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Bioavailability assessment of hexachlorobenzene in soil as affected by wheat straw biochar

Yang Song[a,1], Fang Wang[a,1], Yongrong Bian[a], Fredrick Orori Kengara[b], Mingyun Jia[a], Zubin Xie[a], Xin Jiang[a,*]

[a] State Key Laboratory of Soil and Sustainable Agriculture, Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008, PR China
[b] Department of Chemistry, Maseno University, Private Bag Maseno 40105, Kenya

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ABSTRACT

Biochar incorporation with soil could increase sorption of organic contaminants, thereby reducing their bioavailability. In this study, the effects of wheat straw biochar on the sorption, dissipation and bioavailability of hexachlorobenzene (HCB), a typical persistent organic pollutant (POP), were investigated in laboratory experiments. We observed that HCB sorption by biochar was 42 times higher than that by soil and the sorption isotherm was linear for the concentration range studied. Biochar amendments reduced HCB dissipation, volatilization and earthworm (*Eisenia foetida*) uptake of HCB from soil. Hydroxypropyl-β-cyclodextrin extraction correlated better with the earthworm bioassay than butanol extraction of HCB in biochar-amended soil. The results of both chemical extraction and earthworm bioassay indicate that biochar amendment of soil resulted in a rapid reduction in the bioavailability of HCB, even for the 0.1% biochar application rate. This suggested that wheat straw biochar could potentially be used in immobilizing POPs in contaminated sites.

1. Introduction

Application of biochar into soil has been shown to sequester C, reduce the emission of greenhouse gases, improve soil fertilization and thus plant growth [1–3]. Biochar has also been shown to have a very high affinity and capacity for sorbing organic contaminants since it has a large surface area and high microporosity, among other physico-chemical properties [4,5]. The strong sorption affinity of biochar influences the environmental fate and behavior of organic contaminants in soil [5], especially their bioavailability.

Bioavailability of contaminants dominates their potential degradation and uptake in soil, since organisms mostly utilize contaminants dissolved in soil water [5]. The fact that decreased degradation of benzonitrile, atrazine and simazine has been observed in biochar-amended soil [6–10], and that reduced plant uptake of chlorpyrifos and carbofuran occurred with increasing biochar addition in soil [11], shows that sorption of contaminants by biochar reduces their bioavailability in soil [6,11]. The decreased bioavailability of the herbicides could also result in reduced herbicidal efficacy to weeds [6,12]. For example, barnyard grass survival rating increased with increasing biochar content at potentially damaging diuron or clomazone application rates [6,12]. However, studies have also reported that microbial activity could be stimulated by the elemental nutrients in biochar, thereby enhancing the biodegradation of pollutants such as PAHs and benzonitrile in biochar-amended soil [13,14]. Therefore, assessing the bioavailability of contaminants in biochar-amended soil is of importance.

To assess the effect of biochar on the bioavailability of contaminants in soil, bioassays such as microbial degradation and plant uptake have been performed [7,10,11]. However, these methods are time-consuming and laborious [15]. Chemical extraction methods, such as mild-solvent extraction, have proved to be suitable in bioavailability assessment of contaminants in soils without biochar [15,16]. However, whether chemical extractions are suitable for biochar-amended soil needs to be evaluated.

Most studies about the effects of biochar are based on polar organic contaminants [6–12]. However, reports on the effect of biochar on the bioavailability of non-polar persistent organic pollutants (POPs) are limited [17,18]. The objectives of the present study were therefore (1) to investigate the extent to which amendment of soil with different levels of wheat straw biochar affects the bioavailability of hexachlorobenzene (HCB) – a model non-polar POP and (2) to evaluate the suitability of chemical extraction methods to assess the bioavailability of contaminants in soil in the presence of biochar.

* Corresponding author. Tel.: +86 25 86881195; fax: +86 25 86881000.
E-mail address: jiangxin@issas.ac.cn (X. Jiang).
[1] These authors contributed equally to this work.

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2. Materials and methods

2.1. Chemicals

Hexachlorobenzene (HCB) – a typical POP – was used as a model compound. The HCB standard (>99.5% purity) was obtained from Dr. Ehrenstorfer (Augsburg, Germany). The solvents and all other chemical reagents were of analytical grade and were obtained from Nanjing Chemical factory (Nanjing, China). HPCD (>98% purity) was obtained from Shanghai ANPEL Scientific Instrument Co. Ltd. (Shanghai, China). Anhydrous sodium sulfate was oven-dried at 400 °C for 4 h prior to use.

2.2. Soil sampling

An agricultural soil (Ferri-Udic Argosols, as referred to in Chinese Soil Taxonomy) was collected from a vegetable field in Nanjing, China (32°12′4.6″N,118°50′112.3″E). The soil was sampled from the upper 20 cm, passed through a 2-mm sieve for the incubation experiment and air dried and passed through a 0.15-mm sieve for the sorption experiment, before storage at 4 °C. Analysis for the soil physico-chemical properties was conducted by conventional standard procedures [19].

2.3. Biochar preparation

Wheat straw (*Triticum aestivum* L.) was used to produce biochar under anoxic conditions by a patented biochar reactor (NO.: ZL 2009 2 0232191.9). Prior to biochar production, the wheat straw was oven-dried for 12 h at 80 °C, and then moved to the biochar reactor, which was heated by a step-wise temperature programme. The starting temperature was 200 °C, followed by consecutive elevation to 250 °C, 300 °C, up to a maximum of 500 °C, and the temperature was maintained for 1.5 h at each point. The whole production process, at the final temperature step, was stopped when no further smoke was emitted from the gas exit pipe. The biochar sample was allowed to cool to room temperature, and sieved through a 0.15-mm mesh.

The specific surface area was determined applying the Brunauer–Emmett–Teller (BET) method to nitrogen adsorption isotherms while the pore volume and size were determined using Barrett–Joyner–Halenda (BJH) adsorption and desorption analysis [4]. The biochar functional groups were determined using a Fourier transform infrared (FTIR) spectrometer (NEXUS 870, Thermo Nicolet, USA). The samples for FTIR analysis were prepared in 2% KBr wagers. The infrared spectra were obtained with 2 cm^{-1} resolution and 64 scans between wave numbers of 400 cm^{-1} and 4000 cm^{-1} [20].

2.4. HCB sorption methodology

To compare the sorption affinities of soil and biochar, a batch sorption experiment was conducted. Due to the low water solubility of HCB (6.2 $\mu g\,L^{-1}$ at 25 °C), the HCB was firstly dissolved in acetone, and then added to 10 mL 0.005 M $CaCl_2$ solution in a 30 mL glass tube. The initial concentrations of HCB ranged from 50 to 2000 $\mu g\,L^{-1}$ in this experiment, which were higher than its water solubility. Due to the fact that the acetone used could enhance the affinity of HCB for aqueous phase and thus affect the HCB sorption, the acetone concentration was 0.1% by volume to minimize the cosolvent effect [21]. Then 5 mg or 50 mg of biochar or soil, respectively, was added to the tubes. The use of these masses was to ensure that 60–80% of the added HCB was sorbed by the sorbents [21]. The tubes were immediately closed with Teflon-lined screw caps and rotated on an overhead shaker at 40 rpm for 72 h at 25 °C. A preliminary experiment had shown that sorption could reach equilibrium within 72 h. At equilibrium, the suspensions were centrifuged at 4024 × *g* for 30 min. Then 5 mL supernatants were sampled and extracted twice with equal volumes of *n*-hexane on a vortex shaker for 2 min. The extracts were pooled together, dried with anhydrous sodium sulfate and then concentrated to 2 mL for further gas chromatographic (GC) analysis. All the treatments were conducted in triplicates.

The biochar, after sorbing HCB (2000 $\mu g\,L^{-1}$ HCB concentration), was dried in desiccators to produce the HCB-sorbed biochar (Biochar-HCB). The Biochar-HCB and pure HCB powder samples were analyzed by FTIR as described in Section 2.3.

2.5. Dissipation of HCB in soil affected by biochar

Prior to the start of the experiments, the soil samples were wetted to 20% of soil moisture content and equilibrated for 1 wk at 25 °C in the dark. 0.55 mg of HCB standard, dissolved in 10 mL acetone, was applied to an aliquot of 15 g (dry weight) of soil in a 50-mL glass beaker. After evaporation of acetone, the soil aliquot was mixed and transferred into a glass beaker which already contained 284.7 g (dry weight) of equilibrated soil and 0.3 g (0.1%) of biochar. The total 300 g of soil amended with biochar was mixed by stirring carefully and thoroughly with a spatula, transferred to a 1000-mL incubation flask, and adjusted to 28% soil moisture content. Then 2 g of the spiked soil was sampled with a stainless steel soil borer to analyze the initial concentration of HCB in the soil. The remaining soil was compacted to a volume equivalent to 1.3 g cm^{-3} of soil density. The flask was closed tightly with a rubber plug which contained inlet and outlet tubes, and incubated at 25 °C for 24 wk in the dark. The setups for the 0.5%, 1% and 2% biochar content were conducted in the same way outlined above for the 0.1% treatment. The unamended treatment, without addition of biochar, was used as control. There were therefore a total of 5 treatments: 0% biochar, 0.1% biochar, 0.5% biochar, 1% biochar and 2% biochar, all conducted in triplicates.

During the incubation period, the flasks were aerated once per week for 20 min at an exchange rate of 0.4 L min^{-1}, in a closed laboratory trapping system, to flush out and trap the volatilized HCB (for details on the trapping system, see [22]). After aeration, 10 g of soil was sampled for HCB residues and chemical extraction analysis. For the earthworm bioassay experiment, 25 g soil was sampled after 1 wk, and again after 24 wk, of incubation.

2.6. Residues and volatilization of HCB in soil

The residues of HCB in soil, which means total concentration in soil, were extracted by accelerated solvent extraction (ASE 200, Dionex, USA) [16]. Briefly, 2 g soil samples were homogenized with 5 g diatomaceous earth. The extraction was performed at a temperature of 100 °C and a pressure of 1500 psi with hexane/acetone (4:1, v/v). The extracts were rotary evaporated at 45 °C to about 2 mL and then applied to a silica gel/anhydrous sodium sulfate column, followed by elution with 15 mL hexane/dichloromethane (9:1, v/v). Finally, the eluate was concentrated to 1 mL for subsequent GC analysis.

During the experimental period, the volatile fraction of HCB was trapped with hexane, dried with anhydrous sodium sulfate and concentrated to 1 mL for subsequent GC analysis.

2.7. Bioavailability assessment of HCB in soil

2.7.1. Chemical extraction

Butanol extraction and HPCD extraction – which have been shown to be effective in bioavailability assessment of HCB in soil [16] – were evaluated for their suitability in assessing the bioavailability of HCB in the biochar-amended soil. Generally, 2 g soil was

extracted with 15 mL *n*-butanol or 25 mL HPCD (50 mM) in a glass centrifuge tube by shaking on an orbital shaker at 200 rpm for 2 h (butanol) or 24 h (HPCD), followed by centrifugation at 1448 × *g* for 30 min. Then, 10 mL of the HPCD supernatants was sampled and extracted twice with 10 mL hexane, followed by drying with anhydrous sodium sulphate and concentration to 1 mL for GC analysis. The butanol supernatants were discarded and the extracted soil was washed with 10 mL deionized water followed by exhaustive ASE extraction as described in Section 2.6. The HCB concentration in the butanol extract was calculated by subtracting the concentration in soil after butanol extraction from the total concentration in soil before extraction [16].

2.7.2. Earthworm bioassay

Earthworm (*Eisenia foetida*) was used in a bioassay experiment to evaluate the effectiveness of chemical extraction methods (Section 2.7.1) to predict the bioavailability of HCB, according to the procedure of [16,23]. Briefly, 10 adult worms with a clitellum were exposed to 25 g (dry weight) soils sampled in Section 2.5, adjusted to 30% soil moisture content with deionized water in a 100-mL glass jar, and covered with aluminum foil with several holes. The soils were kept under constant room light at 25 °C for 14 d. After exposure, the worms were rinsed and allowed to purge their gut contents for 48 h on moistened filter papers. The worms were weighed, freeze-dried, and ground with 7 times their weights of anhydrous sodium sulphate and equal weights of quartz sand, followed by ASE extraction using the method described for soil extraction in Section 2.6.

2.8. GC analysis

The concentrations of HCB in all the samples were measured by a gas chromatograph (Agilent 6890, USA) equipped with a DB-5 capillary column (30 m length × 0.32 mm inside diameter × 0.25 μm film thickness), a ^{63}Ni electron capture detector and an HP 7683 auto-sampler. Nitrogen (purity > 99.999%) was used as the carrier gas at a flow rate of 1.5 mL min^{-1}. The column temperature was programmed from 60 °C (1 min) to 140 °C at 20 °C min^{-1} and then to 280 °C (5 min) at 8 °C min^{-1}. The injector and detector temperatures were 220 °C and 300 °C, respectively. The injection volume was 1 μL in the splitless mode. The detection limit was 1 pg μL^{-1}.

2.9. Quality control and data analysis

To estimate the recovery of HCB in the sorption experiment, blank samples without sorbents were prepared and analyzed using the same procedure in Section 2.3. The average recovery of HCB in blank samples was 96.2 ± 2.1%. To estimate the recoveries of HCB residues in soil and in earthworm, a recovery study was carried out by spiking HCB (2 μg) to 10 g of soil or 2 g of earthworm. The extraction and purification of the samples were performed using the procedure described in Section 2.6. The average recoveries for 3 replicates were 91.6 ± 4.3% in soil and 99.9 ± 2.5% in earthworm. To estimate the recovery of HCB extracted by hexane from HPCD, 10 μg mL^{-1} HCB (2.5 μg in 250 μL acetone) was spiked to 25 mL HPCD, followed by extraction with hexane as described in Section 2.7.1. The average recovery for 3 replicates was 96.2 ± 5.2%.

The sorption isotherms of HCB, for both biochar and soil, were generated by fitting the data into the Freundlich model [21]:

$$Q_e = K_f C_e^n \quad (1)$$

where Q_e and C_e are the amounts of HCB sorbed (μg g^{-1}) and the equilibrium solution concentration (μg L^{-1}), respectively; n is an empirical exponent indicative of isotherm nonlinearity and K_f is a Freundlich unit capacity coefficient [(μg g^{-1})/(μg L^{-1})^n].

Table 1
Physico-chemical properties of soil and wheat straw biochar.

	Soil	Biochar
pH	7.56	10.51
Organic matter (%)	3.61	–[a]
Total C (%)	3.10	48.53
Total N (%)	0.14	0.46
Total P (%)	0.09	0.11
Total K (%)	2.31	5.24
Clay (%)	13.61	–
Silt (%)	63.11	–
Sand (%)	23.28	–
Specific surface area (m^2 g^{-1})	–	4.81
Pore volume (cm^3 g^{-1})	–	0.0051
Pore width (nm)	–	5.00

[a] (–) not determined.

The dissipation of HCB in soil was evaluated by fitting the data into a modified first-order kinetics equation [22]:

$$C = C_0[\lambda + (1-\lambda)e^{-kt}] \quad (2)$$

where C (μg g^{-1}) and C_0 (μg g^{-1}) are the concentrations of HCB in soil at time t and time 0 (initial concentration), respectively; λ is the coefficient of non-bioavailable fraction of HCB in soil; k is the first-order rate constant.

The extent of earthworm accumulation of HCB was expressed using a biota-soil accumulation factor (BSAF) [23]:

$$\mathrm{BSAF} = \frac{C_{worm}}{C_{soil}} \quad (3)$$

where C_{worm} (μg g^{-1}) and C_{soil} (μg g^{-1}) are the concentrations of HCB in earthworm (dry weight) and in soil, respectively.

All statistical data analysis was done with SPSS 17.0 and the significance level was $p < 0.05$.

3. Results and discussion

3.1. Biochar properties

The physico-chemical properties of biochar and soil are shown in Table 1. The pH of the biochar was 10.51, which is in agreement with other reported values in literature [2]. The biochar had a total carbon content of 48.53%, which was higher than that reported for wheat ash [24,25]. The specific surface area of biochar was 4.81 m^2 g^{-1}, which is similar with that reported for wheat ash [24].

3.2. Sorption of HCB by soil and biochar

The sorption isotherms of HCB to soil and biochar fitted well into the Freundlich model (R^2 was 0.96 and 0.93 for soil and biochar, respectively) and are shown in Fig. 1. The Freundlich coefficient, n, for soil and biochar were 0.70 ± 0.05 and 0.98 ± 0.09, respectively, indicating that the sorption of HCB to biochar for the concentrations examined was linear. The K_f values for soil and biochar were 2.01 ± 1.27 and 86.16 ± 1.26, respectively, indicating that biochar was 42 times more effective in HCB sorption compared to soil.

For biochar sorption, both non-linear and linear sorption isotherms of organic compounds have been reported and were attributed to surface-adsorption dominant and partition-dominant processes, respectively [4,21]. The linear sorption of HCB by biochar (Fig. 1) might be ascribed to partitioning into the noncarbonized organic phase since the surface area of biochar in this study was not so high (Table 1). Linear partitioning of atrazine to biochar derived at low temperature of 350 °C has also been reported [26]. Besides the surface area, porosity, aromatic components and surface functional groups are also important factors affecting the sorption affinity of biochar [21]. The HCB molecule could enter into the

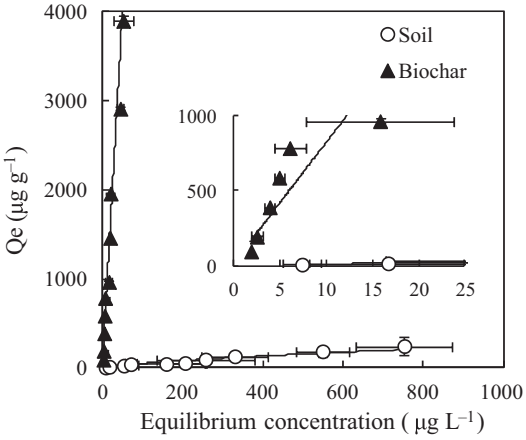

Fig. 1. Sorption isotherms of HCB by soil and wheat straw biochar (dots: measured data; curves: Freundlich model fitted).

mesopores of biochar given that the biochar used had large pore volumes and enough pore width (Table 1). The pore-filling could also result in a linear isotherm [21]. The observed linear isotherm, in spite of the high HCB concentration used in the experiment, indicates the high sorption affinity of the sorbents for HCB. This implies that much higher HCB concentrations would be required for non-linear sorption to occur. The higher K_f values for biochar further emphasize the strong sorption ability of biochar for HCB, and by extension non-polar organic compounds.

3.3. FTIR analysis

The FTIR spectra of biochar before and after reaction with HCB are shown in Fig. 2. Different bands in the spectra represented different vibrations of functional groups in biochar [20]. The broad band at 3600–3100 cm^{-1} was assigned to O—H stretching [27]. The bands at 2967, 2924, 2856 and 1370 cm^{-1} were assigned to aliphatic CH_2 stretching, indicating that the original organic residues – such as polymeric and fatty acids – existed in the biochar [20]. Other bands represent stretches due to C=O in carboxylic and ester groups (1704 cm^{-1}), C=C and C=O in aromatic rings (1590 cm^{-1}), COOH and CHO (1437 cm^{-1}) and aromatic C—H (1200 – 1110 cm^{-1} and 876, 812, 754 cm^{-1}) [4,28]. The benzene skeleton vibration (1340 and 1290 cm^{-1}) and bending vibration of C—Cl (696 cm^{-1}) of HCB were also detected in the biochar-HCB sample,

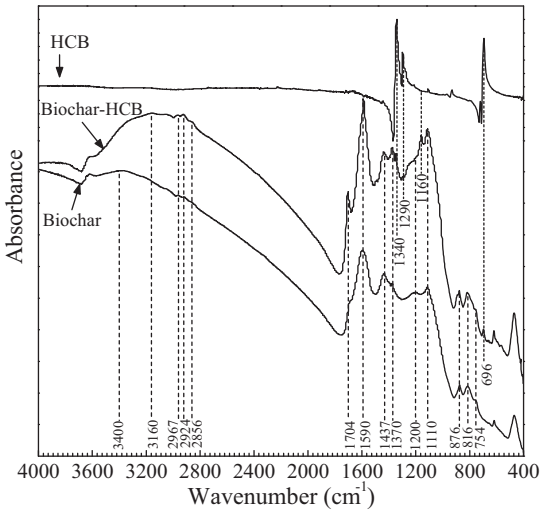

Fig. 2. FTIR spectra of wheat straw biochar before and after reaction with HCB.

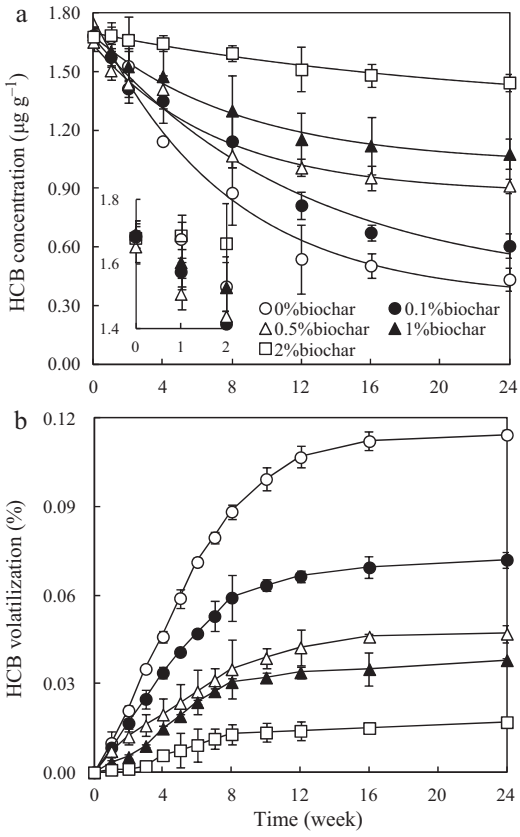

Fig. 3. Time course of HCB residues (a) and volatilization (b) in soils amended with different percentages of wheat straw biochar (dots in (a): measured data; curves in (a): modified first-order kinetics model fitted).

without chemical shift, indicating that physical sorption of HCB to biochar might have occurred.

3.4. Dissipation of HCB from soil

The residues and volatilization of HCB with time in biochar-amended and unamended (0%) treatments are shown in Fig. 3. In the first 2 wk, faster dissipation of HCB was observed in the 0.1% and 0.5% biochar-amended treatments compared to the 0% treatment. This might be due to nutritional stimulation of biochar application for native microorganisms. The nutrients in biochar could be released into soil within 1 wk after application [23] and thereby stimulate soil microbial activity [13]. However, after 4 wk, a significant decrease in HCB dissipation was noted in the biochar-amended soils (Fig. 3a). The HCB residues in soil increased with increasing biochar content while the volatilization of HCB decreased with increasing biochar content (Fig. 3). The 0% treatment showed the highest volatilization at each sampling point and this led to the highest accumulated volatilization losses after 24 wk of incubation. In contrast, significantly lower volatilizations were detected in biochar-amended treatments ($p < 0.05$).

The dissipation of HCB in soil fitted well into the modified first-order kinetics model (Table 2). The non-bioavailable coefficient, λ, increased with increasing content of biochar in soil, indicating decreased bioavailability of HCB in biochar-amended treatments and further indicating that sorption inhibition of HCB bioavailability – rather than nutritional stimulation – was the dominant factor affecting the dissipation of HCB in biochar-amended soil. This could be confirmed, firstly, by the strong sorption affinity of biochar (Fig. 1) and, secondly, by the phenomenon that the lesser the dissipation of HCB, the lesser the volatilization of HCB that occurred

Table 2
Residues of HCB in soils amended with different percentages of wheat straw biochar after 24 wk of incubation and their regression equations fitted into the modified first-order kinetics model.

Biochar amendment	Residue (%)	Modified first-order kinetics model fitted			
		C_0[a]	λ[b]	k[c]	R^2
0%	25.86 ± 3.02	1.78 ± 0.21	0.18 ± 0.06	0.13 ± 0.03	0.98
0.1%	35.99 ± 3.64	1.67 ± 0.31	0.23 ± 0.10	0.08 ± 0.02	0.98
0.5%	55.38 ± 2.31	1.64 ± 0.13	0.53 ± 0.04	0.14 ± 0.03	0.97
1%	63.72 ± 3.89	1.68 ± 0.08	0.61 ± 0.02	0.12 ± 0.02	0.99
2%	85.99 ± 2.56	1.69 ± 0.25	0.76 ± 0.08	0.04 ± 0.02	0.97

[a] C_0: concentrations of HCB in soil at start time.
[b] λ: coefficient of non-bioavailable fraction of HCB in soil.
[c] k: first-order rate constant.

(Fig. 3). Reports have shown that high biodegradation of chlorobenzenes in soil results in decreased volatilization of chlorobenzenes, whenever biodegradation is the dominant process [22,29]. This contrasts with our findings in this study and it can therefore be inferred that HCB was getting sorbed to biochar and becoming non-available for degradation and volatilization processes.

3.5. Butanol and HPCD extractions of HCB from soil

As shown in Fig. 4, the butanol- and HPCD-extraction efficiencies of HCB in soil, expressed as percentages of the HCB extracted by ASE at each sampling time, decreased with increasing aging period. Amendment with biochar significantly reduced the extractability of HCB in soil, indicating the strong sorption ability of biochar. Even for the 0.1% biochar-amended treatment, significantly lower ($p < 0.05$) chemical extraction efficiencies, relative to the 0% treatments, were observed. The HPCD extraction efficiency showed the same trend as the butanol extraction efficiency for different treatments, but was lower than the butanol extraction efficiency over the whole incubation period, regardless of treatment or aging period. This could be explained by the fact that butanol is a mild-extraction solvent while HPCD acted as a sink in the extraction procedure, and this resulted in different interaction mechanisms during extraction [15]. Butanol could directly contact soil or biochar particles during extraction while in HPCD extraction HCB is first desorbed from soil or biochar particles, dissolved into water and then captured by HPCD [30].

3.6. Earthworm accumulation of HCB in soil

Strong sorption of contaminants by biochar may result in the formation of hot spots, containing significantly higher concentrations of contaminants relative to the surrounding soil [7]. Therefore, soil mesofauna such as earthworm might ingest the biochar particles and thus result in high accumulation of contaminants. However, as shown in Fig. 5, both the BSAF and concentrations of HCB in earthworm decreased markedly with increasing biochar application rate and decreased after 24 wk – compared to 1 wk – of incubation, for both biochar-amended and unamended treatments ($p < 0.05$). Li et al. [31] reported that earthworm avoidance, which occurs in soil amended with as low as 10% biochar, could be mitigated by wetting. In the present study, earthworm avoidance might not occur due to the low content of biochar and the high soil water content in the bioassay experiment. Bioaccumulation of hydrophobic organic pollutants by *E. foetida* is an equilibrium process and mainly occurs through their outer epidermis [32]. Therefore, the low earthworm accumulation of HCB in biochar-amended soils could be explained by the reduced concentration of HCB in the soil liquid phase as a result of the strong sorption by biochar, and this

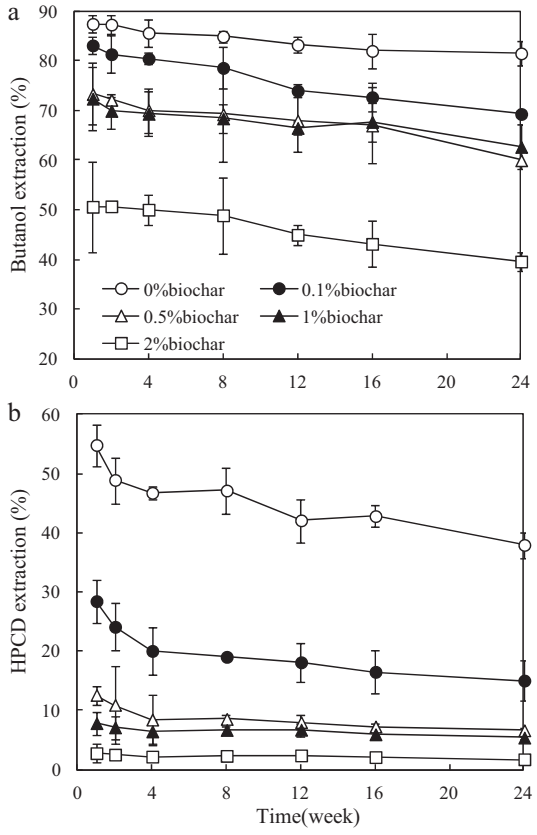

Fig. 4. Butanol extraction (a) and HPCD extraction (b) of HCB from soils amended with different percentages of wheat straw biochar. Extraction efficiencies were the percentages of the HCB extracted by ASE at each sampling time.

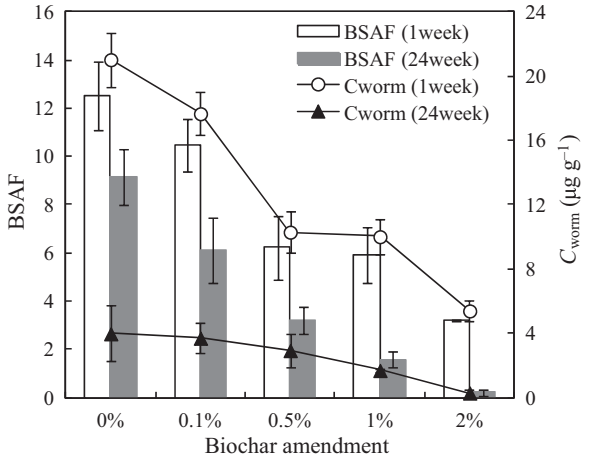

Fig. 5. Biota-soil accumulation factor (BSAF) and the concentrations of HCB in earthworm (C_{worm}) from soils amended with different percentages of wheat straw biochar after 1 wk and 24 wk of incubation.

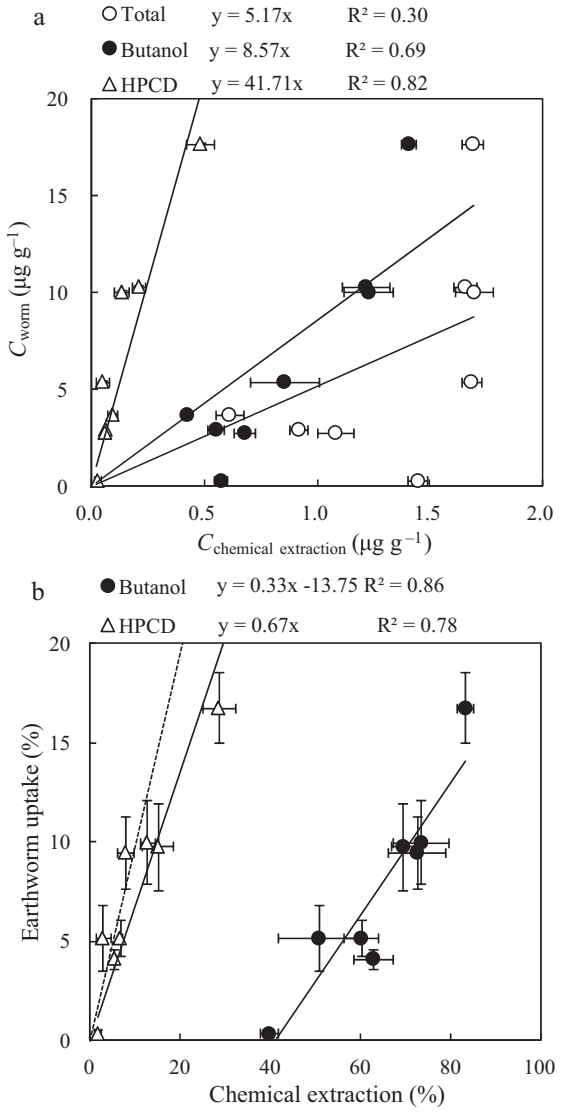

Fig. 6. Correlations between earthworm accumulated concentrations and different chemical extracted concentrations (a) and between chemical extractions and earthworm uptake percentages (b) in biochar-amended soils. The dotted line in (b) is the 1:1 line.

could demonstrate that biochar reduces the risk of HCB transportation in the food chain.

3.7. Evaluation of chemical extractions

The earthworm bioassay experiment was used to evaluate the suitability of chemical extractions to predict bioavailability of HCB in soil. As shown in Fig. 6a, the earthworm-accumulated concentrations of HCB correlated poorly with the total concentration of HCB in soil, but correlated well with butanol and HPCD extractions, indicating that chemical extractions are more reliable than exhaustive extraction in bioavailability assessment. However, the correlation coefficients of both concentrations, and the percentages between HPCD extraction and earthworm uptake of HCB from soil, were not only higher but also closer to the 1:1 line, compared to the butanol extraction (Fig. 6). The correlation coefficient between the earthworm-accumulated concentration and the butanol-extracted concentration of HCB in biochar-amended soil (0.69) was lower than that in soil without biochar (0.98) in our previous experiment [16]. These results indicate that HPCD extraction is more reliable than butanol extraction in bioavailability assessment of HCB in biochar-amended soil and that the suitability of chemical extractions might be specific for soil with and without biochar. Therefore, the selection of chemical extraction methods to assess the bioavailability of contaminants in soil in the presence of biochar needs rethinking.

3.8. Bioavailability of HCB in soil affected by biochar

The reduced dissipation (Fig. 3), reduced HPCD extraction (Fig. 4) and reduced earthworm accumulation (Fig. 5) of HCB in biochar-amended treatments, all indicate that application of biochar reduced the bioavailability of HCB in soil, and this resulted from the strong sorption affinity of biochar [6,10]. The sorption affinity of biochar, after amendment with soil, was different from that in liquid solution medium due to biochar interaction with soil organic matter and minerals over time [2]. The sorption of HCB in biochar-amended soil could be divided into two parts: a part sorbed by soil organic matter and another sorbed by biochar. Compounds sorbed by dissolved organic carbon (DOC) could increase their mobilization and thus bioavailability [33]. However, the DOC released from soil could also be sorbed by biochar [25]. Similarly, the DOC released from biochar could be sorbed by soil, resulting in competition with HCB for sorption sites or even provision of additional sites for HCB sorption on the soil surface [34]. Moreover, the mineral surfaces may cover the surfaces of biochar over time and, therefore, the compounds sorbed in the pore spaces would not be released, resulting in long-lasting reduced bioavailability [5]. Therefore, the sorption and interaction between biochar and soil resulted in reduced bioavailability of HCB.

Both the HPCD extraction and earthworm bioassay results showed the reduction of HCB bioavailability in biochar-amended soil of over half a year, even at the 0.1% application rate (Figs. 4 and 5). On average, the production of wheat straw biochar from field burning would result in a char content of 0.024–0.066% in the soil [4,6]. A higher content may occur in agricultural soils due to the annual burning of wheat residues, and the biochar aged in soil for 2 years still had a high sorption affinity [7,25]. Therefore, biochar in agricultural soils may play an important role in affecting the bioavailability of pesticides or POPs, such as reducing plant uptake [11]. Moreover, the 50 mM HPCD solution could not efficiently extract HCB from biochar-amended soil (Fig. 4b), indicating that biochar not only reduced the bioavailability of HCB in soil, but also reduced the risk of HCB leaching to ground water. Therefore, biochar showed great potential for use in immobilization or stabilization technologies to minimize plant uptake, leaching and transport along the food chain of POPs in contaminated sites. The length of time the pollutants remain strongly sorbed by biochar in soil is of importance and needs more systematic research.

4. Conclusions

Wheat straw biochar has great sorption capacity for HCB, and its sorption for the compound is stronger than that of the soil used in the study. HPCD extraction is more reliable than butanol extraction in bioavailability assessment of HCB in soil, in the presence of biochar. Amendment of soil with biochar significantly decreases the dissipation and volatilization of HCB from soil and thus results in reduced bioavailability of HCB, even for low biochar application rates. Therefore, wheat straw biochar has great potential for immobilizing POPs in soil.

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References

[1] S. Steinbeiss, G. Gleixner, M. Antonietti, Effect of biochar amendment on soil carbon balance and soil microbial activity, Soil Biol. Biochem. 41 (2009) 1301–1310.
[2] S.P. Sohi, E. Krull, E. Lopez-Capel, R. Bol, A review of biochar and its use and function in soil, Adv. Agron. 105 (2010) 47–82.
[3] D. Woolf, J.E. Amonette, F.A. Street-Perrott, J. Lehmann, S. Joseph, Sustainable biochar to mitigate global climate change, Nat. Commun. 1 (2010) 56–65.
[4] Y. Chun, G.Y. Sheng, C.T. Chiou, B.S. Xing, Compositions and sorptive properties of crop residue-derived chars, Environ. Sci. Technol. 38 (2004) 4649–4655.
[5] R.S. Kookana, The role of biochar in modifying the environmental fate, bioavailability, and efficacy of pesticides in soils: a review, Aust. J. Soil Res. 48 (2010) 627–637.
[6] Y.N. Yang, G.Y. Sheng, M.S. Huang, Bioavailability of diuron in soil containing wheat-straw-derived char, Sci. Total Environ. 354 (2006) 170–178.
[7] D.L. Jones, G. Edwards-Jones, D.V. Murphy, Biochar mediated alterations in herbicide breakdown and leaching in soil, Soil Biol. Biochem. 43 (2011) 804–813.
[8] V.A. Loganathan, Y. Feng, G.D. Sheng, T.P. Clement, Crop-residue-derived char influences sorption, desorption and bioavailability of atrazine in soils, Soil Sci. Soc. Am. J. 73 (2009) 967–974.
[9] P. Zhang, G.Y. Sheng, Y.H. Feng, D.M. Miller, Predominance of char sorption over substrate concentration and soil pH in influencing biodegradation of benzonitrile, Biodegradation 17 (2006) 1–8.
[10] P. Zhang, G.Y. Sheng, D.C. Wolf, Y.C. Feng, Reduced biodegradation of benzonitrile in soil containing wheat-residue-derived ash, J. Environ. Qual. 33 (2004) 868–872.
[11] X.Y. Yu, G.G. Ying, R.S. Kookana, Reduced plant uptake of pesticides with biochar additions to soil, Chemosphere 76 (2009) 665–671.
[12] C. Xu, W. Liu, G.D. Sheng, Burned rice straw reduces the availability of clomazone to bamyardgrass, Sci. Total Environ. 392 (2008) 284–289.
[13] L. Beesley, E. Moreno-Jimenez, J.L. Gomez-Eyles, Effects of biochar and greenwaste compost amendments on mobility, bioavailability and toxicity of inorganic and organic contaminants in a multi-element polluted soil, Environ. Pollut. 158 (2010) 2282–2287.
[14] P. Zhang, G.Y. Sheng, Y.C. Feng, D.M. Miller, Role of wheat-residue-derived char in the biodegradation of benzonitrile in soil: nutritional stimulation versus adsorptive inhibition, Environ. Sci. Technol. 39 (2005) 5442–5448.
[15] B.J. Reid, K.C. Jones, K.T. Semple, Bioavailability of persistent organic pollutants in soils and sediments – a perspective on mechanisms, consequences and assessment, Environ. Pollut. 108 (2000) 103–112.
[16] Y. Song, F. Wang, X.L. Yang, C.Y. Liu, F.O. Kengara, X. Jin, X. Jiang, Chemical extraction to assess the bioavailability of chlorobenzenes in soil with different aging periods, J. Soil Sediment. 11 (2011) 1345–1354.
[17] J.L. Gomez-Eyles, T. Sizmur, C.D. Collins, M.E. Hodson, Effects of biochar and the earthworm *Eisenia fetida* on the bioavailability of polycyclic aromatic hydrocarbons and potentially toxic elements, Environ. Pollut. 159 (2011) 616–622.
[18] L. Beesley, E. Moreno-Jimenez, J.L. Gomez-Eyles, E. Harris, B. Robinson, T. Sizmur, A review of biochars' potential role in the remediation, revegetation and restoration of contaminated soils, Environ. Pollut. 159 (2011) 3269–3282.
[19] R.K. Lu, Soil Agricultural Chemistry Analytical Methods, Chinese Agricultural Science and Technology Press, Beijing, 2000.
[20] B. Chen, D. Zhou, L. Zhu, Transitional adsorption and partition of nonpolar and polar aromatic contaminants by biochars of pine needles with different pyrolytic temperatures, Environ. Sci. Technol. 42 (2008) 5137–5143.
[21] X. Wang, B. Xing, Sorption of organic contaminants by biopolymer-derived chars, Environ. Sci. Technol. 41 (2007) 8342–8348.
[22] Y. Song, F. Wang, F.O. Kengara, Y.R. Bian, X.L. Yang, C.Y. Liu, X. Jiang, Improved biodegradation of 1,2,4-trichlorobenzene by adapted microorganisms in agricultural soil and in soil suspension cultures, Pedosphere 21 (2011) 423–431.
[23] B. Wen, R.J. Li, S.Z. Zhang, X.Q. Shan, J. Fang, K. Xiao, S.U. Khan, Immobilization of pentachlorophenol in soil using carbonaceous material amendments, Environ. Pollut. 157 (2009) 968–974.
[24] Y.N. Yang, G.Y. Sheng, Enhanced pesticide sorption by soils containing particulate matter from crop residue burns, Environ. Sci. Technol. 37 (2003) 3635–3639.
[25] Y.N. Yang, G.Y. Sheng, Pesticide adsorptivity of aged particulate matter arising from crop residue burns, J. Agric. Food Chem. 51 (2003) 5047–5051.
[26] X. Cao, L. Ma, B. Gao, W. Harris, Dairy-manure derived biochar effectively sorbs lead and atrazine, Environ. Sci. Technol. 43 (2009) 3285–3291.
[27] B. Chen, Z. Chen, S. Lv, A novel magnetic biochar efficiently sorbs organic pollutants and phosphate, Bioresour. Technol. 102 (2011) 716–723.
[28] X. Cao, W. Harris, Properties of dairy-manure-derived biochar pertinent to its potential use in remediation, Bioresour. Technol. 101 (2010) 5222–5228.
[29] F. Wang, U. Döfler, M. Schmid, D. Fischer, L. Kinzel, H. Scherb, J.C. Munch, X. Jiang, R. Schroll, Homogeneous inoculation vs. microbial hot spots of isolated strain and microbial community: what is the most promising approach in remediating 1,2,4-TCB contaminated soils? Soil Biol. Biochem. 42 (2010) 331–336.
[30] T. Hartnik, J. Jensen, J.L.M. Hermens, Nonexhaustive beta-cyclodextrin extraction as a chemical tool to estimate bioavailability of hydrophobic pesticides for earthworms, Environ. Sci. Technol. 42 (2008) 8419–8425.
[31] D. Li, W.C. Hockaday, C.A. Masiello, P.J.J. Alvarez, Earthworm avoidance of biochar can be mitigated by wetting, Soil Biol. Biochem. 43 (2011) 1732–1737.
[32] J.L. Gomez-Eyles, C.D. Collins, M.E. Hodson, Relative proportions of polycyclic aromatic hydrocarbons differ between accumulation bioassays and chemical methods to predict bioavailability, Environ. Pollut. 158 (2010) 278–284.
[33] S. Tao, F.L. Xu, W.X. Liu, Y.H. Cui, R.M. Coveney, A chemical extraction method for mimicking bioavailability of polycyclic aromatic hydrocarbons to wheat grown in soils containing various amounts of organic matter, Environ. Sci. Technol. 40 (2006) 2219–2224.
[34] A. Cabrera, L. Cox, K.A. Spokas, R. Celis, M.C. Hermosin, J. Cornejo, W.C. Koskinen, Comparative sorption and leaching study of the herbicides fluometuron and 4-chloro-2-methylphenoxyacetic acid (MCPA) in a soil amended with biochars and other sorbents, J. Agric. Food Chem. 59 (2011) 12550–12560.