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Full Length Article

Investigating the Effects of Biochar on Soil Properties and Alleviating Aluminum Toxicity for Improving Cabbage (*Brassica oleracea* var. Capitata) Productivity while Reducing Potash Fertilizer

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Abstract

The potassium (K) is an essential macronutrient and the availability of K in the soil is gradually decreasing which severely affecting crop productivity in the south of China. The purpose of the present study was to investigate the effect of biochar on soil physicochemical properties and to explore the effect of biochar on substituting potash fertilizer in acid soil. Therefore, a pot experiment was conducted with two typical acidic soils (red and yellow-brown soil). The acid soil without biochar significantly inhibited plant growth and biomass accumulation in cabbage while biochar improved the growth parameters and nutrient contents in plant parts. Biochar completely replaced the potash fertilizer in red soil and up to 20% of potash fertilizer in yellow-brown soil. Biochar increased the pH by 1.3 units of acid soil and total soil Al and Al^{3+} in red soil and yellow-brown soils from 2694.71, 538.29 mg kg^{-1} to 1170.58, 412.82 mg kg^{-1} respectively. The leaf Al content was declined from 3879.6 to 614.65 µg g^{-1} in red soil. Taken together, it can be concluded that biochar-amended soil could increase the nutritional status and improve cabbage productivity by alleviating soil Al toxicity and replace potash fertilizer in a short period.

Keywords: Biochar; Cabbage; Acid soil; Potassium; Aluminum toxicity

Introduction

In China, red soil (R) and yellow-brown soil (YB) are typical acid soils in the south of China and this zone is regarded as the main grain producing area (Zhang *et al*., 2013). However, due to high rainfall and leaching of basic cations, some of the essential nutrients including potassium are gradually decreasing while increasing the risks of soil acidification, aluminum (Al^{3+}) toxicity and H^+ toxicity and these factors threaten the productivity of crops (Ma *et al*., 2007; Riaz *et al*., 2018) by inhibiting root growth and plant development. The content of CEC is low and the active Al^{3+} is very high in red soil (Climate, 2006). Moreover, due to a gradual decrease of arable land, farmers must have to use chemical fertilizers to increase crop productivity (Guo *et al*., 2010; Schroder *et al*., 2011; Chang *et al*., 2019). However, this practice can drive soil acidification indirectly. In acid soil (red soil), aluminum is present in the most active form (Al^{3+}) and is toxic for the root growth (Menzies *et al*., 1994; Jia and Zhang, 2008). Low pH and loss of indispensable nutrients are two major factors limiting crop growth and development in acid soil of south China (Zhu *et al*., 2015). Management practice is an important factor that influences soil fertilizer, however, some improper soil measures may affect soil fertilizer restoration, such as pH and organic matter (Zhang and Xu, 2005). Potassium (K) is one of the most important nutrients for the normal growth and development of plants (Romheld and Kirkby, 2010). Plants require a high amount of K for optimizing photosynthesis and crop quality (Jia *et al*., 2019). Potassium is easily reduced by water leaching and potassium deficiency reduces the growth of legume nodulation in red soil (Sangakkara *et al*., 1996). The K usually exists into four forms in the soil, including water-soluble K, exchangeable K, non-exchangeable K and mineral K (Barre *et al*., 2008). Red soil is a typical acidic soil in southern China, the soil is generally characterized by low nutrient and high risk of erosion (Zhang *et al*., 2019a). K availability in acidic soil is very low, while in normal soil, the amount of soil K can be easily fixed (Moterle *et al*., 2016; Singh *et al*., 2018). It has also been reported that there is a significant correlation between soil pH and potassium fixation in some soils (Xu *et al*., 2003).

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Biochar is a biomass, produced by pyrolysis under anaerobic conditions. Biochar is an aromatic carbon-rich material with stable physical and chemical properties (Anderson *et al*., 2011; OK *et al*., 2015; Weber and Quicker, 2018). Biochar has been reported to improve soil quality, pH, organic matter, and nutrients of the soil (Lehmann *et al*., 2011; Berek *et al*., 2016) and it has been suggested that biochar reduces the bioavailability of metals (Ahmad *et al*., 2014; Hasan, 2018). There are different forms of aluminum in the acidic soil (Blaser *et al*., 2008). However, Al^{3+} is the most toxic form of active aluminum (Ryan *et al*., 2009; Zhao *et al*., 2019). Low pH and Al toxicity could affect the antioxidant system of the plant by accumulating reactive oxygen species (Martins *et al*., 2013; Yang *et al*., 2015). The plant defense system plays an important role in the tolerance to stress conditions, and the activities of superoxide dismutase (SOD), catalase (CAT) and peroxidase (POD), and contents of malondialdehyde (MDA) and soluble protein reflect the damages of Al toxicity and response of plant to metal stress (Gechev *et al*., 2003; Bafeel and Ibrahim, 2008).

Biochar possesses a large surface area and porous structure (Cornelissen *et al*., 2013; Sun *et al*., 2015). Biochar holds high K depending on the feedstock and fluctuates during the process of carbonization, so it can retain potassium and releases it slowly (Smider and Singh, 2014). Oram *et al*. (2014) showed that legumes plant parts accumulated high K concentrations by applying biochar. However, few studies have considered biochar as a source of chemical potash especially in the productivity of cabbage (*Brassica oleracea* var. Capitata). Most of the research on biochar is mainly about N, P and heavy metals, and the information is not enough about the effect of biochar on soil K. The mineral K is the most stable form in the soils (Britzke *et al*., 2012). However, the available K can be used by plant, including exchangeable K (potassium in the soil solution) and soluble K (potassium absorbed by soil colloid) (Darunsontaya *et al*., 2012). Moreover, in the south of China, the availability of K in soil is gradually decreasing and severely affecting crop productivity.

Therefore, the specific objective of this study was to investigate the effects of biochar on soil physicochemical properties of two typical soils of China, to improve plant growth under different potash fertilizer levels. Therefore, a pot experiment was designed to study the effect of biochar on increasing soil nutrients availability, especially K while alleviating aluminum toxicity to improve cabbage productivity in acid soil.

Materials and Methods

Experimental Materials

Two typical acidic soils (red soil and yellow-brown soil) were collected at a 0–20 cm depth. Red soil (R) samples were collected from mountainous soil of XianNing, Hubei, and yellow-brown (YB) soil from the field of Huazhong Agriculture University, Wuhan. Prior to homogenizing of soil with fertilizer and biochar, the soil was sieved through 2 mm mesh to remove plant residues and stones. The physicochemical properties of the soils and biochar before starting experimental treatments are shown in Table 1. Biochar was produced from peanut shells (0.5 h total pyrolysis time at 400ºC) and was applied at a rate of 3% of soil (60 t/ha).

Experimental Design and Management

The pot experiment was carried out in the greenhouse of Huazhong Agricultural University, China. The pots (height-140 mm, diameter-170 mm, bottom diameter -115 mm) were filled with 2 kg of soil. The experiment was designed with four treatments in each type of soil, *i.e*., K100 (normal fertilizer), CK80 (3% biochar + 80% K fertilizer), CK60 (3% biochar + 60% K fertilizer), CK0 (3% biochar + 0% K fertilizer). The K100 treatment of fertilizer was applied as 1.16 g NH_4NO_3, 0.88 g KH_2PO_4, 0.28 g KCl, and trace elements modified from Anon nutrient solution (2.86 mg kg^{-1} H_3BO_3, 1.81 mg kg^{-1} $MnCl_2.4H_2O$, 0.22 mg kg^{-1} $ZnSO_4.7H_2O$, 0.08 mg kg^{-1} $CuSO_4.5H_2O$, 0.09 mg kg^{-1} Na_2MoO_4, 48.5 mg kg^{-1} EDTA-Fe). Rests of the treatments were applied with reducing the concentrations of potassium fertilizer by adjusting the content of KH_2PO_4 and KCl. Each soil had four treatments and every treatment had four replicates, (total of 32 pots). The experiment was carried out under natural growth conditions and 70% humidity. After every week, the gravimetric moisture content of soils was determined, and the corresponding weight of water was poured into the pots to maintain soil moisture at 70% of field capacity.

Sample Collection and Analysis

All plants were harvested on 35 days after planting. The soil sample was collect destructively at 0 days (fundamental soil) and 35 days (harvesting time). One part of soil samples were sieved through 0.9 mm and 0.15 mm for physicochemical analyses and enzyme activities, respectively. Plant samples were washed with tap water and thoroughly rinsed with deionized water. The shoot length was measured by a ruler. Fresh biomass and leaf number were counted on 35 days (harvesting time). One part of plant samples was stored at -80ºC for antioxidant enzyme activities and the rest of the part was dried at 60ºC for determination of nutrient contents.

Plant sample determination: The fresh leaves (1 g) were ground in liquid nitrogen with the precooled mortar and phosphate buffer (pH=7.8). The homogenates were centrifuged at 15000 × g for 10 min, and then the supernatant was collected into another tube for determining the following antioxidant enzyme activities. The superoxide dismutase (SOD) activity was determined by nitro blue tetrazolium (NBT) (Giannopolitis and Ries, 1977) and expressed as FW mg^{-1}. The catalase (CAT) activity was assayed by the method of Aebi (1984) and the peroxidase (POD) activity was detected by guaiacol (Liu and Chang, 1994). The soluble protein was determined by Coomassie brilliant blue (Buege and Aust, 1978). The Al content of plant leaves was determined by the extraction method proposed by You (1997).

Soil sample determination: The soils were dried in air to measure physicochemical analyses. The pH was measured in a 1:2.5 soil/water suspension with a glass electrode (CP-401 pH meter). The SOM (soil organic matter) and various forms of potassium were analyzed according to the Soil and Agricultural Chemistry Analysis (Bao, 2000). The active Al^{3+} was determined by the 1 mol L^{-1} KCl and the total Al by 0.5 mol L^{-1} NaOH including hydroxyl compounds, inorganic Al and humic acid of the soil (Pang *et al*., 1986). The method described by Guan (1986) was used for measuring acid phosphatase and urease of soil. The most suitable pH for acid phosphatase is 5.5 (Dick *et al*., 2000).

Statistical Analysis

All statistical analysis were performed using one-way ANOVA and tables were generated by Microsoft Excel 2013. When the F-value was significant, the least significant difference (Duncan) test was used for comparison between the means at $P < 0.05$ by SAS version 9.2.

Result

Influence of Peanut Shell Biochar Amendment on the Growth of Cabbage

Biomass and agronomic characters of cabbage: The results showed that the growth characteristics of cabbage (shoot length, fresh weight, dry weight and leaf numbers) in R soil were significantly increased in the soil amended with biochar as compared with K100 (Table 2). In acid red soil, the biochar significantly replaced potash fertilizer without compromising plant growth parameters and highest growth characteristics were found under CK80 treatments with biochar than other treatments (Table 2). The effect of the biochar on the growth of cabbage in YB soil was not obvious as in R soil. The treatment of CK80 resulted in slightly increased in agronomic characteristics of cabbage (shoot length, fresh weight, dry weight and leaf numbers) compared with the control treatment (K100) (Table 2), while other treatments did not show any improvement of in YB soil.

The results indicated that cabbage growth in R soil was more prominent than YB soil and biochar applied at 3% to soil significantly substituted the potash fertilizer to some extent in response to cabbage growth.

Table 1: Chemical and physical component of control soil and biochar

Property	Soil sample		
	R soil	YB soil	Biochar
pH	4.8	5.45	8.76
OM (g kg^{-1})	1.31	6.78	555.1
TN (g kg^{-1})	0.59	0.96	18.84
TP (g kg^{-1})	0.71	0.96	2.59
TK (g kg^{-1})	16.36	19.37	8.48
Tal (μg kg-1)	3744	342.79	
Al^{3+} (μg kg-1)	540	6.52	
Avail. N (mg kg^{-1})	35	87.5	
Olsen-P (mg kg^{-1})	6.13	8.01	
Avail. K (mg kg^{-1})	96	152	
Water. K (mg kg^{-1})	10	28	
Slowly. K (mg kg^{-1})	238	380	

Nutrient content and nutrient Al content of cabbage: The response of plant nutrient content under biochar was measured (Fig. 1A, B, C). In R soil after addition of biochar, the contents of N and K in plants were increased by 6.67% and 152.49% in CK80 treatment compared with control treatment (K100). Interestingly, the treatment of CK80, CK60 and CK0 increased the K contents by 152.49%, 118.07%, and 84.67%, indicating that biochar might have increased the bioavailability of K. However, there was no significant effect of biochar on P contents.

In YB soil, the effect of biochar was not same as in R soil, the biochar treatment significantly decreased the N, P, and K content of plants, when compared with control treatment (K100) and there was no significant difference in N and P contents with biochar treatments (Fig.1 A, B, C).

The results indicated a pronounced decreased in the Al content of plant parts grown in acid red soil amended with biochar as compared with the K100 (Fig. 1D). The leaf Al content was declined from 3879.6 to 614.65 $\mu g\ g^{-1}$ in red soil (Fig. 1D), similarly, in YB soil, biochar decreased Al contents from 544.6 to 237.13 $\mu g\ g^{-1}$ in CK80 treatment as compared with CK100 (Fig. 1D). The results suggested that biochar could mitigate Al toxicity by decreasing bioavailability to plant.

The oxide resistance enzymes of cabbage: In R soil, biochar amendment resulted in a decrease of POD and SOD activities than the control treatment (K100). The POD activity was decreased by 97.8% in CK60 treatment, (Fig. 2A) and the SOD activity by 61.29% compared with K100 treatment (Fig. 2B). However, biochar slightly increased the CAT activity by 27.7% than control treatment (Fig. 2C). Moreover, the results showed that the leaf MDA level was decreased significantly with biochar (Fig. 2D), and declined from 4.12 $\mu mol\ g^{-1}$ in K100 to 1.62 $\mu mol\ g^{-1}$ in CK60 treatment. The soluble protein content of leaf was increased and the highest content (3.81 $\mu g\ g^{-1}$) was found in CK60 treatment (Fig. 2E).

Table 2: The biomass and agronomic characters of cabbage at different levels potash fertilizer and biochar

Soil type	Treatment	Shoot length (cm)	Fresh weight (g)	Dry weight (g)	Leaf number
	K100	$1.55^{c} \pm 0.13$	$0.06^{b} \pm 0.01$	$0.01^{c} \pm 0.01$	3^{c}
	CK80	$10.43^{a} \pm 0.43$	$19.68^{a} \pm 2.82$	$2.23^{a} \pm 0.22$	7.25^{a}
R soil	CK60	$8.55^{b} \pm 0.64$	$17.99^{a} \pm 5.08$	$1.76^{b} \pm 0.19$	6.25^{b}
	CK0	$8.38^{b} \pm 0.48$	$18.02^{a} \pm 1.92$	$1.79^{b} \pm 0.18$	6.75^{ab}
	K100	$13.5^{b} \pm 0.24$	$41.63^{a} \pm 1.53$	$3.54^{a} \pm 0.36$	9^{a}
	CK80	$14.23^{a} \pm 0.60$	$40.25^{a} \pm 5.11$	$3.85^{a} \pm 0.61$	9.75^{a}
YB soil	CK60	$13.23^{b} \pm 0.21$	$35.47^{b} \pm 1.74$	$3.58^{a} \pm 0.10$	8^{a}
	CK0	$13.43^{b} \pm 0.15$	$32.74^{b} \pm 2.49$	$3.26^{a} \pm 0.09$	8.5^{a}

R soil: red soil, YB soil; yellow brown soil, K100 (normal fertilizer), CK80 (3% biochar with 80% K fertilizer), CK60 (3% biochar with 60% K fertilizer), CK0 (3% biochar without K fertilizer). Different letters in each column indicates significant difference at $P < 0.05$ probability level

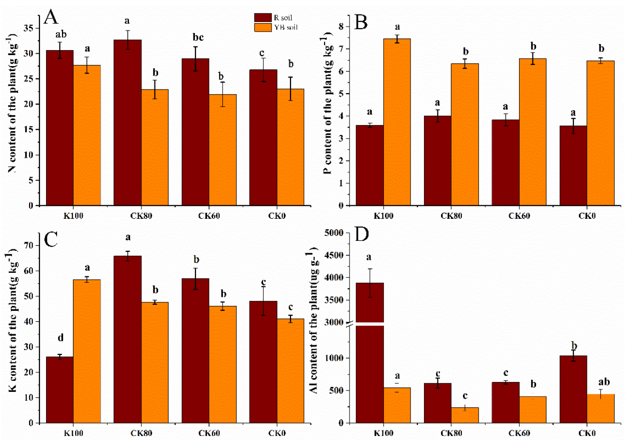

Fig. 1: Changes in the N、P、K and Al content of cabbage at different levels of potash fertilizer and biochar, compared with normal fertilization. R soil: red soil YB soil; yellow-brown soil, K100 (normal fertilizer), CK80 (3% biochar with 80% K fertilizer), CK60 (3% biochar with 60% K fertilizer), CK0 (3% biochar without K fertilizer). Different letters in each column indicate significant difference at $P < 0.05$ probability level. Error bars indicate the standard error are calculated from four repeats

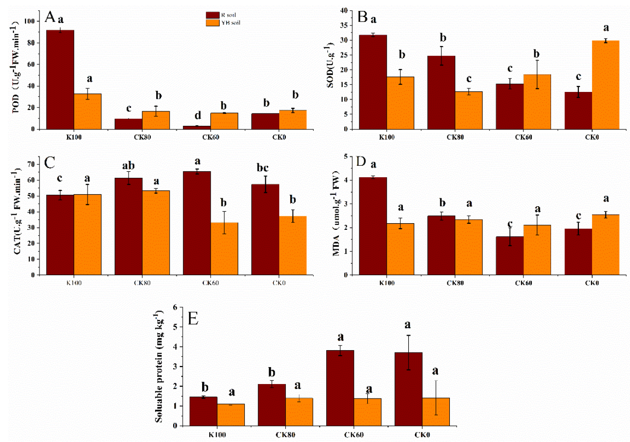

Fig. 2: Changes in the oxide resistance enzymes of cabbage at different level potash fertilizer and biochar, compared with normal fertilization. R soil: red soil YB soil; yellow-brown soil, K100 (normal fertilizer), CK80 (3% biochar with 80% K fertilizer), CK60 (3% biochar with 60% K fertilizer), CK0 (3% biochar without K fertilizer). Different letters in each column indicate significant difference at $P < 0.05$ probability level. Error bars indicate the standard errors are calculated from four repeats

In YB soil, due to different soil physicochemical properties, the growth of cabbage showed variations. The CK60 treatment led to a decrease of POD and CAT activities by 53.13%, and 26% compared with control treatment (K100), respectively (Fig. 2A, C). The SOD activity was decreased to its minimum value under the CK80 treatment and was increased by reducing the level of potash fertilizer (Fig. 2B). The level of MDA did not show a significant difference among all treatments (Fig. 2D, E**)**.

Influence of Biochar on Nutrients and Physicochemical Characteristics of Different Soils

Aluminum of the soil: Data from biochar-amended soil and the control soil samples are shown in Fig. 3. The results indicated that the contents of Al ions in R soil were higher than that of YB soil. The total active Al was decreased considerably in R soil with biochar amendment and decreased from 2694.71 to 1170 mg kg^{-1} in K100 compared to control treatment (Fig. 3A). The Al^{3+} was also decreased from 538.20 to 347.35 μg g^{-1} in K100 treatment as compared with the control treatments (Fig. 3B).

The YB soil also showed the same tendency, both the total active Al and Al^{3+} were decreased by biochar treatments. The CK0 treatment significantly decreased the total active Al from 306.10 to 142.67 mg kg^{-1} with respect to the control treatment (Fig. 3A). The CK80 treatment led to a significant decrease of Al^{3+} than without biochar from 12.37 to 7.25 mg kg^{-1} in CK0 treatment compared with control (Fig. 3B).

Potassium of the soil: The potassium can be divided into four types on the basis of dissolution in the soil: water-soluble K, exchangeable K, non-exchangeable K and mineral K. In red soil, the biochar (CK80) treatment significantly increased the content of water-soluble K (22.33 to 34.67 mg kg^{-1}) compared with the control treatment (K100) (Fig. 4A). Similarly, the exchangeable K and non-exchangeable K were increased by biochar amendment comparing with the control treatment (K100). The maximum exchangeable K and non-exchangeable K were found in CK60 treatment and increased by 104.60%

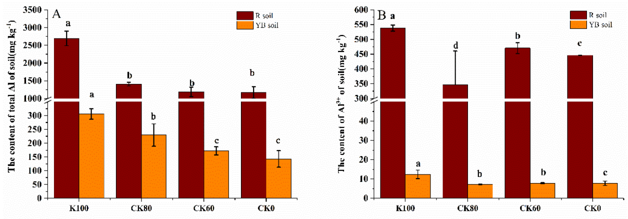

Fig. 3: Changes in aluminum ions of different soil at different level potash fertilizer and biochar, compared with normal fertilization. R soil: red soil YB soil; yellow-brown soil, K100 (normal fertilizer), CK80 (3% biochar with 80% K fertilizer), CK60 (3% biochar with 60% K fertilizer), CK0 (3% biochar without K fertilizer). Different letters in each column indicates significant difference at $P < 0.05$ probability level. Error bars indicate the standard errors are calculated from four repeats

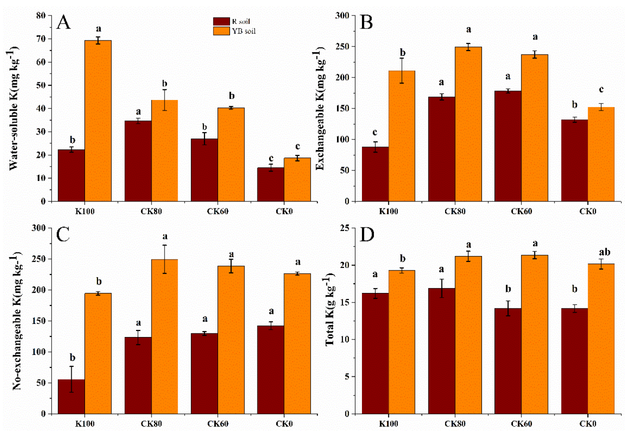

Fig. 4: Changes at the different form potassium of different soil at different level potash fertilizer and biochar, compared with normal fertilization. R soil: red soil YB soil; yellow brown soil, K100 (normal fertilizer), CK80 (3% biochar with 80% K fertilizer), CK60 (3% biochar with 60% K fertilizer), CK0 (3% biochar without K fertilizer). Different letters in each column indicates significant difference at $P < 0.05$ probability level. Error bars indicate the standard errors are calculated from four repeats

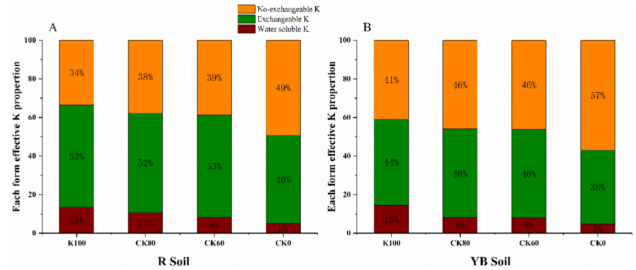

Fig. 5: Changes at each form effective K proportion of different soil at different level potash fertilizer and biochar, compared with normal fertilization. R soil: red soil YB soil; yellow brown soil, K100 (normal fertilizer), CK80 (3% biochar with 80% K fertilizer), CK60 (3% biochar with 60% K fertilizer), CK0 (3% biochar without K fertilizer). Different letters in each column indicates significant difference at $P < 0.05$ probability level. Error bars indicate the standard errors are calculated from four repeats

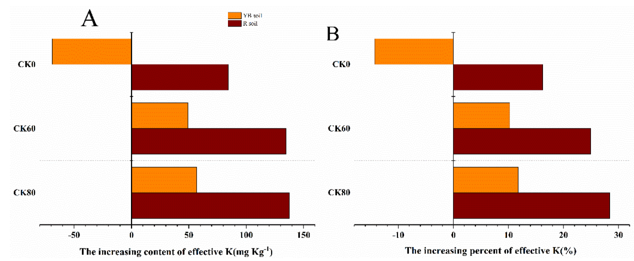

Fig. 6: Changes at available potassium and increment percent of different soil at different level potash fertilizer and biochar, compared with normal fertilization. R soil: red soil YB soil; yellow brown soil, K100 (normal fertilizer), CK80 (3% biochar with 80% K fertilizer), CK60 (3% biochar with 60% K fertilizer), CK0 (3% biochar without K fertilizer). Different letters in each column indicates significant difference at $P < 0.05$ probability level. Error bars indicate the standard errors are calculated from four repeats

and 133.42% respectively (Fig. 4B, C). The highest content of total K was 16.88 g kg^{-1} in CK80 treatment (Fig. 4D). The results showed that water-soluble K, exchangeable K and non-exchangeable K representing effective K were improved significantly with biochar treatment in relation to control treatment (K100). The effective K treatment increased by CK80, CK60 and CK0 were 137.42 mg kg^{-1}, 134.89 mg kg^{-1} and 84.3 mg kg^{-1} respectively, and was remarkably higher than the CK treatment, and the increasing rate was 28.41%, 24.95% and 16.21%, respectively (Fig. 6A).

Compared with red soil, the different potassium forms in YB soil showed variations. Biochar significantly decreased water-soluble K level, the lowest content was 18.67 mg kg^{-1} under the CK0 treatment (Fig. 4A) while the other effective potassium forms were increased with biochar amendment as compared with the control treatment (K100). The most significant effect on exchangeable K was occurred with the CK80 treatment, increased from 211.19 to 250 mg kg^{-1} in K100 treatment while the lowest content was 152.36 mg kg^{-1} in CK0 treatment (Fig. 4B, C). Similarly, biochar treatments resulted in an increase of total K irrespective of K concentrations applied to the soil (Fig. 4D). It's worth noting that in YB soil, the treatments of CK80 and CK60 increased K by 11.79% and 10.22%, respectively compared with the K100 treatment (Fig. 6B). Thus, there was a significant increase of effective K in R soil and YB soil after biochar addition.

In R soil, the proportion of non-exchangeable K was increased significantly from 34% to 49% by CK0 treatment when compared with control treatment (K100). The highest decrease in water-soluble and exchangeable K was noted with the CK0 treatment and decreased from 13%, 53% to 5% and 46% respectively (Fig. 5A). In YB soil, the proportion of each effective K form showed similar changes. Compared with the control treatment (K100), the non-exchangeable K was increased up to 57%

while the water-soluble K and exchangeable K were declined by 6 and 16%, respectively in CK0 treatment (Fig. 5 B).

Enzyme activities of soil: Soil enzymes play an important role in soil biological process and nutrient uptake by the plant and directly related to the physical and chemical properties of soil. The activities of acid phosphatase and sucrose of R soil was significantly decreased with biochar treatments. The activities of urease and sucrose of YB soil was significantly decreased by biochar treatment. There was no significant difference in the activities of urease in R soil and acid phosphatase in YB soil among biochar treatments with the control treatment ($P < 0.01$, Fig. S2).

The application of biochar resulted in an increase of soil pH by 0.8–1.2 unit in R soil (initial soil pH=4.8), particularly in CK0 treatment, the highest pH was 5.72 under the CK0 treatment. Similarly, biochar increased pH more than 1.0 unit in YB soil (initial soil pH=5.45), the highest pH was 6.77 in CK0 treatment (Table S1). The activity of urease was negatively related to pH, especially in YB soil and the correlation reached a significant level (Table 3). In addition, the urease was positively correlated with available N in YB soil (Table 3). The activity of sucrose was directly affected by factors such as pH, OM and chemical properties. OM level in R soil and YB soil were generally increased with biochar amendment during the incubation time compared with control treatment (K100) (Table S1). There was a negative relationship between the activity of sucrose and pH, Olsen-P, Available-K, while positively relationship between the activity of sucrose and OM, Available-N in R soil (Table 3). In addition, the relationship showed the same tendency between the enzyme activities, pH and available - N in YB soil (Table 3). The relationship between the activity of acid phosphatase and pH, Olsen-P was negative in R soil (Table 3).

Discussion

Previous studies reported the positive effect of biochar on soil physicochemical properties and plant growth in different types of soils (Mohamed *et al*., 2015; Farhangi-Abriz and Torabian, 2018; Zhang *et al*., 2019b). Moreover, biochar has been reported to mitigate heavy metal toxicities (Lin *et al*., 2018; Riaz *et al.*, 2018b). It is well known that biochar has an obvious effect on soil structure, nutrient retention and crop productivity (Agbna *et al*., 2017). However, the effect of biochar as a substitute of K fertilizer in improving cabbage productivity has not been well elucidated especially in yellow-brown soil and red soil of China which are prone to K deficiency and high Al toxicity. In our study, acid soil without biochar amendment severely inhibited the plant growth parameters and availability of essential nutrients, however, biochar significantly improved cabbage growth and biomass accumulation in acid red soil (Fig. S1). Biochar not only increased the soil nutrients but also reduced the Al concentrations both in soil and plant parts as well as substituted potash fertilizer.

Al toxicity is regarded as a major limiting factor for plant growth in acid soils, which hinders many biochemical processes and restricts the uptake of nutrients across cell membranes. In our study, the total active Al was decreased considerably in R soil with biochar amendment and decreased from 2694.71 to 1170 mg kg^{-1} in K100 compared to control treatment (Fig. 3A). The Al^{3+} was also decreased from 538.20 to 347.35 $\mu g\ g^{-1}$ in K100 treatment as compared with the control treatments (Fig. 3B). The results showed that biochar amendment to soil resulted in decrease uptake of exchangeable Al in the plant parts. Biochar forms a stable compound with Al due to the porous structure of biochar, which makes the soil exchangeable Al into a low-activity organic complex Al (Gondek *et al*., 2018; Lin *et al*., 2018). Biochar is alkaline in nature and can increase the pH of the soil. As shown in Table S1, the pH of R and YB soil were 4.59 and 5.33 under treatment of K100, while the pH of R and YB soil were 5.72 and 6.77 under treatment of CK0. Thus, the biochar could alleviate Al toxicity of soil and reduce the absorption of Al by plants (Qian and Chen, 2013; Yuan and Xu, 2015).

Several studies have suggested that biochar could improve the bioavailability of macro-nutrients and substantially increases available K when incorporated into the soil (Bu *et al*., 2017; Gonzaga *et al*., 2017), which in turn increases soil fertility and maintains optimal growth of the crop. In our study, biochar led to increase of some nutrients but decreased other nutrients in cabbage tissues. Biochar clearly increased K and decreased leaf N content in cabbage grown in R soil. The increase in K content could be attributed to the structure of biochar because K is most available nutrient in the biochar. In the present study, the P and K contents of the plant were significantly improved, especially K. In our study, we found biochar can replace potash fertilizer significantly and the proportion of non-exchangeable K was increased in R soil. It might be due to that biochar has great porosity and specific area (Gonzaga *et al*., 2017), and can transform water-soluble and exchangeable K to non-exchangeable K. However, the effects of biochar were not prominent in YB soil. The reason could be that the exchangeable K and water-soluble K contents were high in YB soil. In order to maintain the balance of potassium, the other forms of potassium transform into non-exchangeable K (Singh *et al*., 2002). The possible another reason could be that the soil (pH, water content) influences the release of nutrient from biochar (Biederman and Harpole, 2013).

Biochar is enriched with mineral nutrient elements (Park *et al*., 2011; Alburquerque *et al*., 2014; Mukherjee *et al*., 2014). Biochar, a nutrient-rich material, has been found to increase plant nutrient uptake (Lehmann *et al*.,

Table 3: Correlation between soil enzyme activities and physical and chemical properties of different soil

Item	Soil Sample					
	R Soil			YB Soil		
	Urease	Sucrose	Acid phosphate	Urease	Sucrose	Acid phosphate
pH	-0.12	-0.945**	-0.408	-0.732**	-0.654*	0.106
OM	-0.066	0.834**	0.256	0.022	-0.335	0.046
Avai.N	-0.03	0.87**	0.175	0.603*	0.748**	0.136
Olsen-P	-0.318	-0.869**	-0.446	0.013	-0.035	0.108
Avai.K	0.08	-0.634*	0.228	0.515	0.479	0.349

Note: n= 12; *, $P < 0.05$, **$P < 0.01$ R soil: red soil YB soil; yellow brown soil, K100 (normal fertilizer), CK80 (3% biochar with 80% K fertilizer), CK60 (3% biochar with 60% K fertilizer), CK0 (3% biochar without K fertilizer)

2003). Bai *et al*. (2015) observed that the soil P availability was increased significantly after the addition of poultry litter biochar. Lehmann *et al*. (2011) and Gonzaga *et al*. (2017) also found a reduction in plant N with the addition of biochar into the soil, indicating the rise of ammonia volatilization with the increase of soil pH (Table S1). The increase of carbon by biochar affects the mineralization, fixation, immobilization of soil N (Dempster *et al*., 2012; Wang *et al*., 2016). Biochar might increase soil P availability through different theories including (a) by enhancing soil P availability by decreasing P adsorption, (b) biochar may influence P adsorption with Fe oxides when initial P content of the soil is very low. (c) P concentration of biochar could be slowly released through P mineralization and interaction with soil organic matter (Cui *et al*., 2011; Slavich *et al*., 2013).

Soil enzyme activity is one of the important indexes to evaluate soil fertility and reflects the intensity and direction of various biochemical processes in soil (Velmourougane *et al*., 2013; Kedi *et al*., 2013). The enzyme activity can also be affected by biochar chemical properties (Baldrian *et al*., 2013). In our study, soil enzymes showed variable changes after biochar amendment. It was noted that the activities of urease, acid phosphatase and sucrose of YB soil were greater than that of R soil (Fig. S2). Some research results indicate that soil physicochemical properties could be changed by biochar, such as pH and organic matter (Yao *et al*., 2017). Urease is an amide enzyme that catalyzes urea (Table S1). In addition, pH is one of the key factors affecting soil urease activity (Huang *et al*., 2017), and the pH of R soil is lower than YB soil. Some studies found that soil enzymes mainly adsorbed to soil organic matter and inorganic particles in the form of physical or chemical bonding, or with humus complex (Burns *et al*., 2013; Kedi *et al*., 2013). While the biochar possesses a high ratio of pores and surface area, therefore, the activity of sucrose was decreased with the addition of biochar. In addition, the reason for this correlation ascribed the changes of bacterial and fungal diversity in acidic soil treated with biochar (Winquist *et al*., 2014; García-Delgado *et al*., 2015). The relationship between acid phosphatase and pH, Olsen-P was negative in R soil. On the one hand, the optimum pH value of acid phosphatase is 5.5, if the pH of the soil is high, the activity of acid phosphatase will be low (Pfeiffer, 2010). On the other hand, biochar could bring the amount of inorganic P that could inhibit the acid phosphatase (Allison and Vitousek, 2005; Zhai *et al*., 2015).

When plants suffer adversity, such as salt, drought, acid toxicity and environmental stresses, in order to deal with external stress, the physiological and biochemical characteristics of plant activate the corresponding coping mechanisms, of which the most important is antioxidant enzyme system (Prochazkova *et al*., 2001). In R soil, the cabbage was highly under acidic and Al stress, and accumulated reactive oxygen species, ultimately damaged the plasma membrane. In order to alleviate the damage of plasma membrane, the activities of POD, SOD and CAT are generated in cells of living organisms through many metabolic pathways to decompose free radicals and decrease membrane peroxidation (Zhao *et al*., 2018). However, the efficient antioxidant system consisting of SOD, POD and CAT could help the plant to survive under adverse conditions of the environment (Yan *et al*., 2018). Interestingly, the biochar increased the pH value of soil, and relevant studies reported that soil pH value is the most important factor affecting the active concentration of toxic metal ions in plants (Rees *et al*., 2014). Moreover, the concentration of soluble protein was decreased by biochar.

Conclusion

Biochar has been reported to improve soil physical and chemical properties of acid soil. The results showed that acid soil without biochar significantly reduced crop growth and accumulated high contents of Al in the soil. However, biochar improved the growth of the cabbage and reduced the contents of Al in the soil as well as in the plant parts. Moreover, biochar amendment to soil resulted in increased nutrients of the soil and substituted the K fertilizer. In this experiment, the fertility of the YB soil was relatively high and the nutrient of R soil was poor, and acid and Al stress were more serious, so the substitution effect of K fertilizer in R soil by biochar was more obvious than YB. Taken together, it is suggested that biochar can replace K fertilizer in red soil while about 20% of potash fertilizer in yellow-brown soil. These findings could be helpful in understanding the effects of biochar on physicochemical properties of soil and chemical fertilizer especially K.

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