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

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).

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.

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).

A soil sample (10.0 g) was extracted with 20.0 mL of acetonitrile and 5 g sodium chloride by vortexing for 10 min. Then the mixture was sonicated for additional 30 min. After centrifuged at 6000 rpm for 15 min, a portion of the supernatant (10.0 mL) was withdrawn and dried under a nitrogen stream (water bath at 40 °C). The residues were redissolved in 1.0 mL of acetonitrile. The final extract was passed through a 0.45 μm Teflon syringe filter. The residue of chlorantraniliprole (CAP) was determined by LC-MS/MS. The recoveries were between 88.8 and 92.1%, from 87.0 to 88.7%, and from 86.0 to 92.8% for the CAP residues in the soils, BC450-amended soils, and BC850-amended soils, respectively, with the fortified concentrations ranging from 1.0 to 50 mg kg^{-1}. Minimum five replicates of soil samples were analyzed for each trial.

2.6. LC-MS/MS analysis method

The LC-MS/MS system was an Agilent HPLC (1200 SL) equipped with 6410 triple quadrupole tandem mass spectrometer, using a Zorbax Column (Eclipse SB-C$_{10}$, 2.1 mm × 30 mm, 3.5 μm particle size), a isocratic mobile phase (water: acetonitrile, 20:80, containing 0.1% formic acid), flow rate 0.1 mL min^{-1}, injection volume 2 μL, and ESI positive mode. The MS/MS parameters were nitrogen at 40 m Torr, capillary potential 4000 V, drying gas 350 °C, collision energy 20, MRM transitions m/z 484 > 285 (quantitation) and 484 > 453 (identification), 484 > 177 (identification). The limit of quantitation was set to be 0.05 mg kg^{-1} for earthworm and soil samples.

2.7. Data analysis

All the sorption data were fitted using the Freundlich equation:

$$q = K_f C^{1/N_f} \tag{1}$$

Where K_f is the Freundlich constant and gives the capacity of the sorbent, N_f the Freundlich exponent presenting an indication of the favorability, q the CAP concentration on sorbent at equilibrium time, and C the CAP concentration on solution at equilibrium.

To assess the statistical differences among the earthworm uptake of CAP from soils, a Duncan's multiple range test was conducted with Statistical Analysis System Version 6.12.

3. Results and discussion

3.1. Sorption of CAP

Sorption data for CAP on the all soils well fit by the Freundlich isotherm equation with $R^2 \geq 0.95$ (Table 3). The adsorption isotherm model describes how simulate the pesticide interacts with the soils (adsorbents). The well fitted data indicate homogenous distribution of active sites on the adsorbents. It is important to

Table 3
Freundlich constants for the sorption of chlorantraniliprole in soils with and without the amendment of biochars.

Sorbents*	K_f (L kg^{-1})	N_f	R^2
BS	2.30	0.72	0.98
BS +0.5%BC450	2.35	0.72	0.98
BS +0.5%BC850	146	0.70	0.95
YS	1.80	0.91	0.96
YS +0.5%BC450	1.98	0.81	0.97
YS +0.5%BC850	204	0.75	0.97
RS	0.94	0.94	0.97
RS +0.5%BC450	1.08	0.84	0.98
RS +0.5%BC850	161	0.75	0.97
PS	1.58	0.83	0.97
PS +0.5%BC450	2.21	0.78	0.99
PS +0.5%BC850	195	0.65	0.97
FS	1.09	0.85	0.98
FS +0.5%BC450	2.25	0.72	0.98
FS +0.5%BC850	231	0.70	0.98

K_f is Freundlich affinity coefficient, N_f is Freundlich exponent. R^2 is the determination coefficient.

* BS, YS, RS, PS, and FS refer to black soil, yellow soil, red soil, purple soil and fluvo aquice soil, respectively.

optimize the use of adsorbents and the findings would be a critical guidance for design and use of biochar adsorption systems on pesticides.

As can be seen among the data in Table 3, for soils without biochar amended, BS has the highest capacity of CAP sorption (largest K_F), compared to the four soil sorbents (> YS > PS > F-S ≈ RS). This may be due to the content of organic matter and other physical and chemical properties of the soils. The difference in-between is relatively small and overall small K_F indicates low sorption with a small or little difference.

Due to the nonlinearity of the sorption isotherms, to facilitate the comparison of the sorption affinity of soils with and without amendment of biochars, the single point sorption constant K_d value was calculated at the equilibrium concentration (C) of 1 mg L^{-1}. It is observed that, amendment with biochar BC450 resulted in the increase of K_d values by 2.2%, 10.0%, 14.9%, 39.9% and 139.1%, respectively, for soil BS, YS, RS, PS and FS. The sorption capacity does not increase significantly, except for soil FS, indicating the capacity of CAP sorption is only slightly increased by addition of BC450.

However, the amendment of 0.5% BC850 to the soils raises the K_d values to 64, to 113, to 171, to 123, and to 212 times for the BS, YS, RS, PS and FS soils, respectively. These data strongly demonstrate a significant enhancement in capacity of CAP sorption with 0.5% BC850. Since such a small amount of biochar is amended, i.e., the addition of biochar by 0.5% weight, it suggests that biochar plays a dominant role in overall sorptivity of the amended soils systems. Allen-King et al. (2002) proposed that black carbon materials including biochar, charcoal and soot, which are physically more rigid than other kinds of soil organic carbon, would exhibit non-linear adsorption with high sorption capacity due to its high specific surface area. BC850 is a biochar material developed under high temperatures with higher specific surface areas and larger pore volumes in comparison with BC450 (Yu et al., 2006), which is expected to be more prominent in sorption enhancement when incorporated in the soils.

Biochar BC850 amendment totally changed the sorptivity of the 5 soils to the order of FS > YS > PS > RS > BS (Table 3). This is thought to be due to the varied performance in terms of sorption capacity of the added biochar, as the sorptivity of BC850 amended soils were dominated by the added biochar. The mechanism could be that, after the biochar was amended in soil, the active sites on biochar are interacting with the soil component and blocked, leading to enhance the efficiency of the sorption of CAP on biochar amended soils in a different magnitude, due to the different physical–chemical properties of the soils. Similar results also reported by Zhang et al. (2010) reported that the magnitude of sorption enhancement for phenanthrene by biochar amendment depended on the soil indigenous organic carbon content. Liu et al. (2010) also found that 3-chlorophenol sorption in the soils containing rice-straw ash was less than the combination of pure ash and the soils. It has been proved that soil water soluble organic matters (such as humic and fulvic acids) could be sorbed by biochar, leading to competition with the added organic substances for limited sorption site and/or pore block of biochar, thus decreasing its sorption capacity (Koelmans et al., 2009; Kwon and Pignatello, 2005; Pignatello et al., 2006). The lowest magnitude of sorption enhancement for biochar amendment in soil BS was easily to be understood due to its highest content of organic matter (4.6%), Table 2, comparing to the other four soils. The other soils, RS, YS, FS and PS, have a relatively small difference in content of organic matter, the big differences of biochar amendment in sorption enhancement (Table 3) might be attributing to the different properties of soil organic matters (solubility, molecular size, etc.) (Koelmans et al., 2009; Cornelissen and Gustasspm, 2006). Besides the soil organic matter, the soil clay

should be another important factor that affects the sorptivity of biochar in soil. The small particle of clay sheet might deposit on the surface of biochar, block the pore and reduce the surface area. For example, soil FS have lowest content of clay (12%, Table 2) and organic matter (1.2%, Table 2) among the five soils, the impact on the sorptivity of the added biochar was the smallest, which resulted in the highest magnitude of sorption enhancement by biochar amendment in soil FS. The content of organic matter in soil YS (1.7%) was a little higher than that soil RS (1.5%), but the clay content was much lower (16 vs. 56%). The magnitude of sorption enhancement by amending the same amount of biochar (0.5%) in soil YS was higher than that of soil RS. The role of different types of soil clay on the sorptivity of biochar need to be further investigated.

3.2. Uptake of CAP by earthworm

Recently, Wang et al. (2012) observed that the degradation of CAP occurred slowly in both soils and biochar amended soils. For example, a 15-day cultivation period led approximately 8–12% of the CAP lost from the soils and the half-life was found to range from 115 to 289 days (Wang et al., 2012). Therefore, a 14-day cultivation period was set in this study. The data of CAP residues in the tissue of earthworm cultivated in CAP fortified soils are shown in Figs. 1 and 2.

It is observed that, in Fig. 2, the effect of CAP fortification concentration is obvious. For instance, at the higher CAP concentration (100 mg kg^{-1}), for both original soils and biochar amended
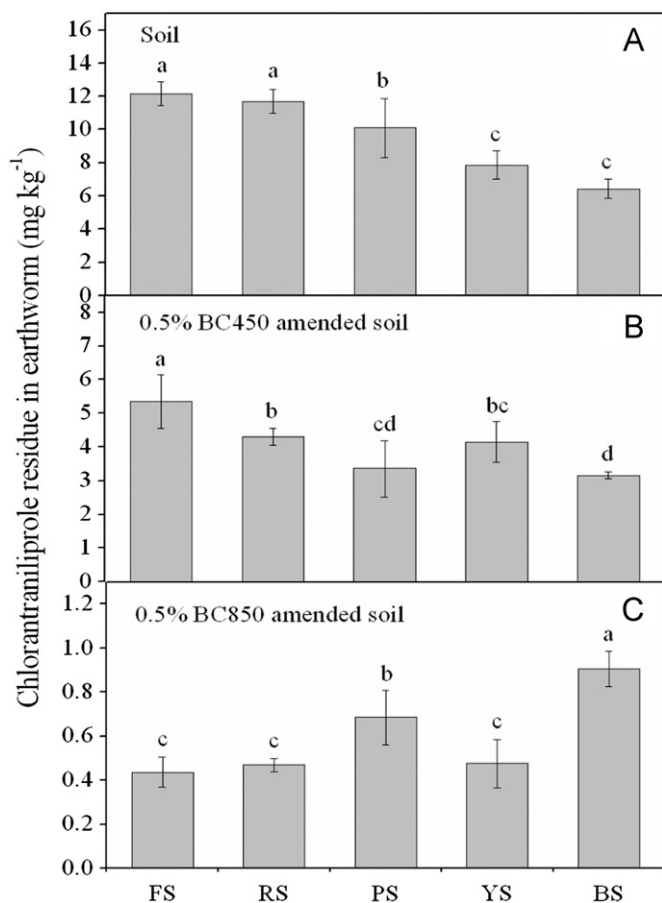

Fig. 1. Chlorantraniliprole residue in earthworms. Soils fortified with 10.0 mg kg^{-1} CAP. Error bars are standard deviation. Different letters (a, b, c, ab, and bc) above the same bar type indicate significant difference (Duncan, $p < 0.05$). FS, RS, PS, YS and BS refer to fluvo-aquic soil, red soil, purple soil, yellow soil and black soil, respectively.
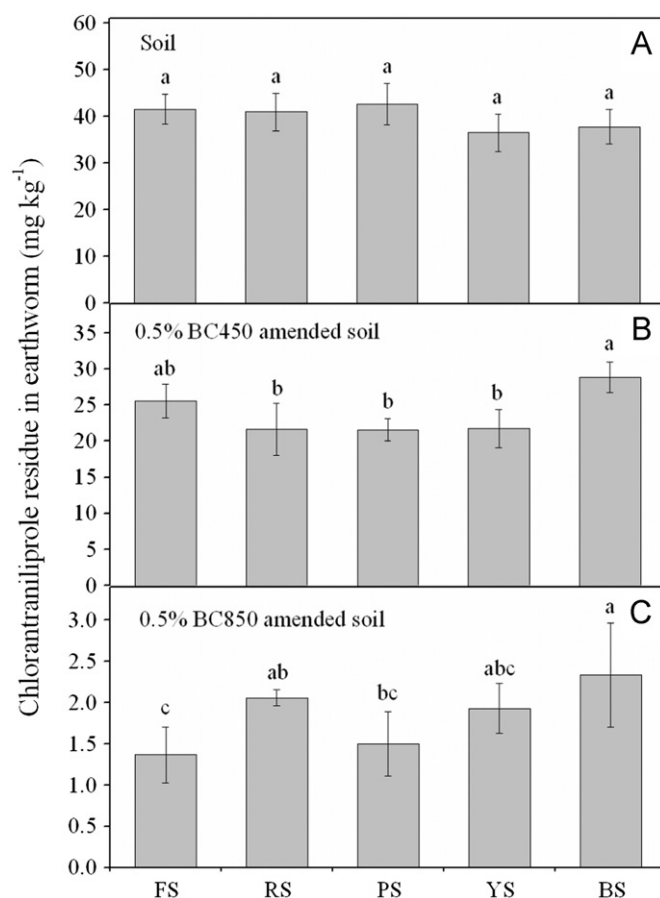

Fig. 2. Chlorantraniliprole (CAP) residue in earthworms. Soils fortified with 100 mg kg^{-1} CAP. Error bars are standard deviation. Different letters (a,b, c, ab, bc, and abc) above the same bar type indicate significant difference (Duncan, $p < 0.05$). FS, RS, PS, YS and BS refer to fluvo-aquic soil, red soil, purple soil, yellow soil and black soil, respectively.

soils, the CAP uptake by earthworms in the five soil samples is almost identical within the experimental error. For example, in Fig. 2, the CAP uptake is found to be approximately 40 mg kg^{-1} in original soils (FS, RS, PS, YS and BS), 25 mg kg^{-1} in soils (0.5% BC450), and 1.7 mg kg^{-1} in soils (0.5% BC850), respectively. This indicates that the high level fortification had possibly saturated the systems and a maximum CAP uptake was reached.

It is also observed that, in Fig. 1, at the CAP concentration (fortified at 10.0 mg kg^{-1}), the CAP uptake by earthworms in the five soil samples changes by amending of biochars. For example, in Fig. 1(C), the CAP uptake is approximately 12 and 6 mg kg^{-1} in FS (original soil) and BS (original soil), and is 0.4 and 0.9 mg kg^{-1} in FS (0.5% BC850) and BS (0.5% BC850), respectively; This indicates that the differences are due to soil properties and interactions between soils and the biochar amended. Therefore, it can be concluded that the properties of soils are also important to performance of biochar in soil in terms of reducing the pesticide bioavailability.

The amendment with biochars appears to lead to a prominent decrease in the bioavailability of CAP in soils. As expected, most prominent effect is observed in soils with biochar BC850 amendment, Figs. 1 and 2. At the level of CAP 10 mg kg^{-1} (Fig. 1), the average CAP uptake by earthworms is 9.65 mg kg^{-1} for initial soils, 4.05 mg kg^{-1} for soils (0.5% BC 450), and 0.59 mg kg^{-1} for soils (0.5% BC850), respectively. A similar pattern is observed in Fig. 2 that at CAP fortified at 100 mg kg^{-1}, the average CAP uptake decreases from 39.89 (original soils) to 1.83 mg kg^{-1} (soil, 0.5% BC850).

It was proposed that there are two typical uptake routes by earthworm (Belfroid et al., 1995). The first one is the simple passive diffusion of contaminants across the dermis of the receptor, and the second is that the contaminants are ingested together with soil, resulting in the diffusion of the contaminants across the gastrointestinal tract and accumulation in the lipid-rich earthworm tissues (Belfroid et al., 1995; Lanno et al., 2004; Jacqueline and Kevin, 2004; Douglas et al., 2000). Substances that are dissolved in the solution surrounding soil particles or weakly associated with the active sites soil/biochar surfaces are considered to be environmentally bioavailable to the earthworm for dermal uptake. Since CAP has a low K_{ow} value (log K_{ow}=2.77), it is assumed that CAP uptake from soils to earthworms be mainly through a passive diffusion pathway which determines the bioavailability of CAP to the earthworms (Belfroid et al., 1995; Lu et al., 2004). The main reason for decreased CAP uptakes in biochar amended soils is likely due to the enhanced CAP sorption by active sites on soil/biochar surfaces leading to a lower CAP concentration (less available) in the bulk-like soil water. Furthermore, it has been reported that biochar in soil could reduce the food availability in soil, and earthworm prefer to ingesting soil in a char and soil mixture (Topoliantz and Pong, 2003; Gomez-Eyles, et al. 2011). It is therefore lead to that *E. fetida* in biochar amended soil consumed less food and biochar, which also resulted in less CAP sorbed by biochar or by soluble organic matter ingested by the earthworms.

4. Conclusions

This study reveals that biochar application in agricultural soils not only enhances, but even also dominates the pesticide sorption in soils with strong biochar (like BC850) amendment, and thus markedly reduces the CAP uptake by earthworms. The magnitude of sorption enhancement and degree of reduction of bioavailability vary based upon the nature of the soils, especially in case of BC850 amendment, presumably mainly due to the interactions between soil soluble organic matters and biochar active surfaces resulting in the attenuation of the sorptivity of biochar. Therefore, studies on environmental behavior of pesticide sorbed by biochar amended soils are important and this study provides understanding of and help in risk assessment on pesticide in soils with biochar. Furthermore, the results delivered in this work are the initial effects and further work on the long-term effects on biochar amendment will be investigated.

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