



Changes in heavy metal mobility and availability from contaminated wetland soil remediated with combined biochar-compost



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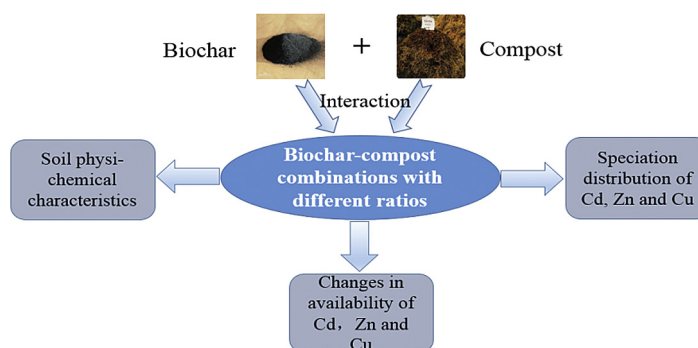
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HIGHLIGHTS

- 20% and 40% biochar addition in amendment combinations result in the higher soil pH.
- The pH changes explained the availability changes of Cd and Zn.
- Cu availability was related to high WEOC and total Cu content in compost.
- The increased organic binding fraction of Cu derived from the transformation of Fe/Mn oxide and residual fractions.

GRAPHICAL ABSTRACT



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ABSTRACT

The combination of biochar and compost has been proven to be effective in heavy metals contaminated wetland soil restoration. However, the influence of different proportions between biochar and compost on immobilization of heavy metals in soil has been less studied up to date. Therefore, we investigated the effect of different ratios of biochar-compost mixtures on availability and speciation distribution of heavy metals (Cd, Zn and Cu) in wetland soil. The results showed that applying all amendment combinations into wetland soil increased gradually the total organic carbon (TOC) and water-extract organic carbon (WEOC) as the compost percentage rose in biochar-composts. The higher pH was obtained in a certain biochar addition (20% and 40%) in combinations due to efficient interaction of biochar with compost. All amendments could significantly decrease availability of Cd and Zn mainly from pH change, but increase available Cu concentration as the result of increased water-extract organic carbon and high total Cu content in compost. Moreover, amendments can decrease easily exchangeable fraction and increase reducible of Cd and Zn greatly with increase of compost content in combinations, while amendments containing compost promote transformation of Cu from Fe/Mn oxide and residual fractions to organic bindings. These results demonstrate that different ratios of biochar and compost have a significant effect on availability and speciation of heavy metals in multi-metal-contaminated wetland soil.

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1. Introduction

Lake wetland is a kind of important ecosystem to human. However, the wetland is gradually decreasing and contaminated seriously in recent years due to the strong interference of anthropogenic activities (Li et al., 2013; Liang et al., 2016; Liu et al., 2015; Wu et al., 2015). The heavy metal adsorbed into the sediments by water particles is easy to be released from sediments due to the change of hydrodynamic and physicochemical conditions, thus causing secondary contamination and ecological environment deterioration (Bonanno et al., 2017; Zhang et al., 2014). Therefore, there has been extensive concern about heavy metal pollution in wetland and it is urgent and essential to wetland restoration.

The efficiency of contaminated site remediation relies on the effectiveness of organic amendments to reduce bioavailability of heavy metals. Compost produced from spontaneous microbial oxidation of agricultural straw, livestock manure and organic waste under aerobic condition, has been proven to be a very effective amendment for soil polluted by heavy metals (Beesley et al., 2010; Clemente and Bernal, 2006; Karami et al., 2011; Tang et al., 2014b). Compost added in contaminated soil can decrease mobile and exchangeable metal fraction by transforming it into organic bound (Manios et al., 2003; O'Dell et al., 2007). In addition, compost is also a kind of high quality organic fertilizer which can replenish various nutrients, increase microbial biomass and improve soil physicochemical properties (Clemente et al., 2012; Mackie et al., 2015; Schulz et al., 2013; Huang et al., 2008). Biochar, a solid residue from biomass pyrolysis under low oxygen conditions, has also gained increasing literature mainly because of polyaromatic and microporous structures, the large specific surface area, various surface functional groups and high cation exchange capacity (Keiluweit et al., 2010; Wang et al., 2012, 2013a; Xu et al., 2014; Liang et al., 2015a; Tang et al., 2014a). These characteristics make biochar sorb heavy metals easily and thus reduce soil ecotoxicity (Beesley et al., 2011; Tang et al., 2012; Yang et al., 2015; Wang et al., 2015b, 2017).

In order to reinforce the effect of two effective soil repair agent, compost and biochar can be mixed thoroughly to improve each other's properties. Because biochar surface is able to be oxidized by humus and microorganism in compost and biochar has an influence on compost humification process and provide favorable environment for microbial growth (Jindo et al., 2012; Wu et al., 2016a, 2016b). Combination of compost and biochar to restore soil has been researched widely in recent years. It had been observed by Beesley et al. (2014) that the mixture of biochar and compost at 1:1 (v/v) ratio could significantly reduce Cd and Zn concentration in soil pore water (Beesley et al., 2010). Beside, combining amendments had higher efficiency for reducing soil toxicity by means of the decreases in mobile and exchangeable heavy metals and increases in soluble nutrients simultaneously (Beesley et al., 2014). Other researches proved that combined compost and biochar (C+B) with 1:1 (w/w) ratio led to a higher reduction of the bioavailability and mobility of heavy metals and made the biggest improvement in soil microbial biomass (Zeng et al., 2015). In addition, the application of biochar could change soil properties such the total organic carbon (TOC), cation exchange capacity (CEC) and pH, and promote soil fertility as well as plant growth when combined with compost (Schulz et al., 2013; Zeng et al., 2015; Agegnehu et al., 2015). However, these studies are conducted at certain ratio of biochar and compost, and very few works are conducted to investigate the impacts of various ratios between biochar and compost on contaminated soil.

Detailed knowledge about changes of heavy metals in contaminated wetland soil with or without biochar-compost mixtures is required for a better understanding of the mobilization and

immobilization of metals and the controlling processes. Therefore, in this study we investigated the effects of biochar-compost combinations with different ratios on the mobility and availability of metals and aimed to (1) evaluate the changes in the physicochemical properties of wetland soil amended with variable biochar-compost mixtures after 60 d of incubation; (2) examine the effect of combined biochar-compost on the availability of cadmium (Cd), zinc (Zn) and copper (Cu) in contaminated wetland soil by CaCl_2 -extraction procedure and elucidate the underlying controlling processes mechanistically; and (3) assess the efficacy of biochar-compost combinations with various ratios as immobilizing agent to reduce the mobility of these elements in soil by sequential extraction procedure.

2. Materials and methods

2.1. Sampling site and soil collection

The contaminated soil sample in this study was derived from wetland of Dongting Lake. The local climate is abundant sunshine and rainfall of 1200 mm per year, and thus provide ideal habitat for various species (Yuan et al., 2014; Liang et al., 2015b; Hua et al., 2015). However, because of urbanization, mining production and agricultural activities, the wetland soil was heavily polluted by heavy metals and this resulted in the degradation of ecosystem function and destruction of the regional ecological environment which caused long-term risks to human survival and development (Liang et al., 2016; Zhang et al., 2016; Liang et al., 2015c, 2017).

Bulk soil sample was collected from 0 to 15 cm soil depth of five points in Lujiao Port, Yueyang, Hunan province (29°09'29.62"N, 113°0'4.98"E) in dry season from November to March and then representative soil sample was generated by mixing soil samples thoroughly from different points in laboratory. After mixing, the soil sample was air dried at shade place for 3 weeks and biological debris were removed by ground and sieved to <2 mm.

2.2. Organic amendments preparation and soil treatments

The rice husk biochar (B) was produced by slow pyrolysis process at 500 °C for 1 h under continuous flow N_2 condition and then cooled to room temperature, and finally was sieved to < 2 mm (Beesley et al., 2014). The compost (C) was made from the mixture of pig slurry (80% fresh weigh) and wood chips (20% fresh weigh) through two months composting process in aerobic condition.

To investigate the effect of biochar-compost combinations on availability and solubility of heavy metals in selected wetland soil, biochar-compost mixtures with various ratios between both amendments were blended thoroughly with the polluted soil (Table 1). Then amended soils and soil-only control were placed into 1000 mL pots and then incubated at room temperature for two months. Each treatment had three triplicate. During the period of incubation, deionized water was added to maintain 60% water holding capacity every 48 h. Soil samples were collected after one week (T1) and two months (T8) and then ground to pass through sieves to availability and speciation analysis of metals.

2.3. Physicochemical analysis for soil and organic amendments characterisation

The pH was tested in 1:2.5 (w/v) ratio of soil in deionized water with pH meter (Hanna instruments inc., 3221, USA). Total organic carbon (TOC) was examined by the loss-on-ignition method (Wright et al., 2008). Water extract solution was obtained by 1:10 (w/v) soil to deionized water, shaken for 3 h, and separated by centrifugation at 3000 rpm for 20 min, then filtered to remove

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