1}, respectively, 35 psi nebulizer pressure, and nitrogen (99%) used as the collision gas. LC–MS system control and data analysis were performed with MassHunter Software (Agilent Technologies). A quantitative analysis of pharmaceutical compounds was performed in multiple reaction monitoring (MRM) modes. LC–MS limits of quantification (LOQ) as well as mass transitions are listed in Tables S5 and S6, respectively. Absolute recovery values for all plant parts are listed in Table S7.

Data and Statistical Analysis. Bioconcentration factors were calculated as the summed concentrations of carbamazepine and its metabolites (∑CBZ) in a specific organ (mol g^{-1}) divided by ∑CBZ in the soil (mol g^{-1}) at the end of the season (0–20 cm). The plant-to-soil ratio (mol mol^{-1}) was calculated as the total amount of ∑CBZ in the shoot divided by the amount of ∑CBZ in the soil. A statistical analysis (non-parametric Wilcoxon/Kruskal–Wallis test

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