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Research article

Phytoavailability of Cd and Pb in crop straw biochar-amended soil is related to the heavy metal content of both biochar and soil

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ABSTRACT

Crop straw biochar incorporation may be a sustainable method of amending soil, but feedstock-related Cd and Pb content is a major concern. We investigated the effects of heavy metal-rich (RC) and -free biochar (FC) on the phytoavailability of Cd and Pb in two acidic metalliferous soils. Biochar significantly increased soil pH and improved plant growth. Pb in soil and plant tissues significantly decreased after biochar application, and a similar pattern was observed for Cd after FC application. RC significantly increased NH_4NO_3-extractable Cd in both lightly contaminated (YBS) and heavily contaminated soils (RS). The Cd content of plants grown on YBS increased, whereas it decreased on RS. The Cd and Pb input–output balance suggested that RC application to YBS might induce a soil Cd accumulation risk. Therefore, identifying heavy metal contamination in biochar is crucial before it is used as a soil amendment.

1. Introduction

Biochar is produced by the incomplete pyrolysis of biomass under the partial or total absence of oxygen (Cao et al., 2009). Crop residues, wood chips, and animal manure serve as biochar feedstocks (Tang et al., 2013). Recently, the pyrolysis of crop straw into biochar and using it as a soil amendment has begun to attract attention in China (Fan et al., 2012). Biochar has a large surface area, high porosity, an alkaline pH, is ideally suited for sequestrating C in soil, and can act as a long-term soil C store for hundreds of years (Atkinson et al., 2010; Pietikäinen et al., 2000; Sohi et al., 2010). For these reasons, recent studies have highlighted the benefits of biochar, e.g., by improving soil properties (Van Zwieten et al., 2010), increasing crop biomass (Xu et al., 2015), and remediating polluted soils (Bian et al., 2014; Karami et al., 2011; Park et al., 2011).

In China, it is common practice to burn crop straw in the open air after harvesting. According to preliminary statistics, the total annual quantity of crop straw in China is 600 million tons, approximately a third of which is burned (Cao et al., 2006; Zhu et al., 2005). Biochar made from crop straw has been widely used as a soil amendment (Shen et al., 2014). Previous studies have indicated that the addition of crop straw biochar could reduce the phytoavailability of heavy metals in the soil. For example, Houben et al. (2013) conducted an incubation experiment and found that the addition of 10% (w/w) biochar significantly decreased 0.01 M $CaCl_2$-extractable levels of Cd, Zn, and Pb in contaminated soil by 71%, 87%, and 92%, respectively. Bian et al. (2014) reported that the application of crop straw biochar to contaminated paddy soils significantly decreased rice Cd uptake. Lu et al. (2014) found that rice straw biochar was effective in reducing shoot Cu and Pb concentrations, while bamboo biochar was effective in reducing Cd. The authors suggested that the influence of biochar on heavy metal bioavailability varied, not only with the biochar feedstock and application rate, but also with the metal species studied (Lu et al., 2014). These previous studies demonstrated that soil remediation with biochar could effectively reduce the phytoavailability and ecotoxicity of Cd and Pb, and provided a theoretical basis for the amendment of soils polluted by heavy metals.

Soil heavy metal contamination is a worldwide problem (Gray et al., 2006). Approximately 2.0×10^7 ha of farmland (occupying 19.4% of total farmland) in China has been contaminated by heavy

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metals (mainly Cd and Pb), predominantly in paddy fields (Ministry of Environmental Protection P.R.C. and Ministry of Land and Resources P.R.C., 2014). The contaminated paddy soil might be remediated using various measures and remain in crop production (attempted to use as industrial raw materials), in the next few years. Accordingly, plenty of heavy metal-rich rice straw should be produced for crop straw accumulates considerable amounts of Cd and Pb (Bian et al., 2014; Wang et al., 2015). The heavy metal-rich straw will be mainly returning to field directly or as biochar. After the pyrolysis of crop straw into biochar, the risk of Cd and Pb being incorporated into the soil may increase. The objective of this study was to investigate the effects of biochar application on Cd and Pb levels in contaminated soils.

2. Materials and methods

2.1. Soil and biochar

A lightly contaminated soil was collected (0–20 cm depth) at Guiyang City, Guizhou Province, China, which was derived from Quaternary red clay and classified (Chinese Soil Taxonomy) as a yellow-brown soil (YBS). Its total Cd and Pb content was 0.91 mg kg^{-1} and 25.27 mg kg^{-1}, respectively, and the NH_4NO_3-extractable Cd and Pb content was 0.02 mg kg^{-1} and 0.46 mg kg^{-1}, respectively. A heavily contaminated soil was collected (0–20 cm depth) at Zhuzhou City, Hunan Province, China, which was derived from Quaternary red clay and classified (Chinese Soil Taxonomy) as a red soil (RS). The total Cd and Pb content was 1.47 mg kg^{-1} and 76.53 mg kg^{-1}, respectively, and the NH_4NO_3-extractable Cd and Pb content was 0.48 mg kg^{-1} and 4.36 mg kg^{-1}, respectively. After collection, the soils were air-dried and passed through a 10-mm mesh sieve for a pot experiment. Representative subsamples were then collected and passed through a 2-mm mesh sieve for property analysis. Selected properties of the soils (e.g., soil pH, organic carbon, total Cd and Pb, etc.) were measured using routine analytical methods and are listed in Table 1.

Heavy metal-free biochar (FC) was made from ramie stick, and heavy metal rich-biochar (RC) was made from Cd-contaminated rice straw. The ramie stick was obtained from Taoyuan County, Hunan Province and was planted in clean soil. The Cd-contaminated rice straw was obtained from Zhuzhou City, Hunan Province and the rice was planted on heavy metal-contaminated paddy soil. The two types of biochar were produced by pyrolysis under limiting O_2 conditions, as produced by combustion. Both processes were carried out at 350 °C–550 °C for 1 h. After combustion, the biochar was in powder form and did not require further grinding. The biochar was then passed through a 5-mm sieve before use. The properties of the two biochars are listed in Table 1.

2.2. Pot experiment

The FC and RC were homogeneously mixed with the two soils at rates (w/w) of 0% (control, CK), 0.5% (F1 and R1), and 1% (F2 and R2). Four replicates of each treatment were tested. Each soil (12.0 kg) was then placed in plastic pots that were 25 cm high and 31 cm in diameter, and incubated outside for 7 days (2 May to 8 May 2012). After incubation, chemical fertilizers were applied to each pot at an amount equivalent to 6.0 g N per pot as urea (13 g per pot), 4.5 g P per pot as calcium magnesium phosphate (86 g per pot), and 13.0 g K per pot as potassium sulfate (29 g per pot), which were thoroughly mixed with the soil as basal fertilizers. Then, four-leaves tobacco seedlings (K326, *Nicotiana tabacum*) were transplanted into pots on 11 May 2012 at a density of one seedling per pot. During the growth period, the roots were irrigated twice with 75% thiophanate-methyl wettable powder to treat black root rot, and mancozeb and Bilken viricide of 600–800 times were applied to prevent climate spot and brown spot (Han et al., 2013). The pots were kept outside with a natural day/night regimen and watered as required. Urea (2.0 g N per pot) and potassium sulfate (3.5 g K per pot) were applied as a top-dressing fertilizer to all of the treatments on 30 May 2012, and 2.0 N per pot to all of the treatments on 10 May 2012. The plants were harvested two months after planting. The plant samples were separated into three parts, i.e., leaves (15 leaves), stems, and roots. All of the tissues were washed with deionized water twice. After the surface water was removed with filter paper, the tissues were oven-dried at 60 °C and the weights were recorded. To determine the Cd and Pb concentrations, the tissues were ground and passed through a 0.3-mm sieve. At the same time as harvesting, soil samples were collected from each pot, air-dried, and ground to pass through a 1.0-mm sieve.

2.3. Analysis

To determine the total Cd and Pb concentrations in the soil and in plant materials (leaves, stems, and roots), the samples were digested using mixtures of aqua regia-$HClO_4$ and HNO_3–$HClO_4$ (open system), respectively. The 1 mol L^{-1} NH_4NO_3 extraction method, modified by Zhu et al. (2012), was used to determine the extractable Cd and Pb content of the biochar-amended soils. Concentrations of Cd and Pb in the solutions were determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-

Table 1
Properties of soils and biochars.

Materials		YBS	RS	FC	RC
pH		4.24	4.27	10.02	8.99
SOC	$(g \cdot kg^{-1})$	14.9	19.2	469	452
Total N		1.13	1.54	13.4	15.5
Total P		0.75	0.71	1.77	1.68
Total K		13.67	13.5	20.7	79.1
C/H		–	–	19.0	17.1
Cation exchange capacity	$cmol \cdot kg^{-1}$	9.59	11.14	90.52	90.36
Specific surface area (BET)	$m^2 \cdot g^{-1}$	–	–	5.2	3.4
Pore size	nm	–	–	4	3.8
Total Cd	$(mg \cdot kg^{-1})$	0.91	1.47	0.84	17.66
Total Pb		25.27	76.53	11.41	15.6
Extractable Cd		0.02	0.48	–	0.29
Extractable Pb		0.46	4.36	0.32	0.45

YBS, Yellow-brown soil; RS, Red soil; FC, heavy metal-free biochar; RC, heavy metal-rich biochar. Extractable Cd, 1 mol L^{-1} NH_4NO_3-extractable Cd; extractable Pb, 1 mol L^{-1} NH_4NO_3-extractable Pb; – not determined.