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Effect of biochar amendment on the bioavailability of pesticide chlorantraniliprole in soil to earthworm

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ABSTRACT

To evaluate the effect of biochar amendment on the bioavailability of chlorantraniliprole (CAP) in soils with different physico-chemical properties, the uptake of CAP from various soils by earthworms was studied. It was observed that the biochar amendment of the soils affected the sorption of CAP, but the magnitude of the sorption enhancement by biochar amendment among the soils was varied, presumably due to the attenuation of the sorptivity of the biochar when amended in the soil. The amendment with biochars leads to a decrease in the bioavailability of CAP in the soils to earthworms, and more prominent for biochar BC850 amendment. In the soil with a CAP concentration of 10 mg kg^{-1}, the residue of CAP in the earthworm tissues was found to be 9.65 mg kg^{-1}, in comparison with that the CAP residue was 4.05 mg kg^{-1} in BC450 amended soil and 0.59 mg kg^{-1} in BC850, respectively. The degree of bioavailability reduction by same level of biochar amendment was different among soils with different properties. The results demonstrate that the properties of soils are important to performance of biochar in soil.

1. Introduction

Biochar produced from pyrolysis of biomass with limited or no oxygen supply has been shown to be effective in sorption and sequestration of organic contaminants, due to its great surface area, high nanoporosity and other physiochemical properties (Lehmann, 2007; Glaser et al., 2009; Cornelissen et al., 2005). In the literature, it was reported that addition of a small amount of greenwaste such as crop residue chars to soil greatly enhanced the sorption of a number of contaminants, such as diuron (Yang and Sheng, 2003; Yu et al., 2006), atrazine and simazine (Zheng et al., 2010), chlorophenol (Liu et al., 2010), and phenanthrene (Zhang et al., 2010). Yu et al. (2006) observed in their previous work that, for biochar derived from pyrolyzation of red gum (*Eucalyptus* spp.) chips, sorption coefficients, isotherm non-linearity and apparent sorption-desorption hysteresis significantly increased with increasing content of biochar in the soil, and more prominent for biochar derived under higher temperature due to the presence of high micropores and specific surface area of the soil. The enhanced sorption by amending soil with biochar strongly influenced the fate and behavior of organic compounds such as pesticides in the environment. For example, in soil amended with biochar, the degradation of benzonitrile (Zhang et al., 2005) or acetamiprid (Yu et al., 2011) was retarded, the herbicidal efficacy of diuron on barnyard grass (Yang et al., 2006), and atrazine and trifluralin on annual ryegrass (Nag et al., 2011) was found to be weakened, the plant uptake of insecticide chlorpyrifos and carbofuran was also reduced (Yu et al., 2009), and the extractability and toxicity of pentachlorophenol in sediment was decreased (Lou et al. 2011). This study focuses on the performance for biochar amendment in soils with different properties, especially when the bioavailability of insecticide from the soil to earthworms is taken into consideration.

Recently, production and soil application of biochar is highly recommended by the policy makers and scientific communities due to its significant environmental and agricultural benefits, such as mitigating climate change by sequestration of carbon and reduction in the emission of greenhouse gases (Lehmann et al., 2006; Woolf et al., 2010), modifying soil physical–chemical properties (DeLuca et al., 2006; Lehmann and Rondon, 2006), altering the soil nutrient availability and increasing crop production (Chan et al., 2007; Graber et al., 2010; Major et al., 2010), improving soil microbial activity (Steiner et al., 2008) and strengthening mycorrhizal associations (Warnock et al., 2007). The new strategy together with other practices, such as combustion of biomass and fossil fuel, occurrence of natural vegetation fires, and some agricultural activities (for example, direct burning of plant in field for landing cleaning), has contributed to the high

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level of biochar found in soils (Young et al., 2005). The increasing input of biochar to soil and its heterogeneous effects have pressed for an appropriate balance between its environmental and agricultural benefit and its impact on the insecticide fate and bioavailability.

Chlorantraniliprole (CAP) belongs to anthranilic and phthalic diamide insecticides (Lahm et al., 2005). It shares a typical mode of action on the insect ryanodine receptor and has been widely used to control a broad spectrum of insect pests (Lahm et al., 2005). CAP was characterized as persistent and mobile in terrestrial and aquatic environments (USEPA, 2008). Extended use of CAP might cause accumulation of residue in soil from year to year, and lead to potential risk to soil organisms. In the present study, biochar produced from red gum chips (*Eucalyptus* spp.) at two different temperatures were mixed into five Chinese agricultural soil samples, respectively. The uptake of CAP by earthworm from the soils with amending biochar and the sorption behavior was determined. We chose earthworm as indicator in our bioavailability study for it have a particularly intimate contact with the soil, consuming large quantities and having little external barrier to the soil solution, and it was an ideal organism for assessing the bioavailability of chemicals in soil (Lanno et al., 2004). The objectives were to identify the effectiveness of biochars in reducing the uptake of CAP from the soils to earthworms, and to study the influence of biochar amendment on the bioavailability of CAP in agricultural soils with different properties. The results will be helpful for researchers to evaluate the impact of biochar on the environmental fate and toxicity of the insecticide when being applied in agricultural soils.

2. Materials and methods

2.1. Chemicals

Chlorantraniliprole (CAP), purity 99.7%, was purchased from Sigma–Aldrich (St. Louis, MO, USA). Its solubility in water at 20 °C is 0.88 mg L^{-1} and octanol/water partition coefficient at pH 7 (K_{ow})=7.2×10^2 (USEPA, 2008). The stock solution of CAP was prepared in acetone. Deionized water was supplied by a lab water purification system (EPED Water Pro Plus System, Nanjing, China). Sodium azide and calcium chloride of analytical grade and all solvents were of HPLC grade and obtained from Merck Chemicals (Shanghai, China).

2.2. Biochar and soil samples

The biochars were produced from red gum wood (*Eucalyptus spp.*) at two different temperatures (450 and 850 °C) and thus referred to as BC450 and BC850, respectively, in the manner as described elsewhere (Yu et al., 2006). These biochar materials, BC450 and BC850, were ground into powders followed by passing through a 200 μm sieve. The specific surface area (SSA) and pore size distribution of the two biochars were evaluated using BET nitrogen adsorption techniques at 77 K using a method reported previously (Yu et al., 2006). Typical characteristics of these two biochar materials are listed in Table 1.

Soil samples used in this study were collected from 0 to 0.15 m of the ground surface. There were five different locations: a black soil collected from a wheat field near Harbin City of Heilongjiang Province, Northeast China (BS), a paddy soil collected from a paddy field near Wuxi City of Jiangsu Province, East China (YS), a red soil collected from a vegetable field near Nanchang City of Jiangxi Province, Southeast China (RS), a purplish soil collected from a wheat field near Ya'an City of Sichuan Province, Southwest China (PS), and a fluvo aquice soil collected from a paddy field near Zhengzhou City of Henan Province, North Central China (FS). The five soils are typical agricultural soils in China. The soil samples were air-dried at 40 °C, ground and passed through a 2-mm sieve and stored in plastic bag at room temperature. The selected physical and chemical properties of the soil are given in Table 2.

Biochars amended soils used in this study were set at 5 g biochar kg^{-1} soil. The biochar amended soils were thoroughly mixed on a rotary shaker for 3 day before their use as sorbents for sorption, and bioavailability experiments.

Table 1
Typical characteristics of biochar materials.

Biochar materials	SSA ($m^2\,g^{-1}$)	Pore size (nm)
BC450	27	1.1
BC850	566	0.49

Note: Specific surface area (SSA).

2.3. Earthworm uptake

An aliquot of 50.0 g of the soil sample was weighed into a sterile glass container (7.5 cm diameter, 15 cm height). Each sample was treated with 5.00 mL of 1000 or 100 mg L^{-1} of CAP stock solutions, resulting in a CAP fortified initial concentration of 100 or 10 mg kg^{-1}, respectively;then the mixture was homogenized on the rotary shaker in dark for 24 h. Acetone was allowed to evaporate in darkness at room temperature for 2 days. Deionized water was added to adjust water content in the soils to approximately 70% of the maximum water-holding capacity (i.e. 14.7, 13.3, 11.3, 10.9 and 9.7 ml of water was added to 50.0 g of soil BS, RS, YS, PS and FS, respectively). The containers were sealed with a plastic wrap and kept in darkness at 25 ± 1 °C to allow aging for 24 h. Three replicates were prepared for each treatment.

The earthworms used in this study were *Eisenia foetida* (Sarigng), which were cultivated in laboratory. After the aging step, five mature worms with similar body weight (about 500 mg) were introduced into each container. The containers were covered with gauze and maintained under conditions at 25 ± 1 °C and 70% of relative humidity for 14 days. Soil moisture was maintained by adding the required amount of water by controlling the weight at a two-day interval. At the end of earthworm cultivation, no avoidance and no deaths occurred in any of the replicate incubations.

2.4. Sorption experiment

Sorption of chlorantraniliprole (CAP) was carried out by the batch equilibration technique as described in many other studies (Yang and Sheng, 2003; Yu et al., 2006). The soils were suspended in 10 mL of 0.01 mol L^{-1} $CaCl_2$ solutions (containing 0.5% NaN_3, as an inhibitor of microbial activities) spiked at concentrations of 0.05, 0.1, 0.2, 0.4, 0.8, 1.6 mg L^{-1} of CAP, respectively. The amounts of sorbent used in the experiments were adjusted to allow for 30–80% of the CAP added to be sorbed at equilibrium. The suspensions were shaken on the rotary shaker in darkness at room temperature at 120 rpm for 24 h. After shaking, the suspensions were centrifuged at 4500 rpm for 30 min. An aliquot of the supernatant was passed through a Teflon syringe filter (0.45 μm) followed by LC-MS/MS analysis. The amount of CAP sorbed by the sorbent was calculated by the difference between the initial and final CAP concentrations in the solutions. Three replicates were prepared for each treatment.

2.5. Determination of chlorantraniliprole (CAP) residue in earthworm and soil

At the end of 14-day incubation, the earthworms were taken out of the container. After removed from the soil, the earthworms were kept on a moistened filter paper for 24 h to allow purging of gut contents (Belfroid et al., 1995) followed by being rinsed with sterile water and dried with a dry filter paper, before they were weighed. The earthworms were cut into small pieces (approximately 1 cm) and placed in a 50 mL screw-capped glass tube containing a mixture of 2 g of sodium chloride and 20.0 mL of acetonitrile. The mixture was homogenized by a T18 basic Ultra Turrax blender (IKA) for 2 min followed by centrifuging at 4800 rpm for 30 min. An aliquot 10 mL of the supernatant was then withdrawn and evaporated to dryness under a nitrogen stream. The residues were dissolved with 1.00 mL of acetonitrile and passed through a 0.45 μm Teflon syringe filter. The CAP residues were analyzed by LC-MS/MS. The recoveries were between 83.8 to 90.2% for CAP residues in the in earthworms tissue, with the fortified concentrations ranging from 0.1 to 50 mg kg^{-1}. Minimum five replicates of earthworms were analyzed for each trial.

Table 2
Selected physical and chemical properties of the soil samples.

Soil	Organic matter (%)	pH	CEC (cmol kg^{-1})	Silt (%)	Sand (%)	Clay (%)	Soil texture
BS	4.6	7.5	27.64	38	40	22	Loam
YS	1.7	6.6	16.41	54	30	16	Clay sandy loam
RS	1.5	4.4	10.33	27	16	56	Clay loam
PS	1.2	7.9	20.57	40	42	18	Loam
FS	1.2	8.0	8.71	11	77	12	Sandy loam

Note: Cation exchange capacity (CEC).