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# Contrasting effects of biochar nanoparticles on the retention and transport of phosphorus in acidic and alkaline soils<sup> $\star$ </sup>

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# ABSTRACT

Land application of biomass-derived biochar has been increasingly recommended as a beneficial soil amendment for nutrients (such as N, P) retention. However, the small-scale biochar particles, especially those in the nano-scale range, may carry nutrients downward the soil profile, reducing nutrition retention and posing a potential risk to the groundwater. In this study, column experiments were conducted to investigate the retention and transport of phosphorus (P) in two acidic and two alkaline soils as affected by wood chip-derived biochar nanoparticles (NPs). In acidic paddy and red soils, biochar NPs facilitated the retention of P, increasing by about 24% and 16%, respectively, compared to the biochar absence. It is because biochar NPs stabilize soil Fe/Al oxides and dissolved organic carbon (DOC), thereby reducing the release of Fe/Al oxides- and DOC-associated P. In contrast, in alkaline huangmian and chao soils, retention of P was reduced in the presence of biochar NPs, decreasing by about 23% and 18%, respectively. It was mainly due to the increased transport of Fe/Al oxides-associated P in effluents. Moreover, biochar NPs could also act as a P carrier, mediating the retention of P. The diffusive gradients in thin films provided in-suit measurement of labile P in soil profiles, showing much lower labile P from retained P in acidic soils than that from alkaline soils though the labile P with biochar NPs presence was increased in all soils. Our findings indicate that biochar NPs have contrasting effects on the retention of P in acidic and alkaline soils, implying the cautious land applications of biochar for nutrients retention in soils with different acidities.

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# 1. Introduction

Phosphorus (P) is an essential element for plant growth and a key agricultural input into soils. Farmers often apply large amounts of P fertilizers into soils to enhance crop production, especially in China. Excessive application of P fertilizers has caused the release of P into surface and/or groundwater via runoff, drainage, irrigation, or infiltration, posing negative risks to the water systems (Yao et al., 2011a; Jaisi et al., 2011; Lv et al., 2012). High P level ultimately is a major factor in the eutrophication of freshwater and coastal sea water ecosystems (Karaca et al., 2004; Yao et al., 2012). Moreover, P leaching has become an important limitation to the utilization

https://doi.org/10.1016/j.envpol.2018.04.050 0269-7491/© 2018 Elsevier Ltd. All rights reserved. efficiency of P fertilizers in agricultural production. Therefore, it is important to understand the retention and transport behaviors of P to better optimize their benign use in agronomic and environmental advantages for soil P retention and release.

Biochar has recently been used as a low-cost sorbent to retain P due to its large specific surface area, internal porosity, and rich polar and nonpolar surface sites (Yao et al., 2011a; Yao et al., 2012; Yao et al., 2011b; Yao et al., 2013; Mukherjee et al., 2013; Lehmann and Joseph, 2009; Cui et al., 2016; Macdonald et al., 2015). It could directly be applied to agricultural fields to improve soil fertility by reducing the leaching loss of nutrients (Laird et al., 2010a). However, the possible negative impacts associated with the land application of biochar must also be taken into consideration (Hale et al., 2012; Oleszczuk et al., 2013). Recent studies have shown transport behavior of nano-scale biochar in porous media (Wang et al., 2013a, 2013b; Zhang et al., 2010; Chen et al., 2017). These small 'reactive' biochar nanoparticles (NPs) may carry







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contaminants down along the soil profile and enter the groundwater system. Once leaching, biochar NPs might affect the retention and dissemination of P, giving rise to the release of P. To the best of our knowledge, few studies have looked at the effects of biochar NPs on the retention and transport of P in natural soils (Yao et al., 2011a, 2012).

Leaching of P from agricultural soil is an intricate process that depends on soil properties, such as solution pH, clay minerals, Fe/Al oxides, and organic matter (Luengo et al., 2007; Zhong et al., 2007; Borggaard, 1983; Uchimiya et al., 2010). For example, the sorption of P by soils decreases with the increase of pH due to stronger electrostatic repulsion, thereby decreasing the retention of P, while decreasing pH increased the adsorption capacity of P onto soils (Jiang et al., 2015). The negatively charged P could attach onto the surface of Fe/Al oxides, which makes large proportions of P turn into unavailable forms (Arai and Livi, 2013). Due to its heterogeneous, part of dissolved organic matter maybe positive through protonation (Yan et al., 2017). Thus, P can sorb onto dissolved organic matter by electrostatic interaction. When incorporated into soil, biochar can alter soil physical and chemical properties (Xu et al., 2012; Laird et al., 2010b; Chen et al., 2011). The positive electricity on the surface of Fe/Al oxides (amphoteric minerals) are neutralized by the addition of the negatively charged biochars, leading to the agglomeration and immobilization of Fe/Al oxides (Fang et al., 2016). Moreover, biochar addition might aid in stabilizing soil organic carbon due to sorption to biochar NPs and occlusion within aggregates, thereby reducing the release of soil organic carbon (Hua et al., 2014). Hence, we hypothesize that biochar might influence the retention and transport of sorbed P onto Fe/Al oxides or soil organic carbon complex (Uchimiya et al., 2010; Cui et al., 2011).

The main objective of this study is therefore to investigate the effects of wood chip-derived biochar NPs on retention and transport of P in acidic and alkaline soils. Specifically, retention and transport behaviors of P in acidic and alkaline soils were examined in the absence and presence of colloidal biochar NPs by column breakthrough experiments; pre-deposited biochar NPs or P in soils followed by P or biochar NPs injection were conducted to explore possible mechanisms by how biochar NPs affect the retention and transport behaviors of P; and the diffusive gradients in thin films (DGT) technology was used to acquire the in-suit measurement of labile P from retained P in soils as affected by biochar NPs. The results are expected to increase our knowledge on land applications of biochar for nutrient retention.

## 2. Materials and methods

#### 2.1. Soils and biochar NPs

Four types of soils (0-20 cm) were collected from Jiangsu (paddy soil, PS), Jiangxi (red soil, RS), Shaanxi (huangmian soil, HS), and Henan (chao soil, CS). The collected soils were air-dried, crushed, and sieved between 600 and 710  $\mu$ m (650- $\mu$ m median grain size). Selected physicochemical properties of the soil aggregates such as pH, total organic carbon content, specific surface area, zeta potentials, elemental compositions, etc. were characterized (S1 in Supporting Information).

Biochar was produced from wood chips under N<sub>2</sub>-atmosphere at pyrolysis temperature of 500 °C. The biochar NPs were obtained by completely grinding the biochar into powders and passing through a 200-mesh sieve. Characterization of the physicochemical properties of the biochar NPs such as pH, particle size, specific surface area, elemental compositions, etc. was described in our previous study (Chen et al., 2017).

### 2.2. Sorption of P onto soils and/or biochar NPs

Batch sorption experiments were conducted to understand the sorption capacity of P onto soils and/or biochar NPs. The P stock solution was prepared by dissolving NaH<sub>2</sub>PO<sub>4</sub> (analytical grade) into deionized (DI) water. All sorption experiments were carried out in duplicate. First, 0.50 g soils were weighted into 50-mL centrifugation tubes with a series concentrations of 25 mLP solutions (0.010-2.0 mM, diluted with P stock solution) for the experiment of P sorption by soils. The mixtures were unbuffered and their pH values were 5.84 for PS, 5.45 for RS, 7.36 for HS, and 7.16 for CS, respectively. Second, 0.50 g soils with 5% (wt/wt) biochar NPs were added into a series of 25 mLP solutions (the same as above) to investigate the sorption of P onto biochar NPs and soils. The pH values of mixtures were 6.68 for PS, 6.31 for RS, 7.68 for HS, and 7.48 for CS, respectively. After rolling about 15 h at the speed of 30 r min<sup>-1</sup> which was preliminarily determined as a condition to allow the mixtures to reach equilibrium, the soil suspensions were centrifuged at the speed of 4000 rmin<sup>-1</sup> for 20 min and filtered through a 0.45-µm filter. In addition, the soil solutions were obtained from soil suspensions at a soil to DI water ratio of 1:20 after centrifuging at 4000 r min<sup>-1</sup> for 20 min and filtering through a 0.45-µm filter (Fang et al., 2011). In order to study the effect of soil solution on the sorption of P onto biochar NPs, biochar NPs  $(200 \text{ mg L}^{-1})$  were suspended in 1.0 mM P with the presence of soil solutions of PS, RS, HS, and CS. The biochar NPs suspensions in 1.0 mM P without soil solution were used as control. At the end of sorption equilibrium, the biochar NPs suspensions were centrifuged at 10000 r min<sup>-1</sup> for 50 min, and then filtrated through a 0.22-µm filter to completely separate biochar NPs from the solution. The concentration of P in supernatant was analyzed by molybdenum blue method using a UV-vis spectrophotometer (UV-2450, Shimadzu Co., Ltd., Japan) at the wavelength of 790 nm (Chen et al., 2015). Ascorbic acid was used as reducing agent in this method to avoid the influence of ion (such as Fe) in the soil solution on the detection of P. The amount of P adsorbed was calculated by the difference between the initial and equilibrium concentration in filtrate.

### 2.3. Column transport experiments

Column transport experiments were conducted in 1.2 cm  $(diameter) \times 8 \text{ cm}$  (length) glass chromatography columns, which were wet-packed with the soil aggregates (650-µm median grain size, prepared above). The column porosity was determined gravimetrically to be 0.54-0.57 (Table S1). Detailed procedures of column packing and saturating were described in our previous study (Chen et al., 2017). Following the column saturated with DI water, the NaBr conservative tracer was injected into the four types of soil columns with the targeted flow rate  $(0.25 \text{ mLmin}^{-1})$  to obtain the hydrodynamic properties of soil columns by fitting NaBr breakthrough curves (BTCs). Bromide tracer concentration was quantified using a bromide ion-selective electrode (PBr-1, Kangyi Instrument Co., Ltd., China). The BTCs of bromide tracer in the PS, RS, HS, CS, and sand columns were fitted using the CXTFIT code (Fig. S1), indicating that the average pore-water velocity of the four types of soil and sand columns was almost the same in this study (Wang et al., 2015). After the tracer experiment, about 16 pore volumes (PVs) of 1.0 mM P solutions without and with  $200 \text{ mg L}^{-1}$ biochar NPs (Exp. 1–4 and Exp. 5–8, respectively, Table S1) were injected into the soil columns using a peristaltic pump (BT100-2], Baoding Longer Precision Pump Co., Ltd., China). The transport of P (1.0 mM) without and with biochar NPs  $(200 \text{ mg L}^{-1})$  in sand columns was used as control. The pH of influent P solutions without and with biochar NPs was unbuffered and the pH was about 5.28 Download English Version:

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