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Biochar reduces the bioavailability of di-(2-ethylhexyl) phthalate in soil

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HIGHLIGHTS

- Biochar increases the retention of di-(2-ethylhexyl) phthalate (DEHP) in soils.
- High soil organic carbon content can decrease the bioavailability of DEHP.
- Biochar significantly decreases the potential risk of human uptake of DEHP.
- Effect of biochar on DEHP fate depends on soil organic carbon content and biochar types.

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ABSTRACT

A pot experiment was conducted to evaluate the effect of biochars on the bioavailability of di-(2-ethylhexyl) phthalate (DEHP) in two soils using *Brassica chinensis* L. as an indicator plant. The residual concentrations of DEHP tended to be higher in the biochar-amended soils than in the control soils. They were lower ($p < 0.05$) in the high organic carbon content soil (HOC; 2.2%C) than in the low organic carbon content soil (LOC; 0.35%C). The DEHP concentrations in plant shoots grown in the HOC soils were lower than those in the LOC soils ($p < 0.05$). Compared to the control, the biochar addition decreased the DEHP concentrations in shoots grown in the LOC soils; whereas there was no significant difference in the HOC soils. Our results showed that soil OC content as well as biochar properties are the key factors influencing the bioavailability of DEHP in soils.

1. Introduction

Phthalic acid esters (PAEs) are a class of plasticizer compounds most commonly used in the world (Graham, 1973). Their global production is approximately 6.0 million tons per year (Xie et al., 2007), while the current consumption is more than 0.87 million tons per year in China and is predicted to increase (Teil et al., 2006). The compound di-(2-ethylhexyl) phthalate (DEHP) is the most frequently added plasticizer for making polyvinylchloride (PVC) which is used commonly in greenhouse and agricultural mulch. Meanwhile, a previous study showed that only 41% of the DEHP added to the soil was degraded within one year (Madsen et al., 1999), indicating that DEHP is persistent in soil (Shanker et al., 1985). Its low degradation rate and wide use make it the most dominant PAE compound in soil (Ejlertsson et al., 1997; Katayama et al., 2010). Although DEHP has a relatively low acute toxicity compared to other PAEs of small molecules (e.g. di-n-butyl phthalate) (Shanker et al., 1985; Cartwright et al., 2000), it has been listed as a priority pollutant by many countries around the world mainly because of its disrupt endocrine function

Abbreviations: DEHP, di-(2-ethylhexyl) phthalate; LOC, low organic carbon content soil; HOC, high organic carbon content soil; LC, Low organic carbon content (LOC) soil without biochar (Control); LS, LOC soil with 2% straw biochar (w/w); LB, LOC soil with 2% bamboo biochar (w/w); HC, High organic carbon content (HOC) soil without biochar (Control); HS, HOC soil with 2% straw biochar (w/w); HB, HOC soil with 2% bamboo biochar (w/w); OC, organic carbon.

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in humans, such as hepatocellular carcinoma, anovulation and fetal growth retardation (Hauser and Calafat, 2005). In order to avoid the risk of DEHP accumulation in humans, it is important to reduce DEHP pollution in soils and crops to minimize the contamination through the food chain.

Biochar is known as black carbon that is formed by the pyrolysis of biomass and is referred to as a 'super sorbent' for contaminants (Shang et al., 2012). Many studies have shown that soil amendment with biochar could enhance soil adsorption of contaminants and thus reduce their bioavailability and leaching risk (Cabrera et al., 2011; Lü et al., 2012; Song et al., 2013). Some researchers have also investigated the uptake of DEHP in vegetables (Fu and Du, 2011; Wu et al., 2013). However, there is very little information on the effect of biochar amendment on the adsorption of DEHP in soils and on DEHP's bioavailability in biochar amended soils. In this paper, we investigated the effect of biochar on the adsorption and bioavailability of DEHP using *Brassica chinensis* L. as an indicator plant in different soils.

2. Materials and methods

2.1. Chemicals

The chemicals DEHP, acetone, dichloromethane and n-hexane were all analytical grade with purity more than 99.5% (Shanghai Lingfeng Chemical Reagent Co., Ltd., China). A stock solution of 40 mg mL^{-1} DEHP was prepared in acetone.

2.2. Biochar samples

The bamboo sawdust and rice straw were oven-dried at 60 °C for 24 h, subsequently pyrolyzed at 500 °C and held for 3 h in the pyrolyzing furnace. The two biochars were ground and passed through a 0.4-mm sieve prior to use. Some relevant properties of the two biochars are shown in Table 1.

2.3. Soil samples

The soils were taken from the surface layer (0–20 cm depth) of two adjacent fields in Lin'an, Hangzhou, China. Both soils were Ferralosols; one of the two soils has been used for growing vegetables and the related long-term intensive fertilization management has lead to a relatively high organic carbon (OC) content of 2.2%C in the topsoil (HOC), while the second soil has been fallow for approximately the same time period, which resulted in a lower OC content of 0.35%C (LOC). Detailed soil parameters are shown in Table 2.

The air-dried soils were passed through a 2-mm sieve prior to use. We sprayed 100 mL DEHP stock solution onto 1 kg of each soil, which provided a DEHP concentration of 4000 mg kg^{-1}. The treated soils were then gradually diluted with clean soil material until the soil's DEHP concentration was 100 mg kg^{-1}. This final concentration was chosen according to previous research (Yin et al., 2004; Qin et al., 2008), who showed the significant influence of this concentration on plant growth without killing the plants.

Table 2
Selected properties of the high organic carbon content (HOC) soil and the low organic carbon content (LOC) soil in the pot trial.

Soil	pH	[a]CEC (cmol kg^{-1})	Electrical conductivity (ds m^{-1})	[b]OC (%)	[c]TN (%)	Soil texture (%)		
						Sand	Silt	Clay
HOC	6.0	5.1	0.2	2.2	0.2	38.6	45.0	16.4
LOC	5.8	4.1	0.3	0.35	0.03	38.7	44.4	16.9

[a] CEC: cation exchange capacity.
[b] OC%: organic carbon content.
[c] TN%: total nitrogen content.

2.4. Pot experiment

For the experiment the soils spiked with DEHP were then either amended with bamboo or rice straw biochar at a rate of 2% (dry weight, w/w). The controls did not receive any biochar. This resulted in a total of six treatments with three replications. Each ceramic pot (height: 18 cm; diameter: 25 cm) was loosely filled with 3.5 kg of soil. The soils absorbed water from the bottom until the soil surface was wetted. Since the experiment was set in the hottest season in China, we chose *B. chinensis* L. which is resistant to high temperature and grows during summer as the indicator plant. Ten seeds of *B. chinensis* L. were planted at equal spacing in every pot. In each pot, 5 seedlings were kept after transplanting at the stable growth period. All pots were fertilized with urea and KH_2PO_4 at a dose of N 0.25 g kg^{-1}, P_2O_5 0.32 g kg^{-1}, K_2O 0.2 g kg^{-1}, and were arranged in a randomized complete block design in a glass greenhouse. During the growth process, regular watering (2–4 times a week) was maintained to prevent drought stress. After 50 days, *B. chinensis* L. was mature, and its shoots were harvested. The plant shoots were rinsed with deionized water and were then oven-dried at 105 °C for 0.5 h in paper bags to deactivate enzymes, followed by drying at 65 °C to achieve constant weight. A soil sample was taken from each pot with a stainless steel corer (length: 25 cm; diameter: 2 cm) and then air-dried. The shoot and soil samples were then ground to 0.25 mm. Plastic equipment was avoided throughout the procedure to eliminate DEHP background contamination.

2.5. Extraction of DEHP from plant shoots and soils

About 0.2 g of the oven-dried plant sample was weighed into a 35-mL Teflon centrifuge tube and supplemented with 1.0 g anhydrous sodium sulfate (Na_2SO_4) and 10 mL solvent mixture (dichloromethane:acetone = 1:1, v/v). Subsequently, the sample was extracted in an ultrasonic bath for 10 min at room temperature and then centrifuged at 10,000 rpm (11179 g) for 5 min, after which the aqueous supernatant was collected. The remaining sample residue was extracted with another 10 mL solvent mixture following the previous steps. Then the supernatants were combined in a 250-mL separating funnel, and 100 mL 6% Na_2SO_4 solution was added. The funnel was vigorously shaken, and the organic layer was transferred into a 100-mL round-bottom flask and allowed to evaporate until the extracted volume was reduced to about 2 mL using a rotary evaporator (Yin et al., 2003). The concentrated sample was then transferred to a graduated test tube and

Table 1
Selected properties of the straw biochar (SB) and bamboo biochar (BB) used in the pot trial.

Biochar	[a]N (%)	[a]C (%)	[a]H (%)	[a]O (%)	Organic carbon content (%)	pH	Ash content (%)	Electrical conductivity (ds m^{-1})	Specific surface area (m^2 g^{-1})
SB	1.0	56.9	1.9	40.1	51.8	10.0	27.7	5.2	44.0
BB	0.8	85.2	2.7	11.3	82.4	9.4	2.9	0.7	0.2

[a] N, C, H, O% means nitrogen, carbon, hydrogen and oxygen content of the biochar.