Ecotoxicology and Environmental Safety 162 (2018) 348–353

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

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

# Cow manure-loaded biochar changes Cd fractionation and phytotoxicity potential for wheat in a natural acidic contaminated soil

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ARTICLE INFO

*Keywords:*
Cadmium
Fractionation
Accumulation
Biohcar
Contaminated soils

ABSTRACT

The current study aims to investigate the implications of amending a soil contaminated with Cd with peanut residues biochar (BP) solely or in combination with cow manure (CMPB) at different rates on phytotoxicity of Cd for wheat plants and its distribution in a mine contaminated soil. Soil pH and EC increased progressively in soils amended with either PB or CMPB. Exchangeable Cd was decreased while its non-exchangeable fractions were increased. Dry weights of wheat straw, roots and grains increased when soils amended with either PB or CMPB, especially at the higher application rate. Such increases were correlated significantly with the extractable soil-Cd. Concentrations of Cd in roots were higher than those in straw; whereas, the concentrations in grains seemed to be the lowest. Generally, values of bio-concentration and translocation factors did not exceed "1" and decreased with application of either PB or CMPB. In conclusion, enriching biochar with cow manure is a recommended strategy to reduce Cd uptake and translocation to straw and seeds. Moreover, Concentrations of Cd did not exceed the permissible levels in grains when soils amended with the highest rate of CMPB.

## 1. Introduction

Contamination of agricultural soils with heavy metals is one of the important issues worldwide (Kumarathilaka et al., 2018). These metals are brought to soils through the movement, discharge, and dispersion of the effluents and wastes of coal combustion, mining and smelting activities (Yun et al., 2016). Shockingly, these contaminants are non-degradable (Bolan et al., 2014); and their toxicity depends mainly on their availability in the soil (Mohamed et al., 2015) rather than their total contents (Abbas and Abdelhafez, 2013). The high presence of Cd in soils has negative implications on the ecosystem e.g. plant growth, animals and human health (Hussain et al., 2015; Naeem et al., 2016; Rizwan et al., 2016). Remediation of contaminated soils can be conducted by *ex-situ* techniques (Younis et al., 2015), but many of these methods (excavation, landfilling and soil washing) are not appreciated because of their high costs and environmental disturbance (Efroymson et al., 2004). Thus, using organic residues may provide a suitable alternative for remediating soils contaminated with heavy metals (Abbas et al., 2017; Kumarathilaka et al., 2018). Incorporation of organic amendments in soils has received growing interests because of their cost-effective and eco-friendly influences on soil properties such as structure, fertility and quality (Park et al., 2011; Houben et al., 2012; Mohamed et al., 2015). Moreover, such amendments decrease the availability of heavy metals in soil due to sorption, oxidation/reduction, precipitation processes and formation of stable complexes with the functional groups of the organic amendment such as phenolic, carboxylic and hydroxylic (Rehman et al., 2016; Yousaf et al., 2016). The binding capacity of heavy metals with the organic amendment is usually influenced by many factors, including soil type, pH, ionic strength, organic matter, redox potential, cation exchange capacity and metal properties (Ali et al., 2017; Yue et al., 2017). It is worthy to mention that sensible concentrations of the bound heavy metals with the organic amendment may return back to soils during the decomposition process of the organic matter (Yue et al., 2017). Thus, selecting the appropriate

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https://doi.org/10.1016/j.ecoenv.2018.06.065
Received 1 April 2018; Received in revised form 16 June 2018; Accepted 20 June 2018

oxidation resistant amendments i.e. biochar (Han et al., 2018) can be the optimum choice for immobilizing heavy metals in soils for longer time periods (Bian et al., 2014a, b).

Biochar is a porous carbon product and can be obtained by thermal treatment (pyrolysis) of organic matter at a relatively low temperature (350–600 °C) under anaerobic or limited oxygen conditions (Abdelhafezez et al., 2017). The chemical and physical properties of these amendments are highly influenced by the feedstock type and pyrolysis conditions (Zhang et al., 2013; Houben and Sonnet, 2015). Many positive effects are recorded for amending soils with biochar e.g. improving soil chemical (cation exchange capacity and pH), physical (infiltration and soil structure) and biological properties (microbial biomass and enzymes activity). Moreover, biochar can successfully immobilize heavy metals and hence minimize their absorption by the grown plants (Herath et al., 2015; Bandara et al., 2017; Igalavithana et al., 2017) due to the high presence of functional groups e.g. ketone, carboxylic, aldehyde and phenol (Lucchini et al., 2014; Abbas et al., 2017) and high adsorption sites on its surface that form strong complexes with heavy metals (Paz-Ferreiro et al., 2014). However, the effect of biochar application on immobilization of heavy metals depends on various other factors such as the type of soil and the heavy metal, and the applied biochar doses (Park et al., 2011; Mohamed et al., 2015). Many investigations have been conducted to study the implications of different types of biochar on soil characteristics, plant growth and the transformations of heavy metals in soils (Zheng et al., 2012; Bian et al., 2014a, b; Kim et al., 2015; Abbas et al., 2017). However, the efficacy of peanut residues biochar combined with organic manure in reducing phytotoxicity of Cd is not well documented. Accordingly, a contaminated soil with Cd due to mining and smelting activities was selected to attain this aim. The main aim of this study was to evaluate the effect of the investigated biochar alone or combined with cow manure on plant growth and Cd accumulation within the different parts and growth periods of wheat until the physiological maturity growth stage. Moreover, effects of these amendments on soil chemical properties were determined at the end of the growing season.

## 2. Materials and methods

### 2.1. Soil and organic amendments

Surface soil samples (0–15 cm) were collected from the experimental farm in Daye mining area (30° 16' N and 114° 93' E), Huangshi City, Hubei Province, China. Samples were air-dried, and ground to pass a 2 mm sieve. The investigated soil was loamy and polluted with heavy metals due to smelting and mining activities. Peanut residues and cow manure were collected from Huazhong Agricultural University, Wuhan city, Hubei province, China. Peanut residues were converted into biochar through the pyrolysis process at 400 °C under limited oxygen conditions. The properties of soil and organic amendments biochar are presented in Tables 1 and 2.

### 2.2. Pot experiment

A pot experiment was carried out at the greenhouse of Wuhan Botanical Garden of Chinese Academy of Science (CAS), Wuhan (30°35′N, 114°17′E), Hubei province, China from 25 November 2014–2 May 2015. The experiment was organized in a complete randomized block design with 5 replicates. Seven treatments were considered in this experiment including three rates of applied peanut biochar (10, 15 and 20 Mg ha$^{-1}$) and three rates of cow manure enriched with biochar (5CM + 5PB, 5CM + 10PB and 5CM + 15PB Mg ha$^{-1}$) beside of the control treatment (no amendments). The common wheat (*Triticum aestivum* L.) was chosen as an indicator plant in this experiment. Thirty-five plastic pots (20 cm diameter × 20 cm height) were packed uniformly with 4 kg soil together with one of the abovementioned organic treatments. A phosphorus fertilizer was added to each pot at a rate of 0.50 g single superphosphate (5.6% P) with soil packing. Ten grains of wheat were sown in each pot and the soil moisture was brought to 60% of water holding capacity (WHC) using deionized water. The moisture was adjusted gravimetrically to 60% WHC throughout the experimental period. Two weeks later, plants were thinned to achieve five plants per pot. All pots received 0.25 g N (urea, N 46.6%) one month after cropping and 0.13 g potassium sulfate (40% $K_2O$) 45 days after cropping.

**Table 1**
Some physical and chemical properties of the used soil.

| Properties | Values |
|---|---|
| EC (dS m$^{-1}$ in soil paste) | 1.31 |
| pH (in 1:2.5 suspension) | 6.22 |
| Total organic matter (g kg$^{-1}$) | 18.5 |
| Total N (g kg$^{-1}$) | 1.56 |
| Total P (g kg$^{-1}$) | 0.71 |
| Total K (g kg$^{-1}$) | 6.89 |
| Total Cd (mg kg$^{-1}$) | 8.13 |
| Available N (mg kg$^{-1}$) | 17.45 |
| Available P (mg kg$^{-1}$) | 7.24 |
| Available K (mg kg$^{-1}$) | 124.8 |
| Available Cd (mg kg$^{-1}$) | 1.28 |
| $CaCO_3$ (g kg$^{-1}$) | 14.56 |
| Sand (%) | 45.05 |
| Silt (%) | 36.72 |
| Clay (%) | 18.23 |
| Soil texture | loam |

EC = electrical conductivity (dS m$^{-1}$).

**Table 2**
Some chemical properties of the used organic amendments.

| Properties | Peanut biochar | Cow manure |
|---|---|---|
| EC (dS m$^{-1}$ in 1:5 extraction) | 2.59 | 3.24 |
| pH (in 1: 5 suspension) | 8.76 | 7.59 |
| Total organic matter (g kg$^{-1}$) | 802 | 648 |
| Total organic carbon (g kg$^{-1}$) | 465 | 376 |
| Total N (g kg$^{-1}$) | 11.71 | 13.85 |
| Total P (g kg$^{-1}$) | 6.53 | 8.07 |
| C/N ratio | 39.71 | 26.49 |
| Total K (g kg$^{-1}$) | 9.45 | 11.23 |
| Total Cd (mg kg$^{-1}$) | 0.02 | 0.03 |
| Total Ca (g kg$^{-1}$) | 12.01 | 13.78 |
| Total Mg (g kg$^{-1}$) | 7.65 | 9.12 |

EC = electrical conductivity (dS m$^{-1}$).

### 2.3. Soil and organic amendments analyses

Soil particle size distribution was evaluated according to the method of Sheldrick and Wang (1993). EC and pH of soil and organic amendments samples were determined in a suspension of 1:2.5 (w/v) by EC/pH meter (Orion STAR A215). Soil organic carbon (SOC) was estimated by potassium dichromate ($K_2Cr_2O_7$) oxidation at 170–180 °C and then titrated by ferrous sulfate (Walkley and Black, 1934). In the case of biochar and cow manure, the organic matter content was determined by combustion in a muffle furnace at 540 °C for 6 h (Nelson and Sommers, 1996), and then calculated by subtracting their weight before and after the combustion process. FIA-star 5000 analyzer was used to determine total amounts of nitrogen (N) and phosphorus (P) in soil and organic wastes, while the total cadmium (Cd) content was determined by atomic absorption spectrometry (Varian AA240FS) after being digested by a concentrated mixture of $H_2SO_4$/$HClO_4$ (2:1 ratio).

### 2.4. Fractionation of Cd

Distribution of Cd between the different chemical fractions was estimated using the method described by Tessier et al. (1979). Five