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Varying effect of biochar on Cd, Pb and As mobility in a multi-metal contaminated paddy soil

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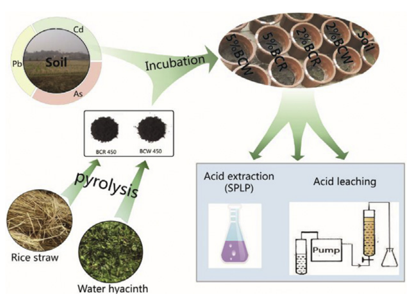
HIGHLIGHTS

- Prolonged Cd immobilization was achieved with BCW under acid precipitation.
- BCW application increased soil Pb leachability upon acid exposure.
- Higher KH_2PO_4-extractable As was obtained with BCW addition.
- BCW incorporation induced little increase in As mobilization with acid input.
- More stringent Pb threshold allowed in biochar need to be proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

Cd, Pb and As stand as the most prominent contaminants prevailing in Chinese soils. In the present study, biochars derived from water hyacinth (BCW) and rice straw (BCR) were investigated regarding their applicability and durability in soil Cd, Pb, and As immobilization under acid precipitation. Total Cd, Pb, and As in both BCs were below the maximum allowed threshold according to biochar toxicity standard recommended by International Biochar Initiative. To evaluate BCs effect on Cd, Pb, As bioavailability and mobility, $CaCl_2$, KH_2PO_4 and SPLP extractions were firstly carried out. In neutral extraction with $CaCl_2$ and KH_2PO_4, significantly reduced Cd/Pb concentrations in $CaCl_2$ extract along with elevated KH_2PO_4-extractable As were recorded with either BC at 2% or 5%. In SPLP with simulated acid rainwater as extractant, comparable Cd, Pb and As levels were determined in SPLP extract with 2% BCW, while slight to significant increase in SPLP-Cd, Pb or As was recorded with other treatments. Longer-term leaching column test further confirmed the high durability of 2% BCW in Cd immobilization under continuous acid exposure. In parallel, little increase in As concentrations in eluate was determined with 2% BCW compared to no-biochar control, indicating a lowered risk of As mobilization with acid input. However, remarkably higher Pb in leachate from both BCW-only control and 2% BCW-amended soils were noticed at the initial stage of acid leaching, indicating a higher acid-solubility of Pb minerals in BCW (most probably PbO) than in tested soil (PbO_2, $PbAs_2O_6$). Taken together, BCW exhibited important potential for soil Cd sequestration with little effect on As mobilization under acid precipitation. But it may simultaneously load highly acid-soluble Pb minerals into soils, resulting in elevated Pb mobility upon acid exposure. Therefore, more stringent threshold for Pb content in biochar need to be put forward to secure biochar application in soils subject to anthropogenic acidification.

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1. Introduction

According to the first national soil pollution survey released recently (4-17-2014) by two government ministries of China, cadmium (Cd) has been identified officially as the most prominent inorganic contaminant in Chinese soil. In parallel, arsenic (As) and lead (Pb) are also ranked two of the top eight inorganic contaminants based on this nationwide survey. Widespread contamination of Cd, As and Pb in cultivated soil has caused substantial transfer and accumulation of these toxicants in food chain (Cui et al., 2004; Li et al., 2014; Liu et al., 2010; Zhuang et al., 2009; Zhao et al., 2015), especially in paddy rice, the most important cereal crop of China feeding more than 60% of Chinese population. In particular, Hunan province, which is regarded as the heartland of Chinese nonferrous mining, has been subject to the most severe farmland contamination with Cd, As and Pb in China due to extensive mining and smelting historically (Sun et al., 2010; Li et al., 2014, 2015; Zhao et al., 2015; Wei et al., 2015). For example, the averaging Cd, As and Pb in mine impacted paddy soils from Qingshuitang (Zhuzhou, Hunan) and Shuikonshan (Hengyang, Hunan) was up to 24–37, 71–253 and 545–2755 mg kg^{-1}, respectively (Williams et al., 2009), far exceeding Chinese national environmental quality standard for agriculture soil in the vicinity of orefield (GB15618-1995, Cd 1.0 mg kg^{-1}, As 30 mg kg^{-1} for flooded soil, Pb 500 mg kg^{-1}). As a result, 95th percentile concentrations of Cd, As and Pb in endosperm grain from the above mining districts were up to 212–2757, 233–585 and 158–537 μg kg^{-1}, respectively, which were remarkably higher than the maximum allowed level of Cd (200 μg kg^{-1}), As (150 μg kg^{-1}) and Pb (200 μg kg^{-1}) in rice grain according to Chinese Hygienic Standard for Grains (GB 2715-2005). Therefore, mitigation and remediation of multi-metal contaminated soil stands as a top priority in China for public health and sustainable agriculture. Biochar (BC) derived from pyrolysis of a variety of biomass under relatively low temperatures (<700 °C) has shown potential in heavy metal immobilization as well as improvement of soil fertility and carbon sequestration (Cao and Harris, 2010). Compared to a wide range of low-cost sorbents, BCs generally exhibit a neutral to alkaline pH (5.9–12.3) with relatively higher cation exchange capacity (CEC) (14.1–44.0 cmol kg^{-1}) (Gaskin et al., 2007; Atkinson et al., 2010; Beesley et al., 2011; Ahmad et al., 2014; Jindo et al., 2014), which resulted in effective immobilization of metal cations mainly through metal precipitation and surface complexation (Inyang et al., 2012; Ahmad et al., 2014; Paz-Ferreiro et al., 2014; Melo et al., 2015). For example, in a recent experiment over three years, Cd and Pb bioavailability in a contaminated paddy field was continuously reduced upon the incorporation of wheat straw biochar (Bian et al., 2014). Similarly, up to 175-fold reduction of Cd, Pb, Cu and Zn in pore water of a mine impacted soil was recorded by the presence of biochar with simultaneously lowered soil toxicity as evaluated by germination and luminescence inhibition tests (Beesley et al., 2014).

However, unlike heavy metal cations, As mobility in soils tends to be enhanced by BCs (Beesley et al., 2014), most probably resulted from the raised soil pH by enriched mineral ash in biochar (Wang et al., 2015). In aerobic soils, arsenate (AsV) is the major As species while arsenite (AsIII) dominates the reducing environment. Under most soil pH (3–10), AsV tends to be negatively charged and exists as $H_2AsO_4^-/HAsO_4^{2-}$ ($pKa_1 = 2.2$, $pKa_2 = 6.9$, and $pKa_3 = 11.5$), while AsIII ($pKa_1 = 9.22$ and $pKa_2 = 12.1$) is generally present as $As(OH)_3$ (pH < 8) and $H_2AsO_3^-$ (pH10-12) (Zhao et al., 2009). As a result, As mobilization tends to occur in alkaline soils (Beesley and Marmiroli, 2011). For instance, following the application of BC into Pb and As co-contaminated soil, enhanced As mobility was demonstrated by higher TCLP-As, in spite of a significant reduction of soil labile Pb (Abdelhafez et al., 2014). Similarly, two-fold higher As in pore water was also determined upon BC incorporation (20% v/v) into two As-contaminated soils with concurrent increase in soil pH (Hartley et al., 2009). Therefore, careful screening of appropriate biochar type and application rate is essential to minimize the associated environmental risks.

In southern China where ferralsol dominates, soils have been subject to the world's most severe acidification due to long-term application of excessive $N{-}NH_4^+$ and acid rain precipitation (Guo et al., 2010). As a result, accelerated mobilization and hence translocation of toxic metals from soil to food crops could occur. Therefore, although BCs exhibit high capability to stabilize toxic metal cations under natural pH as reported by previous studies (Cao et al., 2011; Beesley and Marmiroli, 2011; Houben et al., 2013a; Ahmad et al., 2014; Bian et al., 2014), it is of critical importance to further identify the durability of biochar to sequester heavy metals under continuous acid exposure and the applicability of biochar into soils co-contaminated with metal cations (e.g. Pb, Cd) and As anions.

In the present study, water hyacinth and rice straw, which represent the most problematic invasive species and the most abundant agricultural waste, respectively, in southern China, were chosen as feedstocks for biochar production. The major goal of this study was to investigate the effect of these two types of biochars on Cd, Pb and As mobility and leaching behavior under acid exposure. Furthermore, the underlying mechanisms were elucidated with the aid of scanning electron microscopy with energy dispersive X-ray (SEM-EDX) and X-ray diffraction (XRD).

2. Materials and methods

2.1. Sampling site and soil collection

The multi-metal contaminated soil used in the present study was collected from a typical rice paddy in Zhuzhou, Hunan province (Lat/Long: 27°52′23″N, 113°04′12″E) (Fig. 1). The local climate is subtropical humid monsoon with the average annual rainfall being 1300–1600 mm. And 69% of the annual precipitation occurs between April to September (Du et al., 2013). The traditional cropping system is a winter rape-rice rotation each year. With densely distributed metallurgical smelters and chemical plants in this city, substantial As, Cd and Pb has been loaded into the local field soils primarily through deposition and irrigation. Bulk soil samples were taken from the upper layer (0–20 cm) of three points with a stainless steel shave after rice harvest in December, 2013. A single and representative soil sample was then produced by mixing triplicate 10 kg soil samples collected from the field thoroughly in laboratory. With large debris and biological remnants being removed, the soil was air-dried and sieved to <2 mm prior to use.

2.2. Biochar (BC) preparation and soil treatments

Water hyacinth biochar (BCW) and rice straw biochar (BCR) were produced by slowly pyrolyzing the feedstocks at 450 °C for 1 h under N_2 (Thermo Scientific, BF51732BPMC-1, USA). The heating rate was 6 °C min^{-1}. After cooling to room temperature in a N_2 atmosphere, BCs were crushed and sieved to <2 mm.

To investigate the effect of BCs on As, Cd and Pb mobility in selected paddy soil, BCW and BCR were mixed thoroughly with the soil sample, respectively, at 2% and 5% (w/w) since the optimum biochar application in agricultural soil has been suggested to be 1%–5% (Matovic, 2011). BC-amended soils and soil-only control were then incubated in pots at room temperature with soil moisture being remained at 70% of the field water holding capacity of the substrate. Each treatment had at least three replicates. After one-month of incubation, soil samples were collected and ground