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# The effect of biochar and crop straws on heavy metal bioavailability and plant accumulation in a Cd and Pb polluted soil

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ABSTRACT

Biochar derived from various materials has been investigated with regard to its ability to decrease the bioavailability of heavy metals in contaminated soils, and thus reduce their potential to enter the food chain. However, little attention has been given to the adsorption capacity of untreated crop straws, which are commonly used as a biochar feedstock, especially in soils. Hence, this study was conducted to investigate the effect of crop straws on heavy metal immobilization and subsequent heavy metal uptake by maize and ryegrass in a soil artificially polluted by Cd and Pb. Bamboo biochar, rice straw, and wheat straw were mixed into soil four weeks before the experiment, enabling them to reach equilibrium at 2% (w/w), 1% (w/w), and 1% (w/w), respectively. The results showed that soil pH for both species was significantly increased by all treatments, except when wheat straw was used for ryegrass cultivation. Soil organic carbon was only improved in the rice straw treatment and the soil alkali-hydrolyzable N content was significantly decreased with all of the amendments, which may have contributed to the lack of an effect on plant biomass. Soil available Cd was significantly lower in the rice straw treatment than in the control soil, while Pb levels clearly decreased in wheat straw treatment. The Cd concentration in shoots of maize was reduced by 50.9%, 69.5%, and 66.9% with biochar, rice straw, and wheat straw, respectively. In addition, shoot Cd accumulation was decreased by 47.3%, 67.1%, and 66.4%, respectively. Shoot Pb concentration and accumulation were only reduced with the rice straw treatment for both species. However, metal uptake in plant roots was more complex, with increased metal concentrations also detected. Overall, the direct application of crop straw could be considered a feasible way to immobilize selected metals in soil, once the long-term effects are confirmed.



## 1. Introduction

Heavy metal pollution in soils has become a big issue throughout the world, especially in developing countries such as China (Li et al., 2014). Human activities, such as the mining and smelting industry, excessive soil fertilization, and urban development, which release considerable amounts of heavy metals into the soil, have resulted in a 10.18% total pollution rate in Chinese farmland soil, mainly from Cd, Hg, Cu and Zn (Zhang et al., 2015). Because metals cannot be degraded by microbial or chemical activity, manipulating their bioavailability by certain amendments has become a viable way to ensure food safety when planting crops in heavy metal contaminated sites (Bolan et al., 2014), among which agricultural residues such as rice straw, wheat bran, and papaya wood have been widely studied as low-cost biosorbents (Li et al., 2015).

In China, the total annual output of crop straw is more than $6 \times 10^8$ t, with about $1.1 \times 10^8$, $1.3 \times 10^8$, and $2.3 \times 10^8$ t obtained from rice, wheat, and corn, respectively. Currently, 25% of all crop straw is burned during harvest season to remove crop residues (Shi et al., 2014), which is detrimental to air quality and human healthy. Therefore, effective alternatives need to be developed to provide solutions for recycling the massive amounts of agricultural residues. As natural supplements, containing valuable nutrients and organic carbon, it has been recommended that crop straws be returned to farmland to maintain soil fertility and crop productivity (Wang et al., 2015). Many studies have demonstrated that the return of crop straw to farmland has the potential to increase soil carbon storage and available nutrients (P, K, Ca, and Mg), which is beneficial for plant growth (Zhu et al., 2010, 2015). Although little attention has been paid to the effect of crop straw on the behavior of heavy metals in soils, Li et al. (2015) reported that rice husk and rice straw were effective for removing cadmium (II) in aqueous solutions, and wheat straw has been shown to be capable of adsorbing copper (II), nickel (II) and zinc (II) via ion

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exchange in wastewater (Gorgievski et al., 2013). However, few studies involving pot culture experiments have been conducted (Cui et al., 2008; Huang et al., 2011).

Converting straw to biochar for use as a soil conditioner has become a hot topic in agriculture, environmental science, and other fields, due to its advantages in soil carbon sequestration and $CH_4$ emission reduction (Zhao et al., 2014), and its sorptive capacity for soil pollutants (Lu et al., 2014; Kim et al., 2015; Puga et al., 2015). Biochars could be produced via the pyrolysis of a wide range of organic wastes in addition to crop straws (Lucchini et al., 2014). Like liming materials, biochars also increase the soil pH and hence reduce the bioavailability of heavy metals. In addition, they are capable of immobilizing metals by sorption due to their large surface area (Beesley and Marmiroli, 2011). However, through this mechanism essential plant nutrients may also be immobilized, leading to plant deficiencies in Ca, P, and N, or even decreased competition with cations for metal uptake (Rees et al., 2015). Furthermore, biochars produced at different temperatures have different abilities to adsorb heavy metals. Biochar produced at 200 °C is more effective than biochar produced at 350 °C because the more soluble P enables Pb to be adsorbed (Karami et al., 2011). Melo et al. (2015) also indicated that binding reactions on biochar surfaces are reversible, mainly for Cd (II), which indicates that a continual application of biochar would be required to maintain low soil solution concentrations of metals. However, the performance of specific sorption-desorption mechanisms over time and the environmental impacts on soil organisms of biochar remain unclear (Beesley and Marmiroli, 2011) which restricted the use of biochar on a large-scale.

The abundant supply of crop straw enables biosorbents to be obtained at low-cost. Therefore, the aim of this study was to investigate the influence of the addition of rice straw and wheat straw to soil on heavy metal bioavailability and uptake by plants, compared with biochar application.

## 2. Materials and methods

### 2.1. Soil and amendments

Soil was collected from the top 0–20 cm of a paddy field in Shaoxing city, Zhejiang Province, China. The soil contained 7.0% sand, 71.6% silt, and 22.4% clay and was classified as silty loam soil according to the Chinese soil classification (Gong, 1999). The bulk soil sample was thoroughly mixed, air dried, and passed through a 4-mm sieve prior to initiating the pot experiments. Bamboo biochar obtained from the School of Environmental and Resource Sciences, Zhejiang Agriculture and Forestry University, was produced by a batch pyrolysis facility, with a retention time of 3 h at approximately 750 °C. Rice straw and wheat straw were collected from a local farm, which were ground before use. Selected physicochemical properties of the soil and amendments are listed in Table 1. All of the amendments had a high C/N ratio and contained trace amounts of heavy metals.

### 2.2. Pot experiments

Pot experiments were conducted in a green house in Zhejiang Academy of Agricultural Sciences, between September and November 2015. Four treatments (control, bamboo biochar, rice straw, and wheat straw) and two plant species (maize and ryegrass) were applied. Each treatment was replicated three times. Plastic pots (16 cm in diameter and 18 cm in height) were filled with 2 kg of soil, and 600 mg $kg^{-1}$ Pb (in the form of $Pb(NO_3)_2$) and 2 mg $kg^{-1}$ Cd (in the form of $CdCl_2$) were artificially mixed into each pot. In addition, 2% (w/w, equivalent to 31.2 t $ha^{-1}$) biochar or 1% (w/w, equivalent to 15.6 t $ha^{-1}$) straw was amended to the corresponding treatment. Once all of the experimental units had received the amendments, the pots were irrigated with distilled water to 60% field water holding capacity and allowed to equilibrate for four weeks. Seeds of maize and ryegrass were sterilized in 10% $H_2O_2$ for 15 min, rinsed with tap water, covered with wet filter paper, and allowed to germinate at 30 °C for 48 h. Germinated seeds were sown into pots and three seedlings of maize or thirty seedlings of ryegrass were retained after emerging. Plants were watered every 2–3 days and grown at a temperature of 22–28 °C.

After six weeks of plant growth, plant shoots and roots were collected for analysis. Shoots were cut at the soil surface and roots were carefully separated from soil. They were cleaned with distilled water, oven dried at 105 °C for 2 h, and dried at 75 °C until a constant weight was achieved. The biomass of each pot was recorded. Dried samples were ground and stored for chemical analysis. The soil of each pot was air dried and passed through 2-mm and 0.149-mm sieves.

### 2.3. Chemical analysis

The pH of biochar and straws in water solution were measured at a 1:20(w/v) ratio after stirring for 30 min. Soil pH was measured electrometrically at a 1:2.5(w/v) ratio and soil texture was measured by the hydrometer method. The Walkley–Black method was used to measure soil organic carbon. Total N was measured by the semi-micro Kjeldhal method, and total P was measured by the molybdenum antimony blue colorimetry method. The total heavy metal content in the soil and amendments was analyzed using a HF-$HNO_3$-$HClO_4$ digestion followed by inductively coupled plasma mass spectrometry (ICP-MS, X-Serie2, Thermo Electron, Waltham, MA, USA). Available Cd and Pb in the soil from each pot was extracted by 0.1 M HCl (1:5; w/v) after shaking for 1.5 h and determined by an atomic absorption spectrophotometer (AAS, Solaar Mk2-M6, Thermo Electron). The Cd and Pb concentrations of plant tissues were analyzed by $HNO_3$-$HClO_4$ digestion followed by AAS. All methods described above followed Lu (2000).

### 2.4. Statistical analysis

The primary data were analyzed using OriginPro 8.0(OriginLab Corporation, Northampton, MA, USA), and all analyses were conducted using SPSS18.0 software (SPSS, Chicago, IL, USA). Means

**Table 1**
Selected physicochemical properties of the soil and amendments.

| | pH | Organic carbon (g/kg) | Total P (g/kg) | Total N (g/kg) | Total heavy metal content (mg/kg) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Cr | Zn | Cu | Cd | Pb |
| Soil | 5.65 | 17.5 | 2.45 | 0.653 | 50.7 | 102 | 33.5 | 0.161 | 119 |
| Biochar | 9.68 | 839 | 2.30 | 4.50 | – | 33 | 19 | – | – |
| Rice straw | 7.35 | 374 | 2.13 | 7.34 | 0.047 | 0.282 | 0.013 | 0.0009 | 0.012 |
| Wheat straw | 7.62 | 379 | 2.63 | 8.79 | 0.012 | 0.045 | 0.008 | 0.0004 | 0.003 |