Journal of Hazardous Materials 272 (2014) 121–128

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

A three-year experiment confirms continuous immobilization of cadmium and lead in contaminated paddy field with biochar amendment

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HIGHLIGHTS

- Biochar significantly increased soil pH, organic matter and immobilized soil Cd and Pb.
- Biochar treatment consistently reduced rice Cd and Pb content in three years.
- Contaminated biochar from the study field contained much higher heavy metals than fresh biochar.
- Biochar caused metal immobilization primarily due to the precipitation and surface adsorption.

ARTICLE INFO

Article history:
Received 6 December 2013
Received in revised form 17 February 2014
Accepted 7 March 2014
Available online 20 March 2014

Keywords:
Heavy metal pollution
Biochar
Soil remediation
Aged biochar
Rice paddy

ABSTRACT

Heavy metal contamination in croplands has been a serious concern because of its high health risk through soil-food chain transfer. A field experiment was conducted in 2010–2012 in a contaminated rice paddy in southern China to determine if bioavailability of soil Cd and Pb could be reduced while grain yield was sustained over 3 years after a single soil amendment of wheat straw biochar. Contaminated biochar particles were separated from the biochar amended soil and microscopically analyzed to help determine where, and how, metals were immobilized with biochar. Biochar soil amendment (BSA) consistently and significantly increased soil pH, total organic carbon and decreased soil extractable Cd and Pb over the 3 year period. While rice plant tissues' Cd content was significantly reduced, depending on biochar application rate, reduction in plant Pb concentration was found only in root tissue. Analysis of the fresh and contaminated biochar particles indicated that Cd and Pb had probably been bonded with the mineral phases of Al, Fe and P on and around and inside the contaminated biochar particle. Immobilization of the Pb and Cd also occurred to cation exchange on the porous carbon structure.

1. Introduction

There has been increasing contamination of agricultural land by heavy metals [1]. This pollution in soils has increased the stresses on terrestrial ecosystems and societies [2]. Heavy metal pollution in croplands can result in enhanced dietary exposure through soil–plant–food chain transfer, causing elevated levels of toxic metals in human organs [3]. Of metals produced through anthropogenic activities, Cd and Pb are considered the most harmful for human health and accumulate at highest rates in soils.

Abbreviations: BSA, biochar soil amendment; LA-ICP-MS, laser ablation inductively coupled plasma mass spectrometry; XPS, X-ray photoelectron spectroscopy; SEM, scanning electron microscope; TEM, transmission electron microscope; EDS, energy dispersive X-ray spectroscopy; DAP, diammonium phosphate.

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http://dx.doi.org/10.1016/j.jhazmat.2014.03.017
0304-3894/

Environmental engineers have given high priority to reducing the bioavailability of toxic metals in croplands in order to ensure food security and human health [4].

Rice (*Oryza sativa* L.) is cultivated in large areas of Asia as a major staple crop [5]. Accumulation of Pb and Cd in rice grains has increasingly raised health concerns in many Asian countries including Japan, China, Korea and Thailand [3,6]. Since rice is an important traded commodity and staple food for most of the population, it is now considered to be a priority to reduce levels of Cd and Pb to safe levels [7].

China is the world's largest rice producer with 27% of cropland area being used to cultivate rice [8]. 80% of the nation's total rice production comes from South China [9], where increasing urbanization, mining and metal processing has increased the heavy metal content in rice paddies [10–12]. In a study of rice sampled from Chinese markets, over 10% had Cd levels in excess of the state guideline limit of 0.2 mg kg^{-1} [13]. Another study also observed that more than 70% of rice grain samples from metal-contaminated rice fields across south China were Cd-tainted [14]. Meanwhile, rice grain samples from South China were found to exceed the state guidelines limit for Pb (above 0.2 mg kg^{-1}) [6]. These reports led to serious public concern about food safety in China [15]. A number of soil remediation techniques for metal-contaminated soils have been developed, including chemical treatment, physical treatment, electrokinetics remediation, biological remediation and phytoremediation [4]. However, most of these techniques are not efficient in terms of time, cost and environmental compatibility [16,17]. Therefore, the Chinese government urgently needs new policies and techniques for enabling farmers to produce rice with less heavy metal contamination.

Biochar is an organic carbon-rich material produced via pyrolysis of agricultural bio-waste such as wood chip or crop straw under an oxygen-limited environment [18]. Recent studies have highlighted biochar's role in immobilizing soil heavy metals and reducing their accumulation in plants [19–21]. The reason for this is often attributed to their highly porous structure, active functional groups and generally high pH and CEC [19,21,22]. Short term field trials have shown a reduction in rice grain Cd up to 90% with BSA [20]. However, the long-term effect of biochar on heavy metals immobilization in contaminated soil, and the reaction of biochar with soil heavy metals, has not been systematically investigated in previous studies [19,21].

Therefore, a 3-year field study was conducted to determine if biochar soil amendment (BSA) could consistently reduce soil Cd and Pb bioavailability and the mechanisms that resulted in this reduction.

2. Materials and methods

2.1. Site and soil

The field trial was conducted in a typical rice paddy in Jingtang village, Yixing Municipality, Jiangsu Province, China (31°24′ N and 119°41′ E). The soil was derived from a lacustrine deposit and classified as a hydroagric Stagnic Anthrosol. The topsoil contained organic carbon of 20.20 g kg^{-1}, total N of 5.94 g kg^{-1}, cation exchange capacity of 23.07 cmol kg^{-1} and pH (H_2O) of 5.36. The traditional farming system is a rice-wheat rotation each year. The local climate is subtropical humid monsoon with mean annual temperature of 15.7 °C and mean annual precipitation of 1246.3 mm. The mean precipitation over rice growing seasons for 2010, 2011 and 2012 was 781.7 mm, 492.8 mm and 631.6 mm, respectively. The field soil is being polluted from emissions from a nearby metallurgical smelter that was built in the late 1960s and soil Cd and Pb has attained concentrations of 5 mg kg^{-1} and 100 mg kg^{-1} respectively [23].

2.2. Biochar for soil amendment

Biochar was produced from wheat straw by the Sanli New Energy Company at a maximum temperature between 350 and 550 °C in a vertical kiln [24]. It contained organic carbon 467 g kg^{-1}, total N 5.9 g kg^{-1}, Cd 0.2 mg kg^{-1} and Pb 12.9 mg kg^{-1}, and had a surface area of 8.92 m^2 g^{-1} with a bulk density of 0.6 g cm^{-3} and pH (H_2O) of 10.4 as well as a cation exchange capacity of 21.7 cmol kg^{-1}. The biochar was ground to pass through a sieve of 2 mm prior to use as a soil amendment. The maximum adsorption capacity of Cd^{2+} and Pb^{2+} in solution was estimated at 6 mg g^{-1} and 50 mg g^{-1} with the adsorption isotherms [25].

2.3. Experimental design

Biochar was amended once at the rate of 0 (C0), 10 (C10), 20 (C20), 40 (C40) t ha^{-1} in May of 2010 after the wheat harvest. This was done by spreading the biochar on the soil surface and subsequently mixing it to a depth of 0–15 cm with a plough before leveling the surface. Rice cultivar Wuyunjing-19 (*O. sativa* L., cv. Japonica) was directly sown in each plot in early May each year. For rice production, total N, P and K fertilizers were applied at the rates of 300 kg N ha^{-1}, 204 kg P_2O_5 ha^{-1} and 204 kg K_2O ha^{-1} in the forms of urea, $Ca(H_2PO_4)_2$ and KCl, respectively. The soil was plowed after wheat harvest each year.

The experimental treatments were performed in triplicate and the individual treatment plots were arranged in a complete randomized block design. Each pot of 4 m × 5 m in area was separated with surrounding protection rows 1 m in width and with separated irrigation inlets and drainage outlets. The crop management practices were consistent across treatments and years after biochar amendment.

2.4. Samples collection and analysis

Three samples of topsoil (0–15 cm) were collected from each plot with a stainless steel shave after the rice harvest each year. The soil samples were air-dried and ground with a plastic scroll to pass through a 2 mm sieve. The procedures described by Lu [26] were used to determine the properties of the soil and biochar including pH, total organic carbon, total $CaCl_2$ and DTPA extractable pool of Cd and Pb. Soil available phosphorus (P) and potassium (K) was extracted by sodium bicarbonate and ammonium acetate solution (1:5, w/v), respectively. The extract solution was filtered and analyzed using a Model 410 Flame Photometer for K and using the method from Murphy and Riley [27] for P. For soil silicon (Si) testing, a soil sample was extracted with 0.025 M citric acid following with the procedure described by Lu [26]. The details of these measurements are provided in the supplementary information.

The grain yield of rice was measured in field when harvested each year. Ten plants from each plot were collected randomly when the rice was harvested and these were separated into grain ears, shoot and root tissue samples. The unpolished rice grain was separated from the ears with a thresher. The procedures for plant analysis described by Lu [26] were followed and the details are given in the supplementary information.

2.5. Analysis of biochar particles

Separating and identification of contaminated biochar particles in soil were done following a procedure described by Lin et al. [28]. Random soil cores were collected after rice harvest, which were dispersed by agitation in deionized water (1:10, v/v). The mixture suspension was sieved using a 150 μm sieve, on which biochar particles were manually picked-out with a jeweler forceps under a binocular. The separated biochar particles were carefully washed