



Effect of biochar from peanut shell on speciation and availability of lead and zinc in an acidic paddy soil

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ABSTRACT

Biochar has been used to reduce the mobility and availability of heavy metals in contaminated paddy soils. A pot experiment was carried out to analyze the effects of peanut shell biochar (PBC) on the speciation and phytoavailability of Pb and Zn in contaminated acidic paddy soil using rice (*Oryza sativa* L.) as an indicator plant. Peanut shell biochar was applied to an acidic paddy soil contaminated with Pb and Zn at four rates (0%, 1%, 2%, and 5% w/w), and rice plants were grown in this soil. The soil pH, cation exchange capacity (CEC), water-soluble SO_4^{2-} , dissolved organic carbon (DOC), CaCl_2 -extractable heavy metals, and speciation of heavy metals were determined. Additionally, biomass and concentrations of heavy metals in rice tissues were determined. The application of PBC significantly increased the pH, CEC, water-soluble SO_4^{2-} , and DOC in the paddy soil, but decreased the content of CaCl_2 -extractable Pb and Zn. The CaCl_2 -extractable Pb and Zn showed significant negative correlations with the pH, CEC, water-soluble SO_4^{2-} , and DOC ($p < 0.05$). Following the application of biochar to the contaminated paddy soil, the Pb and Zn concentrations in the CaCl_2 extracts were reduced by 41.04–98.66% and 17.78–96.87% ($p < 0.05$), respectively. Sequential chemical extractions showed a reduction in the acid-soluble Pb and Zn fraction and an increase in the reducible fraction following the addition of biochars. PBC obviously inhibited the uptake and accumulation of Pb and Zn in the rice plants. The Pb concentrations in the rice grain were significantly reduced by 60.32%, with the addition of 5% PBC. Neither of the biochars significantly changed the Zn concentrations in the rice grain. The influence of biochar on Pb and Zn phytoavailability varied not only with the application rate of biochar, but also with the kind of metals. Overall, the use of peanut shell biochar at a high application rate is more effective in immobilizing Pb and Zn in the acidic paddy soil contaminated with heavy metals, especially in reducing the phytoavailability of Pb to the rice plants.

1. Introduction

The contamination of farmland soil with heavy metals is a matter of great concern because it poses a potential health risk for human beings who consume the grain produced on such agricultural soils (Zhao et al., 2015). Lead (Pb) and Zinc (Zn) are the most common heavy metal contaminants in the agricultural soils (Zhao et al., 2015); and Pb and zinc (Zn) often occur together in nature (Chapman et al., 2013), especially in paddy soils that are close to lead and zinc mines. In acidic soils, Pb and Zn are more mobile and are readily available for crop uptake, thus, resulting in their high accumulation in crops (Chapman et al.,

2013; Zhao et al., 2015). Remediation strategies for agricultural soils contaminated with heavy metals are, therefore, urgently required for safe food production. In situ immobilization of heavy metals through adsorption, binding, or precipitation by soil amendments has been widely studied over the last decade as a possible and effective remediation strategy (Kumpiene et al., 2008; Komarek et al., 2013).

Biochars are biological residues that have been combusted under low oxygen to produce porous, low density, carbon-rich materials (Beesley et al., 2011). Recently, biochars have been used in experiments on remediation of acidic soil contaminated with heavy metals to reduce the mobility and availability of the heavy metals, such as Pb and Zn.

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They have been found to be effective in reducing the accumulation of heavy metals within the plants (Park et al., 2011; Lu et al., 2014; Puga et al., 2015a, 2015b; Zheng et al., 2015; Cui et al., 2016; Abbas et al., 2018). The application of chicken manure- and green waste-derived biochars was shown to significantly reduce Pb accumulation by Indian mustard (*Brassica juncea*) through immobilization of the metal (Park et al., 2011). Similarly, sugarcane straw biochar was found to decrease the available concentrations of Pb and Zn in the soil contaminated with mine waste and reduce their uptake by two leguminous plant species (Puga et al., 2015a, 2015b). It was reported that bean stalk biochar and rice straw biochar did not significantly affect the uptake of Pb and Zn in rice (Zheng et al., 2015). However, less attention has been focused on determining the redistribution of Pb and Zn in acidic soils amended with different types of biochars (Cui et al., 2016; Lu et al., 2017). The mobility and bioavailability of heavy metals in the soils is strongly dependent on the redistribution of metals in the soil through adsorption, complexing, reduction, and precipitation process (Lu et al., 2005; Paz-Ferreiro et al., 2014). Sequential extraction is frequently used to decipher the distribution of metals in the soil fractions and to evaluate the mobility and availability of metals in the soils (Ahmad et al., 2012).

Rice (*Oryza sativa* L.) is a major staple crop in southern China. It has been observed that the content of heavy metals exceeds the permissible limits more often in rice grains of crop cultivated in southern China than in the other regions because of the acidic nature of soil in this region, which increases the phytoavailability of heavy metals (Lei et al., 2010; Zhao et al., 2015; Zhu et al., 2016). Many studies have demonstrated that the effects of biochars on the uptake and accumulation of Pb and Zn in rice tissues vary with the feedstock from which the biochars are derived (Khan et al., 2013; Bian et al., 2014; Zheng et al., 2015; Li et al., 2016). The concentrations of Pb in rice grains, leaves, and straw were significantly reduced in soil amended with sewage sludge biochar compared to that in control, but the concentration of Zn in the same tissues was increased (Khan et al., 2013). Wheat straw biochar significantly reduced the concentration of Pb in the roots of rice, whereas there were no changes in the concentrations in the rice grain and shoot (Bian et al., 2014). Rice straw biochar (RBC) and bean stalk biochar (BBC) significantly reduced the concentration of Zn in the roots and shoots, whereas a significant increase in Zn concentration was observed in rice grains following RBC addition. However, no effect was observed after the BBC treatment. Only RBC could significantly reduce the Pb concentrations in the roots, but neither of the biochars could significantly change the concentrations of Pb in the shoots and grains of rice (Zheng et al., 2015). The concentrations of Pb in the stems, leaves, husks, and brown rice were significantly reduced by 74.57%, 81.06%, 79.83%, and 65.00%, respectively, by the addition of 5% rice straw biochar, whereas, in the roots, its concentration increased by 37.23% (Li et al., 2016). These studies showed that the effects of different biochars on the uptake and accumulation of Pb and Zn in rice tissues is inconsistent. Besides, the effect of biochar on the fractionation of Pb and Zn in paddy soils has not fully explained. Furthermore, the effectiveness of biochar for multi-metal immobilization and accumulation in rice tissues have not been much investigated.

Peanut shells are plentiful, inexpensive, common in China, and an attractive feedstock for biochar production (Cheng et al., 2014; Wang et al., 2014; D. Wang et al., 2015; Z.Y. Wang et al., 2015; Ahmad et al., 2017; Chu et al., 2017; Ibrahim et al., 2017). Several studies have shown that peanut shell biochar can effectively adsorb Pb and Zn from aqueous solutions (Guo et al., 2015; D. Wang et al., 2015; Z.Y. Wang et al., 2015), whereas less attention has been given to determining the effectiveness of peanut shell biochar on the bioavailability and rice uptake of Pb and Zn in soils. Therefore, the effects of biochar on the bioavailability of Pb and Zn in contaminated paddy soils need to be investigated in greater detail. In this context, we conducted this study to: (1) study the effects of peanut shell biochar addition on the mobility of Pb and Zn in a contaminated paddy soil and to determine the accumulation of these heavy metals in rice plants, (2) assess the effects of

Table 1

Physico-chemical properties of the paddy soil and biochar used in the study.

Property	Soil	Peanut shell biochar
pH (H ₂ O)	4.41	9.95
Organic C (g kg ⁻¹)	9.31	–
Total C (g kg ⁻¹)	–	133.7
Total N (g kg ⁻¹)	1.06	5.21
Total P (g kg ⁻¹)	–	2.76
Olsen-P (mg kg ⁻¹)	11.64	27.68
CEC (cmol kg ⁻¹)	7.9	141.0
Water-soluble SO ₄ ²⁻ (mg S kg ⁻¹)	174.2	730.1
Acidic groups (mmol g ⁻¹)	–	0.37
Basic groups (mmol g ⁻¹)	–	1.17
Total Pb (mg kg ⁻¹)	278.4	9.9
Total Zn (mg kg ⁻¹)	304.5	61.1

biochar application on the redistribution of Pb and Zn in the contaminated soil, and (3) determine the correlation between Pb and Zn concentrations in rice plants and their transformation in paddy soil after peanut shell biochar application.

2. Materials and methods

2.1. Experimental materials

2.1.1. Soil

Surface soil (0–15 cm) was collected from a paddy field in Shangba village, Xinjiang town, 6 km from the Dabao Mountain mining area in Shaoguan city, Guangdong Province, South China. The soil was collected using spades and stored in polyvinyl chloride bags. The soil samples were thoroughly mixed, air-dried, crushed, and passed through a 2-mm nylon mesh prior to the pot experiment. The properties of soil are listed in Table 1.

2.1.2. Biochar

Peanut shell biochar (PBC) was obtained from Sanli New Energy Company, Henan Province, China; it was produced by pyrolysis at ~350–500 °C. The black carbon content was ~30–35%. The biochar was ground and passed through a 1-mm sieve prior to the pot experiment. The biochar was dissolved in water at a 1:25 (w/v) ratio by stirring for 5 min and equilibration of the solution for 1 h (Gaskin et al., 2008). The pH of the solution was then measured using a PHSJ-3F pH meter (Shanghai INESA Analytical Instrument Ltd. Co., Shanghai, China). The total carbon content of the biochar was analyzed using a previously described method for measuring the soil organic matter (Liu, 1996). The surface functional groups in the biochar were analyzed by Boehm titration (Boehm, 1994). The total N concentration was determined using the semi-micro Kjeldahl method, and total P was determined by Mo-Sb-Vc coloration reagents using a colorimeter (DSH-UV755B UV-Vis Spectrophotometer, Guangzhou SH Biological Technology Co. Ltd., Guangzhou, China) after digestion with H₂SO₄-H₂O₂ used for plant analysis; the available P was extracted with 0.5 mol L⁻¹ NaHCO₃ and measured using colorimetry (Lu, 2000). The cation exchange capacity (CEC) of the biochars was measured using the 1 mol L⁻¹ ammonium acetate (pH 7) method (Lu, 2000). The total heavy metal concentration in the biochar was measured using flame atomic absorption spectrophotometry (FAAS) (Hitachi Z-2300, Japan) after digestion with HCl-HNO₃-HClO₄ acid (Lu, 2000). The concentration of water-soluble SO₄²⁻ was measured in a 1:5 (w/v) mixture of soil and deionized water by spectroscopic barium turbidity method (UVS, UV-1800, Shanghai MAPADA Instrument Co. Ltd., China) (Lu, 2000). The basic properties of PBC are presented in Table 1.

2.1.3. Rice plants

The rice cultivar Boyou 998 was used in the experiment. The seeds of this cultivar were obtained from the Rice Research Institution,

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