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Influence of biochars on the accessibility of organochlorine pesticides and microbial community in contaminated soils

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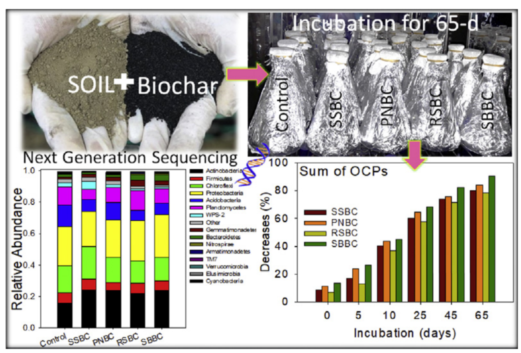
HIGHLIGHTS

- Biochars significantly ($p < 0.01$) reduced OCP accessibility in contaminated soils.
- The application of biochars altered soil microbial community structure over time.
- *Proteobacteria*, *Firmicutes*, *Gemmatimonadetes*, and *Actinobacteria* abundances increased in amended soil.
- *Acidobacteria* and *Chloroflexi* relative abundances decreased following biochar addition.
- Soil microbial community alteration with biochars may be reduced OCP accessibility.

GRAPHICAL ABSTRACT



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ABSTRACT

Biochar can be used as a promising potential substance to reduce the availability of toxic elements and compounds in contaminated soils but its effects on the accessibility of pesticides and microbiological interactions still remain unclear. Here, 65 day incubation experiments were conducted to investigate the efficacy of biochars on the accessibility of 21 different organochlorine pesticides (OCPs), and also to evaluate their influence on soil microbial community. The tested soil was collected from an agricultural field, containing loamy sand texture, and historically contaminated with high concentrations of OCPs. The soil was amended with four different kinds of biochars: sewage sludge biochar (SSBC), peanut shells biochar (PNBC), rice straw biochar (RSBC), and soybean straw biochar (SBBC). The results indicated that biochar-amendments had strong effects upon OCP accessibility over time and can act as super sorbent. Despite greater persistence of OCPs in soil, the application of selected biochars significantly ($p < 0.01$) reduced the accessibility of $\sum$OCPs in the amended soil in the order of SSBC (8–69%), PNBC (11–75%), RSBC (6–67%), and SBBC (14–86%), as compared to the control soil during 0–65 d incubation period. Moreover, the findings from total phospholipid acid (PLFA) and Illumina next-generation sequencing revealed that the incorporation of biochar have altered the soil microbial community structure over time. Higher abundances of *Proteobacteria*, *firmicutes*, *Gemmatimonadetes*, and *Actinobacteria* were found in biochar amendments. However, the relative abundances of *Acidobacteria* and *Chloroflexi* decreased, following biochar addition. The findings of these experiments suggest that biochar addition to soil at the rate of

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3% (w/w) could be advantageous for decreasing accessibility of OCPs, enhancing the soil microbial communities, and their subsequent risk to environment and food chain contamination.

1. Introduction

Biochar exhibits a great potential to be a promising adsorbent for environmental contaminants including pesticides, thereby playing a vital role in reducing the associated risk to humans and ecosystems (Ahmad et al., 2014; Cederlund et al., 2017; Kookana, 2010). Biochar is a solid carbon (C) rich substance produced from pyrolysis of biomass under low/no oxygen (Lehmann and Joseph, 2009; Akhtar and Sarmah, 2018).

Biochar addition may effectively reduce the available fractions by sorption and sequestration of pesticide residues (Ahmad et al., 2014; Kookana, 2010; Martin et al., 2012; Mukherjee et al., 2016; Sopeña et al., 2012; Yang and Sheng, 2003; Yu et al., 2010). The enhanced sorption capacity of biochar strongly depends upon its great specific surface area, organic C content, total porosity, high surface charge and other physicochemical properties (Cabrera et al., 2014; Dechene et al., 2014; García-Jaramillo et al., 2014; Safaei Khorram et al., 2016; Sopeña et al., 2012; Wang et al., 2010). For instance, a study by Yang and Sheng (2003) has demonstrated that wheat and rice biochars were about 2500 times more efficient than soil in adsorbing pesticide residues. Previous studies have also revealed that biochar has a high capacity to adsorb pesticides present in contaminated soils (García-Jaramillo et al., 2014; Spokas et al., 2009; Wang et al., 2010). The application of Eucalyptus biochar has been shown to reduce bioaccessible pesticide concentrations by 5 times than the unamended soil (Sopeña et al., 2012). In another study, Mukherjee et al. (2016) has reported that biochar application increased sorption/sequestration which in turn decreased the extractable fractions of pesticides.

The addition of biochar generally increases soil microbial biomass C and stimulates the microbial activities with or without changing the microbial composition (Ameloot et al., 2013; Lehmann et al., 2011; Quilliam et al., 2012; Santos et al., 2012; Song et al., 2013). On the contrary, addition of biochar can also reduce microbial biomass C and microbial activity as shown by several papers (Dempster et al., 2012; Domene et al., 2014; Khodadad et al., 2011; Mukherjee et al., 2015; Noyce et al., 2016), which could be caused by biochar sorption (Lammirato et al., 2011). Biochar has proven positive effects on soil pH (Major et al., 2010), crop productivity/plant growth/yields (Usman et al., 2016; Waqas et al., 2014; Woldetsadik et al., 2018), bioaccumulation and accessibility of organic and inorganic contaminants (PTEs and PAHs) in soil and food plants (Khan et al., 2015, 2014, 2013; Li et al., 2018). However, there are also some studies showing opposite effects (Bird et al., 2011; Chan and Xu, 2009; Crane-Droesch et al., 2013; Haefele et al., 2011; Calderón et al., 2015; Knox et al., 2015). Moreover, biochar has also been shown to increase and alter dissolved organic matter (DOM) content (Mukherjee and Zimmerman, 2013; Smebye et al., 2016) through stimulating microbial activities (Deenik et al., 2010). There are some previous studies showing the opposite or no effects on microbial activities, abundance or community structure (Jones et al., 2012; Prommer et al., 2014; Tian et al., 2016). The native/intuitive biochar DOM might influence the fate of organic contaminants/pesticides (Docherty et al., 2006; Tang et al., 2016), and could eventually lead to change microbial community (Docherty et al., 2006; Findlay et al., 2003), which is remained as one of the important knowledge gaps. Even with the increasing number of studies on the affinity of biochars for pesticides (García-Jaramillo et al., 2014; Reid et al., 2013; Spokas et al., 2009), its influence on the accessibility of pesticides, and subsequent effects on microbial community have received little attention. The accessible fraction makes it possible to measure the adverse impact of contaminants (pesticides) more accurately than the total concentrations of the contaminants in soil. The total concentrations of the contaminants often result in the over estimation of their environmental risk.

Organochlorine pesticides (OCPs) were selected for this study because of their high toxicity, persistence, bioaccumulation, and deleterious effects on human and ecosystems (El-Shahawi et al., 2010; Sun et al., 2012). The extensive and deliberate application of OCPs across the globe to improve and maximize yields has resulted in extensive environmental contamination (Mumtaz et al., 2015; Wang et al., 2009). Previously, several research papers have been published related with application of biochar including minimization of available potentially toxic elements, nutrients uptake, plant biomasses, arsenic speciation polycylic aromatic hydrocarbons (PAHs) etc. In this particular research, we have focused on totally different aspects of biochar such as accessibility of pesticides in contaminated soil, its effects on soil microbial community structure and DOM changes overtime. It means that this paper covers three aspects of biochar, which were not previously covered by a single paper such as 1) accessibility of OCPs, 2) microbial community structure and 3) soil DOM and its properties which is the novelty of this manuscript. A systemic and comprehensive research is essential to sort out the influence of biochars on pesticide-accessible concentrations, as well as likely changes in the amended soil microbial community. Hence this research work was carried out to investigate how different biochars reduce the pesticide-accessible concentrations over time. The effects of these biochars on microbial community and DOM changes in the amended soils were also assessed.

2. Materials and methods

2.1. Soil sampling and basic analyses

The pesticide-contaminated soil used in the present incubation studies was collected from 0 to 20 cm depth from a highly contaminated agricultural land because of the over-application of pesticides in Ningbo, district Beilun, Zhejiang, China. The plant residues and stones were removed from the soil manually and then the soil was dried under a room temperature before passing through a sieve (2 mm). The collected soil was loamy sand in nature consisting of approximately 70% sand, 28% silt, and 2.0% clay. The total concentrations of OCPs and basic characteristics of soil such as pH, nitrogen (N), sulfur (S), and C contents were determined. A sub-sample (1 kg) was taken from the test soil and freeze dried for further analyses.

2.2. Biochar collection and preparation

The soybean and rice straws were collected from local farmers in the vicinity of Xiamen City, whereas peanut shells were obtained from an oil production facility in the suburb of Xiamen. Sewage sludge was obtained from wastewater treatment plant in Bingbei, Xiamen, China and air dried. Four types of biochars were prepared from their respective feedstock (sewage sludge, soybean straw, rice straw, and peanut shells) using pyrolysis technique for 6 h at 500 °C under continuous flow of nitrogen and used in the incubation experiments. Basic characteristics such as pH, EC, surface area, porosity etc. of these selected biochars were also measured. The values of pH and EC (1:5 w/v) were measured with Accumet XL 60 m, equipped with pH and EC electrodes. The surface area and porosity of biochars were determined with surface area and porosity analyser (Micromeritics, ASAP 2020M + C, USA). Soil particle size was determined with Mastersizer 2000 (Malvern Instruments Ltd., UK), whereas total C, total N, and total S were determined