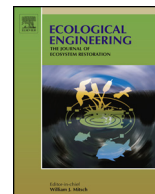




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Short communication

## Biochar soil amendment as a solution to prevent Cd-tainted rice from China: Results from a cross-site field experiment

Rongjun Bian<sup>a</sup>, De Chen<sup>a</sup>, Xiaoyu Liu<sup>a</sup>, Liqiang Cui<sup>a,b</sup>, Lianqing Li<sup>a</sup>, Genxing Pan<sup>a,\*</sup>, Dan Xie<sup>a</sup>, Jinwei Zheng<sup>a</sup>, Xuhui Zhang<sup>a</sup>, Jufeng Zheng<sup>a</sup>, Andrew Chang<sup>c</sup><sup>a</sup> Institute of Resources, Ecosystem and Environment of Agriculture, and Center of Biochar and Green Agriculture, Nanjing Agricultural University, 1 Weigang, Nanjing 210095, China<sup>b</sup> School of Environmental Science and Engineering, Yancheng Institute of Technology, 9 Yingbin Avenue, Yancheng, Jiangsu 224003, China<sup>c</sup> Department of Environment Sciences, University of California, Riverside, CA 92521, USA

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## ABSTRACT

Cadmium contamination in croplands has been a serious concern because of its high health risk through soil–food chain transfer. A sudden emergence of Cd-tainted rice from the South China market urged countermeasures to prevent Cd uptake and accumulation in rice grains from Cd-contaminated rice paddies. A cross-site field experiment with biochar soil amendment (BSA) at rates from 20 to 40 t ha<sup>-1</sup> in metal polluted rice fields was conducted across South China during 2010–2011. Samples both of topsoil and rice grains under BSA treatment were collected after rice harvest and soil extractable Cd pool and rice grain Cd level were analyzed. Across the sites, BSA treatment greatly reduced (by 20–90%) rice grain Cd content, and enabled a safe Cd level (<0.4 mg kg<sup>-1</sup>) of rice grain from all these Cd-contaminated rice fields using a 40 t ha<sup>-1</sup> biochar application except in one site where soil had a Cd content over 20 mg kg<sup>-1</sup>. This could be explained by a reduction in the extractable Cd pool in the biochar treated soil, which was closely correlated to the rise in soil pH with BSA treatment. This study demonstrated a promising role of BSA in preventing dangerous Cd accumulation by rice grain in contaminated rice paddies.

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## 1. Introduction

Cadmium (Cd) has been well known as one of the most important environmental pollutants with its high toxicity to human health (WHO, 1992). Cd contamination in croplands could result in enhanced exposure for human through soil–food chain transfer (Chaney et al., 2004). There had been increasing evidences of cancer-inducing toxicity of Cd<sup>2+</sup> in competition to Ca<sup>2+</sup>, Zn<sup>2+</sup> and Fe<sup>2+</sup> in human body (Satarug et al., 2010). Rice (*Oryza sativa* L.) had been considered as a particular crop that had high Cd uptake with depletion of zinc/iron in its grain (Chaney et al., 2004; Gong and Pan, 2006; Reeves and Chaney, 2008). Consequently, Cd translocation and accumulation in the grain and aerial plant parts of rice could jeopardize of food safety in regions with metal-contaminated rice fields (Kashiwagi et al., 2009). Intake of rice with high levels of Cd could cause “Itai-itai disease”, a dysfunction disease of human related to excessive Cd content in the blood (Nakadaira and Nishi,

2003). The increasing of Cd content in human body relate to consumption of rice grown in contaminated area was observed in a rice-producing region of Thailand, which was linked to an increased occurrence of tubular dysfunction and renal damage (Honda et al., 2010). Therefore, prevention of Cd-tainted rice production would be of urgent need for people with rice as the staple food, particularly in Asian countries.

China had been one of the largest countries with both the largest area of rice paddies and the largest production of rice grain in the world (FAOSTAT, 2011). Possessing 80% of the nation's total rice grain production (DRSESSBS, 2012), rice paddies from South China had been increasingly polluted with heavy metals in Pear River Delta (Wong et al., 2002), in Yangtze River delta (Hang et al., 2009) and in the inland area of Jiangxi and Guangdong provinces (Chen et al., 1999). Moreover, rice in these regions had been grown in acid soils poor in organic matter, increasingly of hybrid rice cultivars and/or with non-submergence water regime, which had been considered enhancing Cd bioavailability to rice grains (Li et al., 2005; Gong and Pan, 2006). In a study of rice grain sampled from markets, Zhen et al. (2008) reported that over 10% of the total grains samples from open markets with Cd levels in excess to the state guideline limit of 0.2 mg kg<sup>-1</sup>. Later on, grain samples

Abbreviations: BSA, biochar soil amendment; SOC, soil organic carbon.

\* Corresponding author. Tel.: +86 25 8439 6027; fax: +86 25 8439 6027.

E-mail addresses: [panggenxing@aliyun.com](mailto:panggenxing@aliyun.com), [gxpan1@hotmail.com](mailto:gxpan1@hotmail.com) (G. Pan).

from metal-contaminated rice fields across South China were reported with a high frequency (70%) of a Cd level over  $0.2 \text{ mg kg}^{-1}$  (Zhang et al., 2009a). More recently, 65% of rice grain samples from all the mine-impacted paddies from Hunan, a province with extensive metal contamination, were predicted to exceed the national food standards for Cd. These reports of high Cd rice had raised serious public consensus of food safety of China (Gong, 2011). In March, 2013, a sudden report of some ten thousands tones of Cd-contaminated rice sold in Guangdong market recalled a public worry and indignation of Chinese rice safety (Chin, 2013). Therefore, there should be an urgent need for China's government to issue a new policy for environmental protection toward a safe production of food for the nation.

Nevertheless, there had been few studies on effective measures to alleviate rice Cd accumulation in contaminated rice paddies. The treatments with liming, fertilizers of calcium-magnesium phosphate and zinc sulfate as well as with manures had been known to help alleviating Cd transfer from soil to rice (Zhang et al., 2009b; Wuana and Okieimen, 2011). However, these techniques had been shown neither consistent effects across wide range of soil conditions nor cost effective in reducing Cd levels in rice grains from contaminated fields (Schnoor, 1997; Martin and Ruby, 2004). Yet, phytoremediation technology, a potential approach of ecosystem engineering for removing Cd from soil (Mulligan et al., 2001), seemed either very costive with an expense of almost 50–200 thousand USD per hectare or excluding crop production before recovered.

Biochar is a carbon-rich material produced via pyrolysis of bio-waste (Lehmann, 2007; Lehmann and Joseph, 2009) and the use of it has been known as an ecological engineering tool to mitigate  $\text{N}_2\text{O}$  emission from croplands while to maintain soil productively (Liu et al., 2012; Zhang et al., 2013; Hossain et al., 2010). The large surface area with functional groups and generally high pH of biochar could be reactive to immobilize heavy metal cations in soils (Beesley et al., 2011). There had been increasing studied on biochar effect on metal mobility in soil (Hossain et al., 2010; Fellet et al., 2011; Méndez et al., 2012). In a previous field experiment, a great reduction in grain Cd content both of rice and wheat was observed with biochar soil amendment (BSA) at 20 and  $40 \text{ t ha}^{-1}$  in a heavily Cd-contaminated paddy from eastern China (Cui et al., 2011, 2012). The purpose of this study was, using a cross site field experiment, to assess if biochar could exert a consistent reduction in rice Cd accumulation in a range of soil conditions and of Cd level in different locations from South China. While synthesizing the results in this study, we try to address that BSA could be a promising practical countermeasure to prevent Cd rice from contaminated rice fields so as to ensure safe production of rice in China.

## 2. Materials and methods

### 2.1. Site of field experiment

A field experiment with BSA was conducted in 5 sites located in the rice production area of South China (Supporting Fig. 1), including YX1 and YX2 in Yixing Municipality of Jiangsu province, YY in Yueyang Municipality of Hunan province, GH in Guanghan County of Sichuan province, and LY in Longyan Municipality of Fujian province of China. Rice production had been more or less stressed due to long term metal contamination in all these sites. The rice paddies varied greatly in total Cd concentration with mostly acid to slight acid soil reaction and relatively similar SOC contents (Table 1). The soil at GH site contained much lower Cd content, which could be considered as the background for rice Cd uptake assessment.

### 2.2. Biochar amendment treatment

Biochar used for soil amendment was produced from wheat straw by pyrolysis at temperature between 350 and  $550^\circ\text{C}$  in a vertical kiln (Pan et al., 2011) and contained organic carbon of  $467 \text{ g kg}^{-1}$ , total N of  $5.9 \text{ g kg}^{-1}$ , Cd of  $0.03 \text{ mg kg}^{-1}$  and ash of 20.8%, and had a surface area of  $8.92 \text{ m}^2 \text{ g}^{-1}$  with a bulk density of  $0.59 \text{ g cm}^{-3}$  and pH ( $\text{H}_2\text{O}$ ) of 10.42 as well as a cation exchange capacity of  $21.7 \text{ cmol kg}^{-1}$ .

BSA was performed before rice transplantation in 2010 in sites of GH and YX1, YX2, and in 2011 in sites of YY and LY. Following a procedure described in detail respectively by Zhang et al. (2013) and by Cui et al. (2011), biochar was amended to surface soil at rates of 0, 20, and  $40 \text{ t ha}^{-1}$  (Treatment C0, C20 and C40 respectively) in all sites except only C0 and C20 treatments in site LY. All the treatments were done in triplicates with a plot area of  $4 \text{ m} \times 5 \text{ m}$  for each replicate and arranged in a randomized complete block design in each site. Rice cultivars cultivated was Wuyunjing 23 of hybrid *Oryza sativa* L., cv. Japonica at YX1 and YX2, Xiangwanxian 12 and Fenyong 559 of hybrid *Oryza sativa* L. ssp. *hsien Ting, Indica* respectively at YY and LY, and D-you202 of Super hybrid *Oryza sativa* L. ssp. *hsien Ting, Indica* at GH. The rice production was managed with local conventional practices consistently across the treatment plots in a single site. For rice growth, chemical N, P and K fertilizers were applied firstly before rice transplanting and secondly during the early stage of rice tillering stage in all sites. Total N, P and K fertilizers were applied at the rate of  $300 \text{ kg N ha}^{-1}$ ,  $204 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$  and  $204 \text{ kg K}_2\text{O ha}^{-1}$  at YX1 and YX2, of  $190 \text{ kg N ha}^{-1}$ ,  $200 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$  and  $140 \text{ kg K}_2\text{O ha}^{-1}$  at YY and LY, and of  $240 \text{ kg N ha}^{-1}$ ,  $150 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$  and  $75 \text{ kg K}_2\text{O ha}^{-1}$  at GH, respectively. All the other crop management practices were kept consistent across the treatments in each site.

### 2.3. Samples collection and analysis

Composite topsoil (0–15 cm) samples were collected of 3 individual random cores in each plot before transplantation and after harvest of a first rice season following BSA respectively in a single site. Soil samples were air dried and ground with a wood scroll to pass a 2 mm sieve for analysis. Sample treatment and analysis of soil properties were performed following the protocols described by Lu (2000).

Soil pH was determined using a 1:5 soil/water ratio with a compound glass electrode (Seven Easy 109 Mettler Toledo, China, 2008). Soil organic carbon (SOC) was determined using wet digestion by potassium dichromate. For total Cd determination, samples were digested with a mixed solution of  $\text{HF-HClO}_4\text{-HNO}_3$  (10:2.5:2.5, v:v:v). For the available pool of Cd, a sample was extracted with 0.01 M  $\text{CaCl}_2$  solution using a soil:solution ratio of 1:5 (m:m), shaken for 2 h and then filtered. Cd in the digest/extract was detected with graphite furnace atomic absorption spectrometry (GFAAS) (SpectrAA 220Z, Varian, USA). A reference sample and a blank were inserted in each batch of digestion and of extraction. The recovery of Cd determination was 91–110%.

From each plot, 10 whole plant samples were collected randomly when rice was harvested and rice grains were obtained with a thresher. After shipping to laboratory, rice grain samples were washed with de-ionized water before oven-drying at  $105^\circ\text{C}$  for 30 min then further dried at  $60^\circ\text{C}$  for 48 h. After drying, the grain samples were shelled and homogenized prior to chemical analysis. A sample of 0.500 g was weighed into a 100 ml digestion flask with 10 ml mixed solution of  $\text{HNO}_3$  and  $\text{HClO}_4$  (8:2, v:v) and left at room temperature overnight. The sample was then digested on an electric heating plate till the solution became clear. Cd in the digest was determined with GFAAS (SpectrAA 220Z, Varian, USA). A reference

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