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Effects of biochars on the bioaccessibility of phenanthrene/pyrene/zinc/lead and microbial community structure in a soil under aerobic and anaerobic conditions

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ABSTRACT

The immobilization of co-contaminants of organic and inorganic pollutants by biochar is an efficient remediation strategy. However, the effect of biochar amendments on the bioaccessibility of the co-contaminants in dry *versus* flooded soils has rarely been compared. In batch experiments, bamboo-derived biochar (BB) had a higher sorption capacity for phenanthrene (Phe)/pyrene (Pyr)/zinc (Zn) than corn straw-derived biochar (CB), while CB had a higher sorption capacity for lead (Pb) than BB. After 150 days of incubation, the amendments of 2% CB, 0.5% BB and 2% BB effectively suppressed the dissipation and reduced the bioaccessibility of Phe/Pyr by 15.65%/18.02%, 17.07%/18.31% and 25.43%/27.11%, respectively, in the aerobic soils. This effectiveness was more significant than that in the anaerobic soils. The accessible Zn/Pb concentrations were also significantly lower in the aerobic soils than in the anaerobic soils, regardless of treatments. The Gram-negative bacterial biomass and the Shannon–Weaver index in the aerobic soil amended with 2% CB were the highest. The soil microbial community structure was jointly affected by changes in the bioaccessibility of the co-contaminants and the soil physiochemical properties caused by biochar amendments under the two conditions. Therefore, dry land farming may be more reliable than paddy soil cultivation at reducing the bioaccessibility of Phe/Pyr/Zn/Pb and enhancing the soil microbial diversity in the short term.

Introduction

Co-contamination of organic and inorganic pollutants has become a serious issue in agricultural soils located near manufacturing regions because of industrial waste production, wastewater irrigation, and pesticide and chemical leakage during agricultural production (Usman et al., 2016). The available fraction of these pollutants in soil can be taken up by crops and transferred through the food chain, eventually posing a threat to human health (Usman et al., 2016). Therefore, immobilization of the co-contaminants in soil, which seeks to reduce their transportation and bioavailability, is an effective soil remediation strategy to reduce these environmental risks (Ahmad et al., 2014; Mohan et al., 2014).

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The use of biochar in environmental remediation has been extensively investigated (Meyer et al., 2011). Biochars can reduce the mobility and bioavailability of the organic pollutants and heavy metals in soils through their large surface area and rich functional groups *via* physical adsorption, cation exchange, hydroxide formation and carbonate precipitation (Sohi et al., 2010; Beesley et al., 2010; Park et al., 2011; Cao et al., 2011). Soil-use (*e.g.*, dry land or paddy soil) can affect the environmental behavior of contaminants in soil and biochar-amended soil (Shankar, 2017). Studies have reported that biochar can reduce the availability of the co-contaminants of organic pollutants and heavy metals in soils under aerobic conditions (Beesley et al., 2010; Cao et al., 2011; Wu et al., 2016). For example, Beesley et al. (2010) reported that amendment with hardwood-derived biochar decreased the concentration of accessible polycyclic aromatic hydrocarbons (PAHs) by more than 50% and induced a 10-fold reduction in the available Cadmium (Cd) in the soil pore water of aerobic soils. The extractability of $CaCl_2$ after 1 hr of incubation was reduced by 25% for zinc (Zn) and 52% for lead (Pb) in the presence of 5% *Miscanthus* straw-derived biochar under aerobic conditions (Houben et al., 2013). Compared with the studies on the immobilizing potential of biochar in aerobic soils, those on the effect of biochar concerning the bioavailability of contaminants in anaerobic soils (*e.g.*, paddy soil) have been less reported. Chen et al. (2008) discovered that the PAH sorption was significantly enhanced in paddy soil amended with pine needles-derived biochar. The amendment of acidic paddy soil with sewage sludge biochar can reduce the amounts of bioavailable arsenic, chromium, cobalt, nickel, and Pb (Khan et al., 2013). Over five years, wheat straw-derived biochar consistently decreased the bioavailable Cd and Pb in a contaminated paddy field (Cui et al., 2016). However, these studies all investigated either organic pollutants or heavy metals. Whether biochar can simultaneously immobilize the co-contaminants of organic pollutants and heavy metals in anaerobic (flooded) soil has rarely been reported. The difference in the bioaccessibility of the co-contaminants in the biochar-amended soils under aerobic *versus* anaerobic conditions also remains unclear. Selection of a reasonable cultivation method for remediated soil amended with biochar is considerably important to ensure safe agricultural production.

The activity and diversity of soil microorganisms that are important for the ecological functions of agricultural soils might be decreased by the combined pollution of heavy metals and PAHs (Bourceret et al., 2016; Cao et al., 2008). The physical properties of biochars (*e.g.*, their pore structure, surface area and mineral content) support the functioning of soil biota (Lehmann et al., 2011). Thus, the relationships among co-contaminants, biochars and microorganisms should be deeply understood. Biochar amendment might increase the microbial diversity of PAH-contaminated soil (Liu et al., 2015). By contrast, Meynet et al. (2012) observed that the activity of PAH-degrading bacteria was more notable in unamended soil than in the soil amended with activated carbon. However, reports comparing the effects of biochar on the soil microbial community structure under aerobic *versus* anaerobic conditions are also lacking. Studying the changes in microbial community structure is helpful for selecting reasonable cultivation methods for contaminated soils amended with biochar.

This study aimed to (1) compare the effects of biochar on the bioaccessibility of the co-contaminants of organic and inorganic pollutants in a field soil under aerobic *versus* anaerobic conditions and (2) investigate the influence of biochar amendments on the microbial community structure under the two incubation conditions. Corn straw-derived biochar (CB) and bamboo-derived biochar (BB) were amended into an agricultural soil that was co-contaminated with phenanthrene (Phe)/pyrene (Pyr)/Zn/Pb. The soils were incubated under aerobic and anaerobic conditions to mimic upland and paddy soils, respectively. A batch sorption experiment was conducted to elucidate the Phe/Pyr/Zn/Pb sorption capacities of the biochars. A phospholipid fatty acid (PLFA) assay was conducted to analyze the soil microbial community structure. To the best of our knowledge, this is the first study to compare the effects of biochar amendments on the bioaccessibility of organic and inorganic co-contaminants and on the microbial community structure under aerobic *versus* anaerobic soils.

1. Materials and methods

1.1. Soil and biochar preparation

An agricultural upland soil co-contaminated with Phe/Pyr/Zn/Pb for more than 40 years was sampled at a depth of 0–20 cm in an area near a steel mill in the suburb of Nanjing, Jiangsu Province. The soil was air-dried and sieved through a 2 mm mesh. The soil had a pH of 7.36 and consisted of 27.60% sand, 63.52% silt, and 8.88% clay. The dissolved organic carbon (DOC) content of the soil was 309 mg/kg, and the total nitrogen (N), phosphorus (P), and potassium (K) contents of the soil were 1.3, 0.57, and 17.4 g/kg, respectively.

Phe and Pyr were chosen as model compounds in this study because they exist widely in PAH-contaminated soils, and in relatively higher concentrations than other PAH compounds (He et al., 2008). The Phe and Pyr concentrations in the soil samples were (258.59 ± 5.92) and (736.36 ± 18.10) μg/kg (dry weight), which exceeded the corresponding environmental quality standards for soils in China (GB 15618-2008) by one and two orders of magnitude. In addition, the Zn and Pb concentrations in the soil were (116.93 ± 14.36) and (38.64 ± 2.34) mg/kg (dry weight), respectively, which exceeded the corresponding environmental quality standards for soils in China (GB 15618-2008) by one order of magnitude.

CB was produced under oxygen-limiting conditions at a final temperature of 300°C using a patented biochar reactor (No. ZL2009 2 0232191.9) (Jia et al., 2013). BB, which is a representative of commercial biochar and produced at 700°C, was purchased from Shanghai Hainuo Charcoal Co., Ltd. The surface area, pore volume, and pore size of these biochars were measured *via* the Brunauer–Emmett–Teller (BET) method using a V-Sorb 2800P analyzer (Gold APP Instruments Corporation, Beijing, China). The elemental compositions were determined using an elemental analyzer (ANA1500, Carlo Erba, Milano, Italy) (Yuan et al., 2011). Table 1 details the physicochemical properties of the biochars.

The concentrations of the ∑16 PAHs in CB and BB were 778.72 and 413.17 μg/kg, respectively, which are both below the recommended maximum limit set by the International

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