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ORIGINAL PAPER

Short-term effects of maize residue biochar on phosphorus availability in two soils with different phosphorus sorption capacities

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Abstract This study investigated the effects of maize (*Zea mays* L.) straw biochar on phosphorus (P) availability in two soils with different P sorption capacities (iron and aluminum dominated slight acid Red earth and calcium dominated alkaline Fluvo-aquic soil). A 42-day incubation experiment was conducted to study how applications of biochar at different rates (0, 2, 4, and 8 % soil, *w*/*w*), in combination with and without mineral KH_2PO_4 fertilizer, affected contents of soil Olsen-P and soil microbial biomass P (SMB-P) and phosphomonoesterase activity. In addition, P sorption characteristics of soils amended with biochar, as well as main properties of the biochar and the soils, were determined. Application of 8 % biochar after 42 days of incubation substantially increased soil Olsen-P from 3 to 46 mg kg^{-1} in Red earth and from 13 to 137 mg kg^{-1} in Fluvo-aquic soil and increased SMB-P from 1 to 9 mg kg^{-1} in Red earth and from 9 to 21 mg kg^{-1} in Fluvo-aquic soil. The increase was mainly due to high concentrations of P in the ash fraction (77 % of total biochar P). Biochar effect on soil Olsen-P and SMB-P increased by higher biochar application rates and by lower P sorption capacity. Biochar application significantly reduced acid phosphomonoesterase activity in Red earth and alkaline phosphomonoesterase activity in Fluvo-aquic soil due to large amount of inorganic P added. We conclude that maize straw biochar is promising to potentially improve soil P availability in low-P soils, but further research at field scale is needed to confirm this.

Keywords Biochar · Fluvo-aquic soil · Phosphorus availability · Phosphorus sorption capacity · Red earth · Soil Olsen-P

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Introduction

Crop residues are valuable agricultural resources as they contain considerable amounts of nutrients. Return of these nutrients, with a satisfactory availability for crop uptake, to the soil is a challenging research and practice task. Burning of crop residues is a traditionally prevalent practice to return the nutrients to soils in many countries including China, but this generates environmental problems including air pollution, emissions of greenhouse gases, serious fine dust problems, and even change of air circulation and monsoon patterns (Gustafsso et al. 2009; Huang et al. 2012). Processing crop residues to produce biochar and applying biochar to soil is recognized as a better way of disposal of crop residues compared with direct burning of residues in the field (Chun et al. 2004; Qian et al. 2013). Moreover, biochar derived from crop residues is increasingly regarded as a multifunctional material for agricultural and environmental applications (Chen et al. 2011). Biochar has many positive effects on soil quality, e.g., increasing soil organic matter content and pH, retaining soil moisture and nutrients, improving soil structure and stimulating microbial activity, and thus promoting plant growth (Asai

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et al. 2009; Zhang et al. 2010, 2012; Anderson et al. 2011; Beck et al. 2011; Haefele et al. 2011; Soinne et al. 2014).

For many agricultural fields in China, application of phosphorus (P) is necessary to maintain a high productivity. A considerable amount of P is removed from soil by harvest of crop grains, and another considerable amount of P is stored in the straws with low use efficiency. A continuous and large demand of P in agriculture would eventually lead to a rapid depletion of P resources, which are mainly nonrenewable phosphate rocks (van Vuuren et al. 2010). From this sense, crop residues should be returned to soil for sustainable P management (Lupwayi et al. 2007; Tao et al. 2012). After charring, concentration of P in biochar is generally two to three times higher than the common values in crop straws, and the volume is substantially reduced. This makes biochar a promising alternative to the direct return of straw especially when incorporation of straw is not feasible due to adverse pedoclimatic conditions.

Several studies have investigated potential effects of biochar application on P availability by changing the soil environment. Atkinson et al. (2010) found that biochar affected soil P availability and plant uptake of P indirectly by changing the environment for microorganisms. DeLuca et al. (2009) observed that the use of biochar altered soil P availability through the biochar's anion exchange capacity or by influencing the activity/availability of cations that interact with P. Moreover, Laird et al. (2010) found that addition of biochar reduced P leaching from a manured soil due to sorption of both orthophosphate and organic P by the biochar. On the contrary, some studies demonstrated that biochar had limited ability to sorb P (Soinne et al. 2014); instead, biochar can even act as a source of soluble P after application to soil (Parvage et al. 2013). Release of P from biochar has also been approved by considerable amount of desorption of P from biochar at zero P level in P sorption experiments (Morales et al. 2013). Availability of P in soil is greatly dependent upon P sorption capacity of soil (Gburek et al. 2005). Thus, it is meaningful to investigate the effect of biochar application on the availability of P in soils with different P sorption capacities. To date, soil fertility is more commonly indicated by physical and chemical soil properties, but biological indicators are becoming increasingly used due to their quick response and high ecological relevance (Nannipieri et al. 2003; Huang et al. 2013). Soil microbial biomass has been recognized as an important source of nutrients to plants because of its fast turnover (Jenkinson and Ladd 1981). Phosphatases can catalyze the hydrolysis of ester–phosphate bonds, leading to the release of phosphate, which can be taken up by plants or microorganisms (Quiquampoix and Mousain 2005). Activities of phosphomonoesterases in soil can be repressed by inorganic P (Nannipieri et al. 2011, 2012) and be dependent on several factors such as soil properties, soil organism interactions, plant cover, leachate inputs, and the presence of inhibitors and activators (Speir and Ross 1978). Thus, activities of phosphomonoesterases in soil may be affected by biochar application and P sorption capacity of soil, which both influence the availability of inorganic P in soil.

Properties of biochar highly depend on feedstocks (Farrell et al. 2014). This study investigated the effect of biochar derived from straw of maize (*Zea mays* L.), one of the most important cereal and forage crops in China, on P availability in soil. The hypotheses tested were the following: (1) biochar application can improve soil P availability due to high concentrations of P in the ash fraction of biochar; (2) soil P availability after biochar application is higher in soil with lower P sorption capacity; (3) acid phosphomonoesterase activity in Red earth and alkaline phosphomonoesterase activity in Fluvo-aquic soil are affected by biochar application and soil P sorption capacity.

Materials and methods

Soils

Two typical Chinese arable soils were used in this study. One was a slight acid soil (pH=6.38) from Dali (25° 53′ 41″ N, 100° 5′ 26″ E, 2,245-m altitude), Yunnan province. It is Red earth according to the soil classification system in China or Ferralic Cambisol according to the soil classification systems by FAO (2006). The other soil was an alkaline soil (pH=8.27) from a long-term experimental field located at Changping (40° 13′ 12″ N, 116° 15′ 23″ E, 44-m altitude), Beijing, and it is Fluvo-aquic soil or Haplic Luvisol (FAO 2006). Soil samples were taken from the field plow layer, i.e., at a depth of 0–20 cm, and air-dried at room temperature, ground, and sieved (<2 mm) before determination of soil characteristics and use in the subsequent incubation and sorption experiments. Red earth had 30 % clay (<0.01 mm), 18 % silt (0.01–0.05 mm), and 52 % sand (>0.05 mm), while Fluvo-aquic soil had 35 % clay, 29 % silt, and 36 % sand. They both had a total phosphorus (TP) content of 0.84 g kg^{-1}, but Red earth had a much lower plant-available P content (Olsen-P 3.01 mg kg^{-1}) than Fluvo-aquic soil (Olsen-P 12.62 mg kg^{-1}). Red earth usually has high Fe and Al contents and thus low level of plant-available P due to strong fixation. A wide distribution of Red earth in Yunnan province makes 25 % of its arable soils have Olsen-P content smaller than 5 mg kg^{-1}. In contrast, Fluvo-aquic soil has high Ca content and its Olsen-P level represents for approximately 50 % of arable soils in Beijing. Detailed descriptions of the soil physical and chemical characteristics are shown in Table 1.

Table 1 Main physical and chemical characteristics of soils

Soil type	Clay[a] (%)	EC[b] (ds m^{-1})	pH	Organic matter (g kg^{-1})	Total P (g kg^{-1})	Olsen-P (mg kg^{-1})	$CaCl_2$-P	Fe[c]	Al[c]	Ca[c]	Mg[c]
Red earth	30	0.059	6.38	32.6	0.84	3.01	0.37	98	1,324	2,440	261
Fluvo-aquic soil	35	0.266	8.27	16.2	0.84	12.62	0.11	14	15	11,900	–

[a] Fraction <0.01 mm

[b] Electrical conductivity

[c] According to the Mehlich-3 method (Nair et al. 2004)

Biochar preparation

The biochar used in this study was produced from maize straw collected from a cropland in a suburb of Beijing. The straw samples were air-dried at room temperature, ground, and sieved (<1 mm). Thereafter, the straw samples were placed in ceramic crucibles, each covered with a fitting lid, and pyrolyzed under oxygen-limited conditions in a muffle furnace (Shanghai Yizhong Electricity Furnace Inc., Shanghai, China). The pyrolysis temperature was gradually raised to 400 °C, at a rate of approximately 20 °C min^{-1}, and then kept constant for 1.5 h (Chun et al. 2004). After pyrolysis, the biochar samples were cooled down to room temperature. Three replicated biochar samples were prepared with the same process as described above. To determine the ash content in the biochar, the biochar was washed with 1.0 M HCl and rinsed with deionized distilled water for several times (Chun et al. 2004). Then the acid-washed biochar was oven-dried at 70 °C overnight. Mass of the ash was the difference between the mass of the original biochar and the mass of the acid-washed biochar. Content of TP in the biochar was determined both before and after acid washing. The TP content in the ash was calculated using the following equation:

$$\mathrm{TP_{Ash}}\left(\mathrm{g\,kg^{-1}}\right) = \left(\mathrm{TP_{unmodified\ biochar}} - \mathrm{TP_{Acid\text{-}washed\ biochar}} \times (1 - \text{Ash content})\right)/m_{\mathrm{Ash}} \quad (1)$$

Incubation experiments

The incubation experiments included nine treatments, and each treatment was carried out with 150 g air-dried soil placed in a plastic cup. In six treatments, each of the two soils was amended with biochar at rates of 2, 4, and 8 % (*w*/*w*) of initial soil in dry weight, with or without addition of KH_2PO_4 at a P rate of 60 mg kg^{-1} soil. Two controls, one with the unamended soil (0 % B) and the other with KH_2PO_4 but without biochar, were included. In the last treatment, soil was amended with the acid-washed biochar at the rate of 4 % (*w*/*w*). Each treatment was replicated three times. Biochar and fertilizer were mixed thoroughly into the soil, which then was wetted with deionized water to 60 % of field water holding capacity. All cups were covered with plastic film, having a small hole to allow gaseous exchange and minimize moisture loss. The cups were incubated at a constant temperature of 25 °C for 42 days. Every 7 days, the weights of the cups were measured and necessary water was supplied to maintain the constant soil moisture content. Each time, 20 g of soil were taken from each incubation cup to determine soil pH, EC, Olsen-P content, and phosphomonoesterase activity.

Analyses

The pH of the soil and the biochar was determined with a pH meter (Mettler Toledo Delta 320), with a soil (air-dried) to water (*w*/*w*) ratio of 1:2.5 and biochar to water ratio of 1:30. The electrical conductivity (EC) was determined by an electrical conductivity meter (DDS-307A). Contents of TP in straw, biochar, and soil were determined using the molybdate-ascorbic acid method, after oxidative digestion of the straw and biochar with concentrated H_2SO_4-H_2O_2 (Tang et al. 2008) and digestion of soil with H_2SO_4-$HClO_4$ (Liu et al. 2010). Plant-available P in the soil was measured according to Olsen et al. (1954), with soil extracted with 0.5 M $NaHCO_3$ and the P in the extract determined colorimetrically using the molybdenum blue method (Murphy and Riley 1962). The P in the soil solution was determined after shaking 10 g of the air-dried soil with 50 mL 0.01 M $CaCl_2$ solution for 30 min (McDowell and Sharpley 2001). The easily available contents of Fe, Al, Ca, and Mg in soil were extracted with the Mehlich-3 solution (Nair et al. 2004) and determined with ion-coupled plasma (ICP, PerkinElmer, Wellesley, USA).

Contents of C, N, H, and O in the biochar were determined by a vario PYRO cube elemental analyzer. The specific surface area and porous texture of the biochar were determined with a Surface Area and Porosity Analyzer (ASAP 2020 HD88, USA). The specific surface area (S_{BET}) was calculated based on the Brunauer–Emmett–Teller (BET) equation (Zheng et al. 2013). The shapes and surface physical morphology of the biochar were examined by a field emission scanning electron microscopy (FE-SEM; SU8000, Hitachi, Tokyo, Japan) at 15 KeV.

Soil microbial biomass P (SMB-P) was determined by fumigation–extraction method (Vance et al. 1987). Soil

phosphomonoesterase activity was determined according to Tabatabai (1982). Two milliliters 0.5 M sodium acetate buffer and 0.5 mL of *p*-nitrophenyl phosphate disodium (PNPP, 0.15 M) as substrate were added to 0.5 g mixture of soil and biochar and incubated at 37 °C for 60 min. After this, 0.5 mL 0.5 M $CaCl_2$ and 2 mL 0.5 M NaOH were added, and the mixture were shaken and filtered. Different pH in buffers were used, i.e., pH 6.5 for measuring acid phosphomonoesterase activity of Red earth and pH 11 for measuring alkaline phosphomonoesterase activity of Fluvo-aquic soil, as acid phosphomonoesterase activity generally prevails in acidic soils, whereas alkaline phosphomonoesterase activity prevails in alkaline soils (Juma and Tabatabai 1978). Acid and Alkaline phosphomonoesterase activity (AP) was expressed as milligrams *p*-nitrophenol (PNP) produced per gram dry weight soil and per hour. The PNP formed was determined at 398 nm.

Phosphorus sorption experiments

Air-dried soil samples (2.5 g) were placed in 100-mL screw cap centrifuge tubes and treated with biochar at rates of 0, 2, 4, or 8 %; each treatment was replicated three times. The soil and biochar were then mixed thoroughly, treated with 50 mL of standard solutions at various P concentrations (0, 15, 30, 40, 50, 60, 70, 80, 90, 100, 120 mg P L^{-1} for Red earth; 0, 15, 30, 40, 50, 60, 70 mg P L^{-1} for Fluvo-aquic soil). The standard P solutions were prepared by dissolving KH_2PO_4 in 0.01 M KCl at pH 7. Two drops of toluene were added to retard microbial activity. The samples were shaken on a reciprocal shaker at 200 rpm for 12 h. After equilibrium, the samples were centrifuged at 1,730×*g* for 15 min. The P in the supernatant was determined according to the molybdenum blue method (Murphy and Riley 1962). The amount of P sorbed by the soil was calculated as the difference between the P added and the P remaining in the solution at equilibrium, according to the following equation:

$$Q_e = (C_0 - C_e)V/m \quad (2)$$

where, Q_e is the sorbed P (mg kg^{-1} soil) at equilibrium, C_0 and C_e (mg L^{-1}) are the concentrations of P in the initial and equilibrium solution, respectively, V is the volume of the aqueous solution (L), and m is the mass of soil (kg).

Statistical analysis

Microsoft Excel (Microsoft Corporation, USA) and SPSS windows version 16.0 (SPSS Inc., Chicago, USA) packages were used for statistical analysis of data. Least significant difference (LSD at P=0.05) was calculated to determine whether means significantly differed among treatments. Unless otherwise stated, the level of significance referred to P<0.05.

Results

Properties of the biochar

The maize straw that was charred at 400 °C yielded the biochar at a rate of 38 %. The elemental analysis showed that the main components of the maize straw biochar were C (76 %), O (13 %), N (5 %), K (4 %), and Ca (1 %) (Fig. 1). The SEM image showed that the biochar consisted of irregular plates and particles of different sizes and that the surface of the biochar was smooth (Fig. 1). The biochar had a specific surface area of 8.57 m^2 g^{-1}, an average pore size of 41.9 nm and a pH of 10.7. Charring process substantially enriched TP concentration from 0.81 g kg^{-1} in maize straw to 3.31 g kg^{-1} in biochar. The biochar amended at rates of 2, 4, and 8 % soil gave 130, 260, and 520 kg P ha^{-1}, respectively, whereas the P added with KH_2PO_4 fertilizer was equivalent to 118 kg P ha^{-1}. Moreover, the concentrations of Olsen-P (15.8 mg kg^{-1}) and $CaCl_2$-P (0.22 mg P kg^{-1}) in biochar were relatively high. After washing with acid, biochar had a TP concentration of 0.94 g kg^{-1}. Despite the ash only made up 17 % of biochar mass, it contained 77 % of TP in biochar, due to high P concentration (14.9 g P kg^{-1} ash).

Effect of biochar application on soil Olsen-P

Content of Olsen-P in both soils increased significantly (P<0.05) after amendment with maize straw biochar compared with the controls without biochar amendment, and the increase was greater at higher biochar application rates. When soils were applied with an increasing rate of biochar from 0 to 2, 4, and 8 %, Olsen-P increased from 3 to 12, 27, and 46 mg kg^{-1} in Red earth and from 13 to 53, 93, and 137 mg kg^{-1} in Fluvo-aquic after incubation for 42 days (Fig. 2). This trend is due to increasing amounts of P added to soils with increasing amounts of biochar, and it demonstrates that the P added with biochar is to a large extent available. Increment of soil Olsen-P after 2 % biochar application was similar to that caused by application of KH_2PO_4 fertilizer at 118 kg P ha^{-1} (Fig. 2).

Fluvo-aquic soil had a higher Olsen-P content than Red earth at initial conditions, despite two soils had the same total P content (Table 1). After application of the same amount of biochar, Fluvo-aquic soil always had a significantly (P<0.05) higher increase in Olsen-P content than Red earth (Fig. 3). In contrast, application of the acid-washed biochar (washing with HCl to eliminate ash) had little effect on soil Olsen-P content. After 42 days of incubation, application of 4 % biochar increased soil Olsen-P by 27 mg kg^{-1} in Red earth and 80 mg kg^{-1} in Fluvo-aquic soil, whereas the acid-washed biochar applied at the same rate increased Olsen-P by only 0.12 and 0.81 mg kg^{-1}, respectively (Table 2). This means that increase in soil Olsen-P by biochar application is

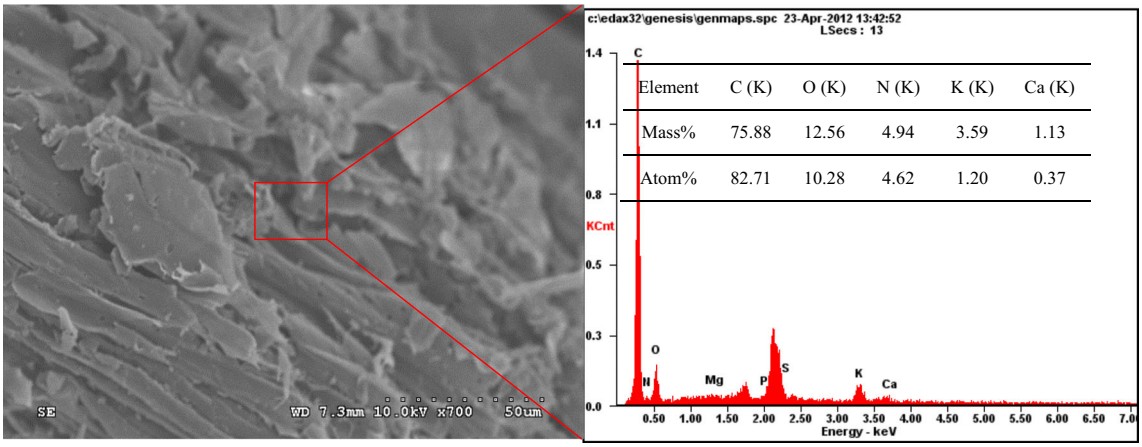

Fig. 1 Structural and elemental analysis of biochar

predominantly derived from ash. This depended on the fact that the acid-washed biochar had a relatively low content of TP (0.94 g kg^{-1}) compared with unmodified biochar (3.31 g TP kg^{-1}).

Effect of biochar application on soil microbial biomass P

Red earth and Fluvo-aquic soil had different trends in SMB-P changes during incubation. In the control of Red earth, SMB-P remained constant below 2.6 mg kg^{-1}, while it ranged from 0.16 (21 days) to 9 mg kg^{-1} (42 days) in the control of Fluvo-aquic soil, without a definite trend (Fig. 3). The SMB-P in Red earth increased by increasing rates of biochar application, whereas this trend was not observed in Fluvo-aquic soil where SMB-P fluctuated. The SMB-P in Red earth amended with biochar firstly increased to a maximum of 7 (2 % biochar), 18 (4 % biochar), and 43 mg kg^{-1} (8 % biochar) and then all declined to about 9 mg kg^{-1} at the end of the experiment. Fluvo-aquic soil also showed this trend, since addition of biochar at rates of 2, 4, and 8 % increased SMB-P to a maximum of 36, 20, and 22 mg kg^{-1} with a successive decline. The treatment with acid-washed biochar did not affect the trend in Red earth treated with biochar, but it significantly affected the SMB-P trend in Fluvo-aquic soil (Table 2).

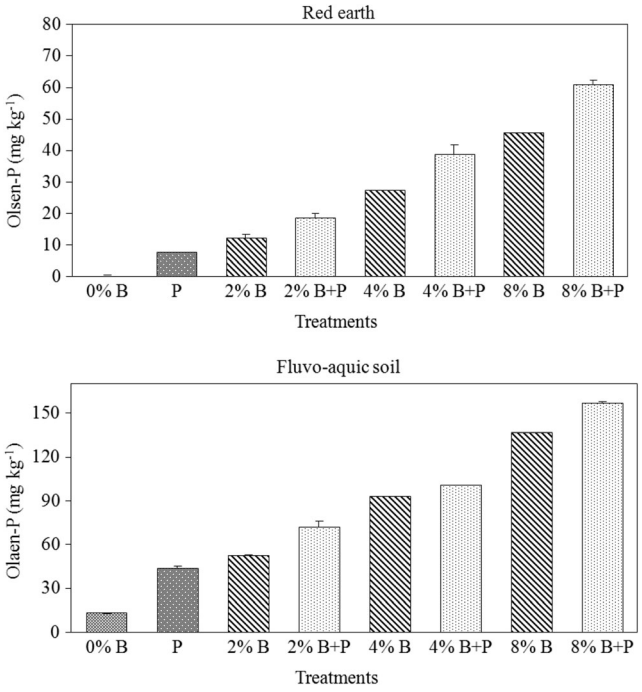

Fig. 2 Soil Olsen-P content after amendment with different rates of biochar and/or KH_2PO_4 fertilizer (118 kg P ha^{-1}) for 42 days. *Error bars* indicated standard deviations (n=3) and all treatments significantly differed with each other within the same soil

Effect of biochar application on phosphorus sorption and soil properties

Overall, sorption of P on Red earth and Fluvo-aquic soil increased by an increasing concentration of P in the soil solution at equilibrium (Fig. 4). However, the two soils had different responses to addition of P solutions. When the same concentration of P was added to soils, the amount of P sorbed by Red earth was always significantly higher than by Fluvo-aquic soil. Red earth reached a P sorption capacity of approximate 1,550 mg P kg^{-1} soil at 19 mg P L^{-1} in the equilibrium solution. Amendment of biochar at rates of 2–8 % to Red earth did not affect P sorption isotherm at all. In contrast, amendment of biochar to Fluvo-aquic soil altered the slopes of the P sorption isotherm curves compared with the control, although their overall pattern was the same. Under 30 mg P L^{-1} in the equilibrium solution, P sorption to Fluvo-aquic soil amended with biochar increased less than the control, as shown by the differences in the slopes of the sorption isotherm curves. The trend was opposite when the P in the equilibrium solution was above 30 mg L^{-1} (Fig. 4). Another great difference in sorption isotherms between two soils was that an obvious negative sorption of P, i.e., desorption of P, was observed from Fluvo-aquic soil at zero P addition, especially at large biochar

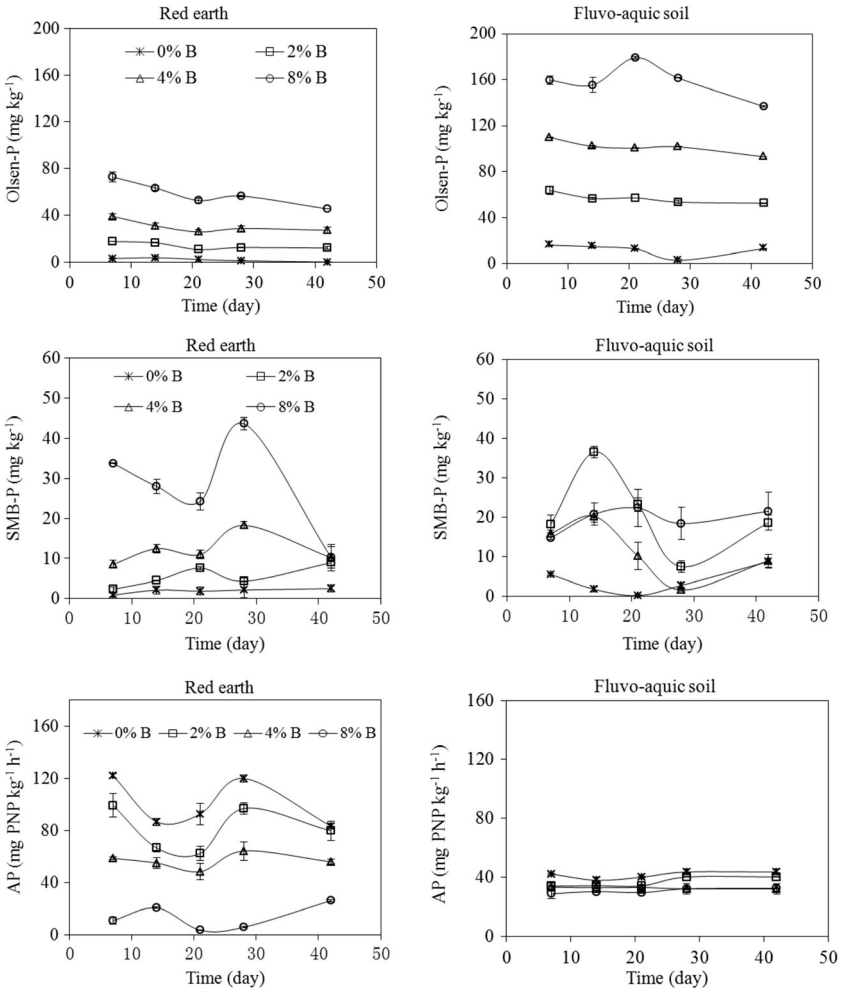

Fig. 3 Changes in soil Olsen-P content, acid and alkaline phosphomonoesterase activity (AP) and soil microbial biomass P (SMB-P, $n=3$) after amendment with different rates of biochar. Acid phosphomonoesterase activity has been determined in Red earth and alkaline phosphomonoesterase activity in Fluvo-aquic soil. An *error bar* was included for each data point to indicate standard deviation

application rates. However, desorption of P from Red earth with a large P sorption capacity was negligible.

Amendment of biochar significantly ($P<0.05$) increased pH of Red earth, e.g., from an initial value of 6.38 to 7.12 after 42 days in the treatment of 8 % biochar. In contrast, the biochar didn't influence the pH of Fluvo-aquic soil (Fig. 5) characterized by an initial pH of 8.27. The biochar significantly ($P<0.05$) increased the EC in both Red earth and Fluvo-aquic soil, and the EC values increased by increasing amounts of applied biochar (Fig. 5). In Red earth, EC also increased substantially with cultivation time, e.g., by 50 % at 8 % biochar addition after 42 days.

Table 2 Change in P availability in different soils amended with 4 % unmodified or acid-washed biochar after 42 days of incubation, compared with the control without amendment of biochar (0 %)

Treatment	Olsen-P mg kg^{-1}	Phosphomonoesterase activity (AP) mg PNP kg^{-1} h^{-1}	Soil microbial biomass P mg kg^{-1}
Red earth			
Unmodified biochar	26.92±0.40 b	−27.4±1.84 a	7.61±3.30 a
Acid-washed biochar	0.12±0.21 c	−11.1±0.98 b	7.08±0.88 a
Fluvo-aquic soil			
Unmodified biochar	80.16±0.23 a	−11.5±3.43 b	0.20±1.62 c
Acid-washed biochar	0.81±0.33 c	+1.56±1.14 c	4.42±1.54 b

AP in Red earth is acid phosphomonoesterase activity and in Fluvo-aquic soil is alkaline phosphomonoesterase activity

Values with different letters indicate significant difference ($P<0.05$) of the means in the same table column ($n=3$)

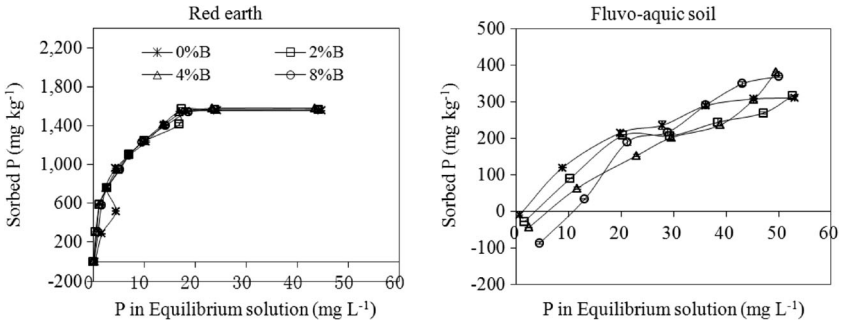

Fig. 4 Phosphorus sorption isotherms of soils amended with different rates of biochar. An *error bar* was included for each data point to indicate standard deviation (n=3)

Effect of biochar application on soil phosphomonoesterase activity

Compared with the control (0 % biochar), amendment of biochar significantly (P<0.05) decreased phosphomonoesterase activities in both Red earth and Fluvo-aquic soil. The decrease was especially obvious in Red earth at the beginning of the incubation experiment (Fig. 3). Biochar affected soil phosphomonoesterase activities to different extents in Red earth and Fluvo-aquic soil. After 42 days of incubation, acid phosphomonoesterase activity in Red earth was reduced by 4, 33, and 69 % as the biochar application rate increased from 0 to 2, 4, and 8 %, respectively. Correspondingly, alkaline phosphomonoesterase activity of Fluvo-aquic soil was reduced by 8, 27, and 26 %. Differing with unmodified biochar, acid-washed biochar caused a relatively small reduction of acid phosphomonoesterase activity in Red earth during incubation and even a slight increase of alkaline phosphomonoesterase in Fluvo-aquic soil (Table 2).

Discussion

The present study investigated the use of biochar as potential amendment/fertilizer to improve P availability in two low-P soils. It is clearly demonstrated that application of 2–8 % biochar significantly increased both Olsen-P and SMB-P in Red earth and Fluvo-aquic soil, with greater effect by increasing application rates (Fig. 3). We have to confess that application of these high rates of biochar may be problematic in practices, e.g., difficult for operational incorporation in the field. However, Red earth, as a common arable soil in South China, has strong P fixation which largely constrains supply of P to crops. Improvement of soil P availability is of especial importance for this type of soil, given the condition that the

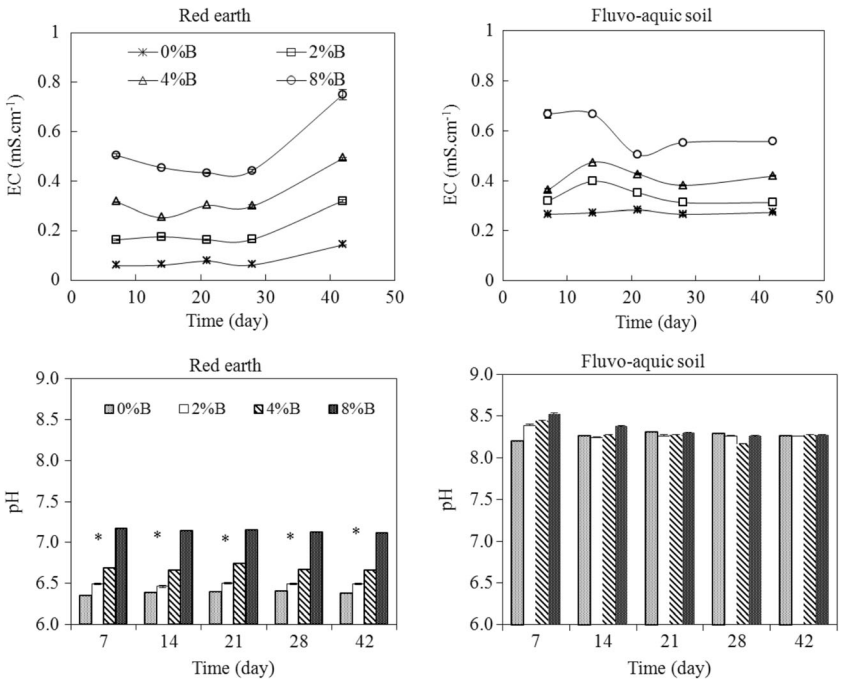

Fig. 5 Changes in soil electrical conductivity (EC) and pH after amendment with different rates of biochar. An *error bar* was included for each data point to indicate standard deviation (n=3). The *asterisk* sign indicates that the pH significantly differed among the treatments in Red earth

optimum P level for crop yield is estimated to be as high as 40 mg Olsen-P kg^{-1} (Li et al. unpublished data). In China, application of P is as high as 140–610 kg P ha^{-1} for production of vegetables and fruits (Li et al. 2007). This is why we used the very high rates of biochar in this study. Because the surplus P may become source of P losses by surface runoff and leaching (Kleinman et al. 2011; Liu et al. 2012), biochar application at high rate should be only used in the fields far away for adjacent water bodies. Other effects of biochar should also be considered when applied at high rates. Biochar is commonly regarded to have a positive liming effect, i.e., increasing pH in acidic soils (Atkinson et al. 2010), due to addition of alkaline metal (Ca, Mg, and K) oxides with biochar (Steiner et al. 2007; Yuan et al. 2011). This is confirmed by biochar application to the slight acid Red earth in the present study (Fig. 5). However, addition of salts with biochar may also increase soil salinity, as indicated by the increase in EC values after biochar application especially at high rates. Therefore, cautions should be taken when applying high rates of biochar.

The P availability in biochar was similar to that in mineral KH_2PO_4 fertilizer. Ash constituted a major part of the TP (77 %) in biochar, and when it was washed off, the effect of biochar on increasing soil Olsen-P was significantly reduced (Table 2). This confirmed the first hypothesis that biochar application can improve soil P availability, which is mainly due to high P concentrations in the biochar ash. When plant tissues are heated, organic C can volatilize at approximately 100 °C, whereas P volatilize at approximately 700 °C (DeLuca et al. 2009). Charring organic materials at 400 °C can transform organic P to inorganic P, mainly as inorganic orthophosphate and pyrophosphate combined with K, Ca, and Mg in biochar (Chirone et al. 2000; Qian et al. 2013). The results imply that unmodified biochar should be used for the purpose of improving soil P availability, whereas acid-washed biochar would have a limited effect.

Increase in soil P availability after biochar application is greater in soil with lower P sorption capacity. The different increase in Olsen-P values in Red earth and Fluvo-aquic soil after amendment with the same rate of biochar (Fig. 3) depends on differences in the chemical properties of the two soils. The P sorption in Red earth, being an acidic soil, is controlled by contents of Fe and Al, whereas in the alkaline Fluvo-aquic soil, phosphate can precipitate as Ca and Mg phosphates. The higher P disappearance in Red earth than in Fluvo-aquic soil treated with the same amount of biochar P (Fig. 4) implies that Red earth has stronger abilities to bind P than Fluvo-aquic soil. As a result, Olsen-P in Red earth increased less than in Fluvo-aquic soil. We also observed an increase in SMB-P, which can act as both a sink and source of P and thus can affect P availability to plants (Achat et al. 2010; Koutika et al. 2013). The increase in SMB-P is likely due to improvement of the soil environment for microbial growth after biochar application (Anderson et al. 2011; Lehmann et al. 2011). Similar to Olsen-P, increase in SMB-P in Red earth was also less than in Fluvo-aquic soil. This is probably because less P is available in Red earth for microbial organisms due to a stronger sorption capacity.

Char materials may also play a role in influencing soil P availability by changing soil pH (Murphy and Stevens. 2010) and P sorption capacity (Laird et al. 2010). It is possible that addition of char materials can reduce the amount of P precipitated with Al and Fe after increasing pH in acidic soils (Atkinson et al. 2010), but reduce P availability in neutral or alkaline soils due to enhanced P fixation by the added metals (DeLuca et al. 2009). It is somewhat surprising that P sorption curve for Red earth was not changed at all by biochar that had a rather high specific surface area. This may be partly due to the increase in soil pH or from competition for P sorption sites as indicated by Soinne et al. (2014) who observed similar results, and partly due to the high P sorption capacity of Red earth. In addition, some of the added P might be immobilized during the P adsorption experiment since toluene does not inhibit completely microbial activity of soil. In contrast, P sorption of Fluvo-aquic soil was considerably altered by biochar addition. Biochar decreased the amount of P sorbed in biochar-soil mixture at low solution P concentrations due to desorption of P from biochar (Morales et al. 2013), but increased P sorption at high solution P concentrations probably due to P precipitation with Ca added with biochar (Qian et al. 2013; Xu et al. 2014).

Biochar application significantly reduced phosphomonoesterase activity in both Red earth and Fluvo-aquic soil, with greater reduction at higher biochar application rates. Nannipieri et al. (2011; 2012) reported that activities of phosphomonoesterases in soil were repressed by inorganic P. It is reasonable that large amounts of inorganic P applied with biochar declined phosphomonoesterases activities in the present study. Repression of phosphomonoesterases activities is likely to be affected by P sorption capacity of soils, as the sorption capacity greatly affects availability of inorganic P in soils. Moreover, the increase in soil EC by biochar addition (Fig. 2) may also account for reduction of phosphomonoesterases activities to some extent. It has been reported that salinity can negatively affect enzymatic activities by causing ion toxicity and denaturing enzyme proteins (Yan and Marschner 2013; Rietz and Haynes 2003).

Conclusions

This short-term study shows a promising potential of using maize straw biochar to improve soil P availability in low-P soils. In China, this is of especial importance as 15 to 92 % of arable fields from Northeast China to South China are estimated to have Olsen-P content below optimum level (Li et al.

unpublished data). Improvement of soil P availability by biochar is mainly due to high concentrations of P in the ash fraction. Biochar effect on soil Olsen-P and SMB-P increases by higher biochar application rates and by lower P sorption capacity. Biochar application can significantly reduce soil phosphomonoesterase activities due to large amount of inorganic P added. However, these findings need to be further confirmed by field experiments over long term, with consideration of possible adverse effects of biochar application at high rates.

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