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Effect of soil biochar concentration on the mitigation of emerging organic contaminant uptake in lettuce

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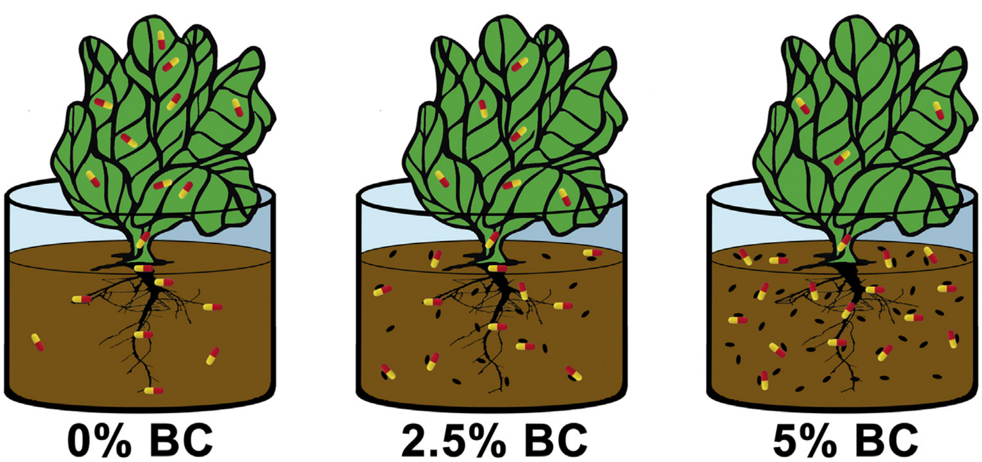
GRAPHICAL ABSTRACT



HIGHLIGHTS

- Several EOCs were taken up by lettuces and translocated to leaves.
- Biochar was used as a mitigation strategy to reduce the amount of EOCs in plants.
- Biochar increased EOC concentration in soil, but reduced their bioavailability.
- IBU EF suggests that the addition of biochar to the soil reduces its biodegradability.

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ABSTRACT

Although crop uptake of emerging organic contaminants (EOC) from irrigation water and soils has been previously reported, successful mitigation strategies have not yet been established. In this study, soil was amended with a wood-based biochar (BC) at two rates (0, 2.5 and 5% w/w) to evaluate the effect on mitigation of EOC uptake (i.e. bisphenol A, caffeine, carbamazepine, clofibric acid, furosemide, ibuprofen, methyl dihydrojasmonate, *tris*(2-chloroethyl)phosphate, triclosan, and tonalide) in lettuce

Abbreviations: BPA, bisphenol A; CAF, caffeine; CBZ, carbamazepine; CFA, clofibric acid; EF, enantiomeric factor; FUR, furosemide; IBU, ibuprofen; MDHJ, methyl dihydrojasmonate; RCF, root concentration factor; TF, translocation factor; TCEP, *tris*(2-chloroethyl)phosphate; TCS, triclosan; TON, tonalide.

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(*Lactuca sativa* L.). After 28 days of irrigation with water containing EOCs at 15 μg L^{-1}, the average EOC concentration in roots and leaves decreased by 20–76% in biochar amended soil relative to non BC-amended soil. In addition, the enantiomeric fractions (EF) of ibuprofen (IBU) in biochar amended soils (EF = 0.58) and unamended soils (EF = 0.76) suggest that the IBU sorbed fraction in BC is more recalcitrant to its biodegradation.

1. Introduction

Biochar (BC) is a solid carbonaceous rich material produced from slow pyrolysis using different feedstocks under a low oxygen atmosphere and at temperatures ranging from 350 to 900 °C. Biochar is applied to agricultural soils to aid in carbon dioxide sequestration, to increase soil water holding capacity and reduce nutrient leaching [1,2]. In addition, BC-amended soils have been shown to increase sorption capacity to pesticides [3], polycyclic aromatic hydrocarbons (PAHs) [4], halogenated phenols [5], veterinary antibiotics such as sulfamethazine [6] and PPCPs [7]. Consequently, mitigation in plant uptake of organic pollutants in BC-amended soils have been reported for PAH contaminated soils [8], pesticides at 50 mg kg^{-1} applied directly to soil (e.g. pyrimethanil, carbofuran and chlorpyrifos) [9,10] and, recently, carbamazepine at 1 mg kg^{-1} [11].

Irrigation water reclaimed from municipal wastewater treatment may contain variable concentrations of emerging organic contaminants (EOCs) ranging from ng L^{-1} up to several μg L^{-1} [12–14]. Among them, pharmaceutical and personal care products (PPCPs), biocides, fragrances, veterinary products, artificial sweeteners and disinfection byproducts (DBPs) have been detected [15]. Accordingly, some EOCs occurring in reclaimed water used for irrigation can be taken up by crops [16–18]. Therefore, strategies to mitigate crop uptake of EOCs have become of great interest from both a food safety and human health perspective.

Biochar has been reported to possess high affinity to some EOCs (BPA, CBZ and IBU). Limited information exists on the absorption–adsorption dynamics and competitive displacement of BC sorbates in the soil-root system, where soil organic matter and BC compete for the EOCs occurring in the irrigation waters [19]. Proposed sorption mechanisms for bisphenol A (BPA) and ibuprofen (IBU) are through π–π electron donor-acceptor interactions and through hydrophobic adsorption for CBZ [20,21]. In contrast, no information exists for other contaminants commonly found in sewage and effluents subjected to different treatment degree including caffeine (CAF), clofibric acid (CFA), furosemide (FUR), methyl dihydrojasmonate (MDHJ), *tris*(2-chloroethyl)phosphate (TCEP) and tonalide (TON).

We hypothesize that amending soils with BC, particularly soils depleted in mineral or organic colloids, will reduce the bioaccessibility of EOCs by plants. Therefore, the objective of this study is to assess the attenuation capacity of BC in soils to mitigate the uptake and translocation by lettuce of 10 EOCs commonly found in reclaimed irrigation water. The study consists of using EOCs with different physical-chemical properties in a soil amended with two rates of BC, 2.5 and 5% (w/w). In addition, the enantiomeric fraction of IBU was calculated in order to assess the impact of BC on EOC biodegradation in the soil.

2. Materials and methods

2.1. Experimental layout

The experiment was conducted in a research greenhouse belonging to the Universitat Politècnica de Catalunya, located in Agròpolis (Viladecans, Barcelona, Spain). Experimental units consisted of 2.5 L cylindrical amber glass pots (Ø = 15 cm and 20 cm high) fitted with a bottom outlet connected to drainage tubing (Ø = 3 cm) and filled with 2.3 kg of air-dried soil sieved to 2 mm as reported elsewhere [22]. To evaluate the effect of amending the soil with BC on the uptake of a mixture of ten EOCs, the following treatments were established: (i) unamended unspiked soil (control), (ii) BC-amended soil at 2.5% and 5% (w/w) with 70 μg of each EOC dissolved in water at 15 μg L^{-1} (30.4 μg kg^{-1} soil + BC dw) and supplied directly into the pot, to avoid adsorption to the irrigation tubing, over eight applications in a four week period beginning twenty-seven days after planting, and (iii) unamended soil and EOCs (30.4 μg kg^{-1} soil dw) supplied as described above. Treatments were replicated five times. In Table 1, the physical-chemical properties of the selected EOCs are listed. One seedling of Batavia lettuce (*Lactuca Sativa* L., cv. Arena) was planted in each experimental unit and watered with a Hoagland and Arnon solution [23] using a time programmed drip irrigation system (V = 100 mL d^{-1}).

The soil used was collected from the surface horizon of a typical Xerorthent soil from the Llobregat River Delta's agricultural area (longitude 2°03′E, latitude 41°17′N) and sieved between 0.12 and 2 mm. The soil had a sandy texture (90% sand, 8% silt, and 2% clay) with a pH of 7.42 ± 0.03 (soil-to-water ratio 1:5) and soil electrical conductivity of 3.8 dS m^{-1} (soil-to-water ratio 1:5). Total organic carbon and total organic nitrogen content was 5 g kg^{-1} and 0.7 g kg^{-1}, respectively. The cation exchange capacity (CEC) was 3.8 meq 100 g^{-1} and exchangeable Ca^{2+}, Mg^{2+}, Na^{+} and K^{+} were 2.82, 0.64, 0.25, and 0.15 meq 100 g^{-1} soil, respectively.

Biochar was produced by Bodegas Torres (Vilafranca del Penedès, Barcelona, Spain) from vineyard wood feedstock and pyrolyzed at 650 °C. Biochar was crushed and sieved to particle sizes between 0.12 and 2 mm. Morphological properties of BC such as surface area (SA), pores or molar H/C are usually the most important factors in sorption of compounds [24]. The N_2-B.E.T SA was 387 m^2 g^{-1}, pore volume was 0.0679 cm^3 g^{-1}, and pore size was 3.26 nm for the BC. Ultimate analysis of BC resulted in C, H, N and S contents of 62.8, 1.1, 0.3 and less than 0.1%, respectively, and a molar H/C ratio of 0.21. Biochar pH was 9.82 ± 0.04 (1:10 solid:solution ratio with deionized water), conductivity was 2158 ± 46 μS cm^{-1} and specific weight was 1.72 ± 0.05. An FTIR spectrum was obtained with KBr pellets and it can be found in SI (Fig. S1). Biochar amended soil pH increased to 7.48 ± 0.04 and 7.56 ± 0.03 with 2.5 and 5% BC amendment, respectively.

2.2. Chemical analysis

At the end of the experiment, soil, plant roots and aboveground biomass, i.e. leaves, from each experimental unit were analyzed. Prior to analysis, roots were soaked in deionized water to remove adhered soil. Roots and leaves were comminuted separately with liquid nitrogen and stored at −20 °C until analysis.

2.2.1. Plant tissue

The extraction of EOCs from plant tissues has been reported elsewhere [25]. Briefly, a matrix solid-phase dispersion method