



Responses of organic and inorganic phosphorus fractions in brown earth to successive maize stover and biochar application: a 5-year field experiment in Northeast China

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Abstract

Purpose To compare the effects of maize stover and its biochar on soil P fractions and investigate the effects of different stover incorporation practices (direct return or pyrolysis) on the transformation of soil P fractions after a long-term field experiment.

Materials and methods Total P, Olsen-P, inorganic P fractions, and organic P fractions were analyzed via a 5-year field experiment growing maize. The treatments were as follows: CK0 (no fertilizer application or amendment), CK (application of mineral NPK fertilizer), ST (application of maize stover at 7.5 t ha⁻¹ along with mineral NPK fertilizer), and BC (application of biochar at 2.63 t ha⁻¹, a rate approximately equivalent to a maize stover biomass of 7.5 t ha⁻¹; the biochar was charred according to a 35% output ratio in the factory). All treatments received N mineral fertilizer at 120 kg N ha⁻¹, P mineral fertilizer at 26 kg P ha⁻¹, and K mineral fertilizer at 50 kg K ha⁻¹ annually.

Results and discussion Relative to the initial fractions in 2013, biochar generally increased the inorganic P fractions (Ca₈-P, Ca₁₀-P, Al-P, and Fe-P), and maize stover generally increased the organic P fractions (MLOP, MROP, and HROP), while both maize stover and its biochar significantly decreased O-P in the soil. After 5 years (in 2017), relative to CK treatment, amendment with maize stover and its biochar increased total P and decreased Olsen-P. The total inorganic P, Ca₈-P, and Fe-P were significantly increased by biochar. Ca₂-P and O-P were significantly decreased by maize stover and its biochar. Total organic P was increased with maize stover and biochar amendment. LOP and HROP were significantly increased under biochar application, and all organic P fractions were significantly increased under maize stover amendment.

Conclusions The application of maize stover and its biochar affected both organic and inorganic phosphorus fractions; biochar had a more advantageous effect on the soil inorganic P fractions, while stover had a greater effect on the content of organic P fractions.

Keywords Biochar · Brown earth · Inorganic P fractions · Maize stover · Organic P fractions

Abbreviations

Ca₂-P Dicalcium phosphate dehydrate
Ca₈-P Octacalcium phosphate
Ca₁₀-P Hydroxyapatite

Al-P Aluminum phosphate
Fe-P Iron phosphate
O-P Occluded phosphate
LOP Labile organic phosphorus
MLOP Moderately labile organic phosphorus
MROP Moderately resistant organic phosphorus
HROP Highly resistant organic phosphorus

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1 Introduction

Phosphorus (P) is a nonrenewable resource and a required nutrient for crop growth and development (Faucon et al.

2015). However, less than 20% of applied P is recovered by crops during the first year of growth. Fe and Al and their oxides in solution in acid soils adsorb P through precipitation and ligand exchange reactions, respectively (Schoumans and Chardon 2015). P is adsorbed and precipitated by CaCO_3 , and calcium-P and magnesium-P compounds are formed in alkaline and calcareous soils (Eriksson et al. 2015). The efficiency of P use by plants is considerably restricted due to high P fixation (Hale et al. 2013). The main source of fertilizer is phosphate rocks, and the reserves are finite. Recent estimates suggest that at the current rate of use, these resources will be exhausted within a few hundred years (Cordell et al. 2009). The potential supply shortages of P fertilizers demand the more efficient usage of these fertilizers and the exploration of new ways to recycle P within agro-ecosystems (Zhai et al. 2014).

Intensive agriculture generates many agricultural residues, and their management and disposal can lead to environmental issues (Intani et al. 2018). Maize stover residues, which contain considerable amounts of nutrients, are valuable agricultural resources. Returning maize residues to the soil such that their nutrients are available for crop uptake is a challenging research topic and practical task (Zhai et al. 2014). The direct burning of crop residues generates several environmental problems. The direct turnover of crop residues is a routine traditional practice for returning nutrients to the soil. However, returning stover directly to the field can result in an uneven distribution of soil moisture, and low emergence rates and yellow, weak or dead seedlings have appeared in maize. Agricultural residues have been pyrolyzed to produce biochar. Producing biochar for soil application has been considered a better way of processing agricultural residues than directly burning or recovering residues in the field (Manolikaki et al. 2016). Biochar pyrolysis is a carbonization technology that thermochemically converts biomass into stable, recalcitrant organic carbon compounds (Lehmann and Ithaca 2015). The advantages of the application of biochar are as follows: generation of bioenergy, increased concentration of plant nutrients, destruction of organic pollutants, and decreased volatile heavy metal content (Samolada and Zabaniotou 2014; Song et al. 2019). The use of biochar is an interesting strategy to improve plant growth and development because biochar can contain various types of nutrients (Asai et al. 2009). Biochar can also promote the growth of plants by improving their resistance to stress conditions (El-Banna et al. 2019).

Important elements, such as carbon (C), nitrogen (N), sulfur (S), oxygen (O), hydrogen (H), and chlorine (Cl), can be eliminated during pyrolysis, while P is retained, providing a potential opportunity for P reuse (Uchimiya and Hiradate 2014). Biochar plays a vital role in soil quality: It increases soil organic matter (SOM) and soil pH, retains soil moisture and nutrients, improves soil structure, and accelerates

microbial activity, thereby stimulating plant growth (Lehmann et al. 2011; Soinne et al. 2014; Efthymiou et al. 2018). Biochar changes the activity and availability of cations (Al^{3+} , Fe^{3+} , and Ca^{2+}). Insoluble Al and Fe phosphate are formed through ligand exchange and precipitation reactions, and P is fixed by adsorption at the surface of biochar (e.g., by oxides of Al and Fe and hydroxide) (Sun et al. 2018). Low P solubility is caused by the formation of metal complexes, such as Ca-P and Al-P (Schmieder et al. 2018). The labile P and NaHCO_3 -P in biochars were much lower than in biosolids, indicating that plant-available P was decreased after pyrolysis (Adhikari et al. 2019). In addition, biochar can increase the amount of microenvironment available for soil phosphatase activity and play a crucial role in transforming organic P into inorganic P in soils (Zhu et al. 2017).

The positive effects of biochar on P levels have been investigated predominantly in low-fertility soils, with few investigations in other typical soils (Nelson et al. 2011; Ngatia et al. 2017). Furthermore, the direct and indirect effects of biochar on soil P cycling, especially P-rich soils, have rarely been reported. One study showed that using maize stover biochar has broad potential to enhance the availability of P in low-P soils and to increase soil available P and soil microbial biomass P (Zhai et al. 2014). Ultisols and Alfisols amended with rice straw biochar (2% w/w) presented 46% and 39% increases in P availability, respectively (0.5 M NaHCO_3 -extractable P). For strongly acidic Ultisols, biochar can significantly increase the Al-P and Ca-P contents and reduce the Fe-P content (Hong and Lu 2018). Information on the effects of biochar on soil P retention and brown earth (one of the main soil types in Northeast China) is sparse. Some of the studies on these topics have been conducted at the laboratory scale or encompassed only a short period of time (18 months) in field conditions (Konczak and Oleszczuk 2018). In such studies, the long-term effects of biochar application cannot be identified.

The great differences in physical and chemical properties between maize stover and its biochar are shown in Table 1. We hypothesized that the effect of maize stover and its biochar on soil P status will be very different. To determine the differences in the effect of different ways of returning maize stover to the field, a long-term biochar, maize stover, and fertilizer management experiment was established in 2013 and used to assess the effects of maize stover and its biochar on the total P, Olsen-P, and organic P fractions as well as inorganic P fractions.

2 Materials and methods

2.1 Materials

Air-dried maize stover was cut into pieces approximately 6 cm in length. The experimental biochar was prepared by the

Table 1 Properties of the amendments and the soil (0–20 cm) in 2013

Property	Maize stover	Biochar	Soil	Unit
pH	7.8	9.2	7.4	
EC	–	–	196.8	$\mu\text{S cm}^{-1}$
CEC	–	–	17.8	cmol kg^{-1}
Total C	429.3	660	11.0	g kg^{-1}
Total N	5.4	12.7	1.2	g kg^{-1}
Total P	3.43	8.87	0.38	g kg^{-1}
Olsen-P	–	120.8	15.9	mg kg^{-1}
Bulk density	–	–	1.31	g cm^{-3}
Organic matter	–	–	13.84	g kg^{-1}
Ash content	3.78	15.57	–	%
Specific surface area	3.43	8.87	–	$\text{m}^2 \text{g}^{-1}$
Average pore size	10.75	16.23	–	nm
Volatile matter	80.14	21.94	–	%
Fixed carbon	16.08	62.49	–	%

pyrolysis of maize stover under a limited supply of oxygen (O_2) at 500 °C in a vertical kiln for 2 h, and 35% of the maize stover biomass was turned into biochar. The biochar was sieved through a 2-mm mesh screen and then thoroughly mixed before being distributed uniformly on the treatment plots and mixed into the topsoil via a rotavator. The basic properties of the two amendments are listed in Table 1.

2.2 Site description and experimental design

The field experiments were performed at the long-term biochar experimental station at Shenyang Agricultural University, Liaoning Province, China (41°49' N, 123°33' E) during the growing season from 2013 to 2017. For a detailed description of the experimental site, see Yang et al. (2017). The brown earth in this experiment is Hapli-Udic Cambisol (FAO classification). The basic properties of the topsoil (0–20 cm) are described in Table 1.

The experiment began in May 2013 with a randomized block design. The treatments were as follows: CK0 (no fertilizer application or amendment), CK (application of mineral NPK fertilizer), ST (application of maize stover at 7.5 t ha⁻¹ along with mineral NPK fertilizer), and BC (application of biochar at 2.63 t ha⁻¹, a rate approximately equivalent to a maize stover biomass of 7.5 t ha⁻¹ that was charred according to a 35% output ratio in the factory). The mineral N, P, and K fertilizers used in this study were urea, calcium superphosphate, and potassium sulfate, respectively. An equal mineral NPK fertilizer (N mineral fertilizer at a rate of 120 kg N ha⁻¹, P mineral fertilizer at 26 kg P ha⁻¹, and K mineral fertilizer at 50 kg K ha⁻¹) was applied in the CK, BC, and ST treatments. Every year, biochar, maize stover, and NPK fertilizers were manually spread on the soil surface and then uniformly mixed into the topsoil with a rotary tiller. Each plot was 3.6 × 10 m²

in area. Each treatment was replicated three times. The planting density of the maize was 60,000 stalks ha⁻¹. The maize plants were mechanically sown in late April or early May and manually harvested in late September each year.

2.3 Soil sampling and chemical analysis

Soil samples were collected from the topsoil (depth of 0–20 cm) before sowing in 2013 and at the end of the growing season in 2017. All soil samples were freed of any vegetation remains, sieved through a 2-mm mesh and then stored in plastic bags before analysis.

The pH of the soil was measured at a 1:2.5 (w/v) ratio, and the pH of the biochar and maize stover was measured at a 1:10 (w/v) ratio (HANNA HI2221, Italy). The electrical conductivity (EC) was measured at a 1:5 (w/v) ratio (BBD-303A, China). The cation exchange capacity (CEC) was measured via the ammonium acetate extraction method, the cations were measured by an ICP-MS (ELAN 6000, PE-SCIEX, USA) (Manolikaki et al. 2016), and the SOM was measured by the method of wet oxidation with $\text{H}_2\text{SO}_4\text{-K}_2\text{CrO}_7$ (Perrier and Kellogg 1960). Total C and total N were measured by an Elementar Vario max Analyzer (Elementar Macro Cube, Germany). Specific surface area and average pore size were estimated by a Surface Area and Pore Porosimetry Analyser V-sorb 4800P (Gold APP Instrument Corporation, China). Volatile matter, ash contents, and fixed carbon were described in Antunes et al. (2017). The maize stover was digested with concentrated H_2SO_4 and 30% H_2O_2 ; then, the P concentration of the maize stover was determined following Murphy and Riley (1962).

The total P contents of the soil and the biochar were determined by treating the samples with H_2SO_4 and HClO_4 at 280 °C for 2 h (Parkinson and Allen 1975). The soil and biochar Olsen-P contents were measured in accordance with the method of Olsen (1954). The P fractionation procedure modified by Chang and Jackson (1957) was used to measure inorganic phosphates with differing solubilities. In brief, 1 g soil samples were extracted in sequential order with the following extractants: 0.25 M NaHCO_3 , shaking for 1 h; for Ca₂-P, 0.5 M NH_4OAc , shaking for 1 h; for Ca₈-P, 0.5 M NH_4F , shaking for 1 h; for Al-P, 0.1 M NaOH -0.1 M Na_2CO_3 , shaking for 2 h, standing for 16 h, then shaking for 2 h; for Fe-P, 0.3 M $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$, stirring for 15 minutes, followed by the addition of 0.5 M NaOH and stirring for 10 min for O-P, and finally 1 M H_2SO_4 , shaking for 1 h, for Ca₁₀-P. The organic P fractions were measured following the method of Bowman and Cole (1978). Briefly, 5 g soil samples were used to extract LOP by shaking for 30 min with 0.5 M NaHCO_3 , and 2 g soil samples were used to extract MLOP by standing for 3 h with 1 M H_2SO_4 ; then, the soil was extracted with 1 M NaOH , standing for 16 h, to measure MROP and HROP. The concentrations of P were determined via the ascorbic acid-

molybdenum blue method with a spectrophotometer (Hitachi U-5100 UV/VIS, Japan) at a wavelength of 700 nm. (Murphy and Riley 2014). Three replicates per fraction were analyzed for each treatment.

2.4 Statistical analysis

All the data are reported as the means \pm standard deviations. One-way ANOVA, which was followed by least significant difference (LSD) tests, was used to test for differences among the treatments, the differences among the P fractions in the same treatment, and the differences in P fractions between 2013 and 2017. PCA was performed on the P fraction data to identify overall trends in the P fractions in response to the different stover incorporation practices. To further investigate the contribution of P fractions to total P and Olsen-P, stepwise regression analysis was performed with total P and Olsen-P as dependent variables and P fractions as independent variables. Pearson's correlation coefficients were used to describe the relationships between each P fraction and both total P and Olsen-P. The differences were considered statistically significant at $p < 0.05$. All statistical analyses were performed using SPSS version 21.0 (IBM, New York, USA).

3 Results

3.1 Total P and Olsen-P

The total P contents of the different treatments are shown in Table 2; the values followed the order BC \approx ST > CK > CK0. The total P contents in the BC and ST treatments were significantly higher (by 17% and 14%, respectively) than in the CK treatment, and the BC treatment yielded the highest total P content among all the treatments. Total P under the different stover incorporation practices in 2017 was increased by 79% and 74% relative to the corresponding values in 2013.

The different stover incorporation practices affected Olsen-P content (Table 2). Relative to that in the CK treatment, Olsen-P in the BC and ST treatments was significantly decreased by 37% and 30%, respectively. Olsen-P in the BC and ST treatments was significantly higher (by 23% and 36%, respectively) than in the CK0 treatment, with no difference between the ST and BC treatments. Olsen-P in the BC and ST treatments was increased by 89% and 71%, respectively, in 2017 relative to the values in 2013.

3.2 Soil inorganic P fraction

The different stover incorporation practices affected the total inorganic P contents (Table 2). The total inorganic P content ranged widely from 225.45 to 372.67 mg kg⁻¹. Relative to the corresponding values in 2013, the inorganic P contents under

the CK, BC, and ST treatments in 2017 were significantly increased, whereas the content in the CK0 treatment was significantly decreased.

As shown in Fig. 1, the inorganic P forms were significantly affected by the different stover incorporation practices. In 2017, compared with that in the CK treatment, Ca₂-P in the BC and ST treatments was significantly lower by 28% and 28%, respectively. As shown in Fig. 3, the Ca₂-P/total P fraction ratio was significantly higher in the CK treatment than in the other three treatments. In the CK0 treatment, Ca₂-P was significantly lower (33%) in 2017 than in 2013, whereas Ca₂-P in the CK treatment was significantly higher (41%) in 2017 than in 2013.

The differences in Ca₈-P among the four treatments in 2017 were significant and followed the order ST > BC > CK > CK0. The Ca₈-P/total P fraction ratio followed the order ST > BC > CK > CK0, and the differences among the treatments were highly significant. The Ca₈-P contents in the CK, BC, and ST treatments were significantly higher (44%, 119%, and 145%, respectively) in 2017 than in 2013; however, Ca₈-P in the CK0 treatment was significantly lower (83%) in 2017 than in 2013.

In 2017, Ca₁₀-P in the different treatments followed the order BC \approx ST > CK > CK0. Ca₁₀-P was highest in the BC treatment and significantly higher in this treatment than in the CK treatment. The Ca₁₀-P/total P fraction ratio in each of the BC and ST treatments was higher than that in the CK treatment. Ca₁₀-P in the CK0 treatment was lower in 2017 than in 2013, and in all treatments, Ca₁₀-P did not significantly differ between 2017 and 2013.

The BC treatment yielded the highest Fe-P among the treatments in 2017. Fe-P in the BC treatment was significantly higher than in the CK treatment, although there was no significant difference between the BC and ST treatments. Among the treatments, the CK0 treatment yielded the highest Fe-P/total P ratio. In the CK treatment, Fe-P was significantly lower (8%) in 2017 than in 2013. There was no significant difference in Fe-P in the CK0, BC, or ST treatments between 2017 and 2013.

Al-P in the CK, BC, and ST treatments was higher in 2017 than in 2013, and Al-P was significantly higher in each of these treatments than in the CK0 treatment. The Al-P/total P fraction ratio was highest in the CK treatment. In the CK0 treatment, Al-P was significantly lower (52%) in 2017 than in 2013, whereas in the other three treatments, Al-P was significantly higher in 2017 than in 2013.

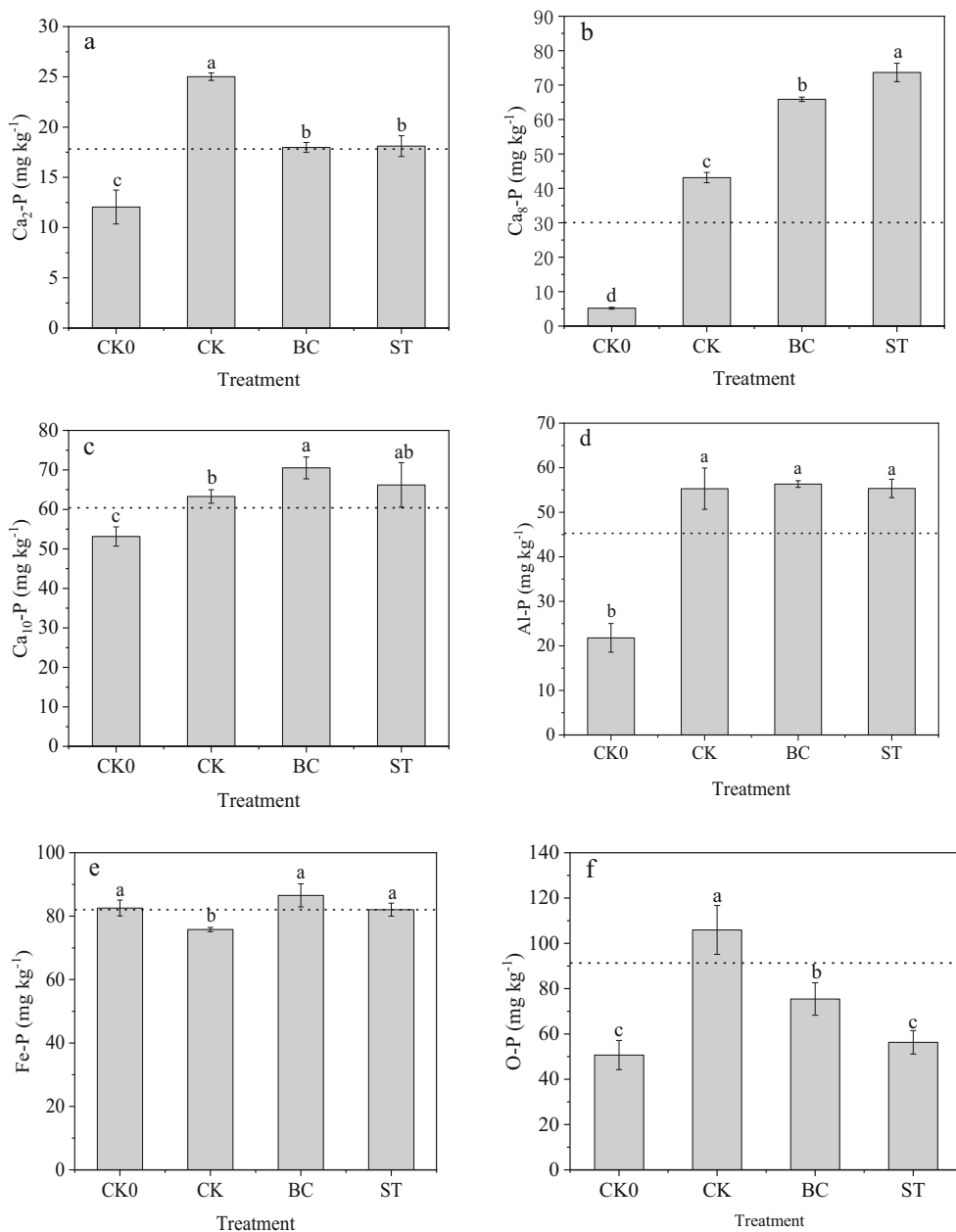
O-P ranged from 50.68 to 105.92 mg kg⁻¹ and followed the order CK > BC > CK0 > ST. Relative to that in the CK treatment, the O-P content in the BC and ST treatments was significantly decreased by 30.50 mg kg⁻¹ and 49.61 mg kg⁻¹, respectively. Among the treatments, the CK treatment yielded the highest O-P/total P fraction ratio and was significantly higher in this treatment than in the other treatments. O-P in

Table 2 Effects of maize stover and its biochar on total P, Olsen-P, total inorganic P and total organic P

	Total P		Olsen-P		Total inorganic P		Total organic P	
	Year 2017 (g kg ⁻¹)	Change from 2013 (%)	Year 2017 (mg kg ⁻¹)	Change from 2013 (%)	Year 2017 (mg kg ⁻¹)	Change from 2013 (%)	Year 2017 (mg kg ⁻¹)	Change from 2013 (%)
CK0	0.45 ± 0.02c	18	22.18 ± 0.69c	39	225.45 ± 8.32c	- 31	137.28 ± 0.87c	9
CK	0.58 ± 0.02b	52	43.17 ± 3.46a	171	368.43 ± 13.70ab	12	145.15 ± 3.16c	16.0
BC	0.68 ± 0.02a	78	27.26 ± 0.10	71	372.67 ± 10.55a	14	169.99 ± 16.39b	35
ST	0.66 ± 0.02a	73	30.08 ± 0.95	88	351.68 ± 11.06b	7	210.96 ± 10.38a	68

Values are expressed as the mean ± standard deviation (*n* = 3). Different letters in the same column indicate significant differences (*p* < 0.05)

Fig. 1 Inorganic P fractions in soils with maize stover and its biochar in 2017 and initial inorganic P fractions in 2013. The dotted lines represent the content of different soil phosphorus fractions in 2013. Different lowercase letters indicate significant differences in the inorganic P concentration of each fraction among different maize stover incorporation practices (*p* < 0.05)



the CK0, BC, and ST treatments was lower in 2017 than in 2013 by 45%, 17%, and 38%, respectively. O-P in the CK treatment increased slightly in 2017 relative to the value in 2013.

3.3 Soil organic P fractions

The effects of the different treatments on total organic P are shown in Table 2. Total organic P fractions followed the order ST > BC > CK > CK0; compared with that in the CK treatment, the total organic P in the maize stover and biochar treatments increased significantly by 17% and 45%, respectively. Among the treatments, the ST treatment yielded the highest total organic P. In the CK, BC, and ST treatments, total organic P was significantly higher in 2017 than in 2013.

The effects of the different treatments on the organic P fractions are shown in Fig. 2. LOP increased significantly in response to the return of maize stover to the field (Fig. 3). LOP was significantly higher in the BC and ST treatments than in the CK treatment. The LOP/total P fraction ratio was significantly higher in the BC and ST treatments than in the other treatments. Compared with those in 2013, the LOP values in the CK0 and CK treatments in 2017 decreased significantly

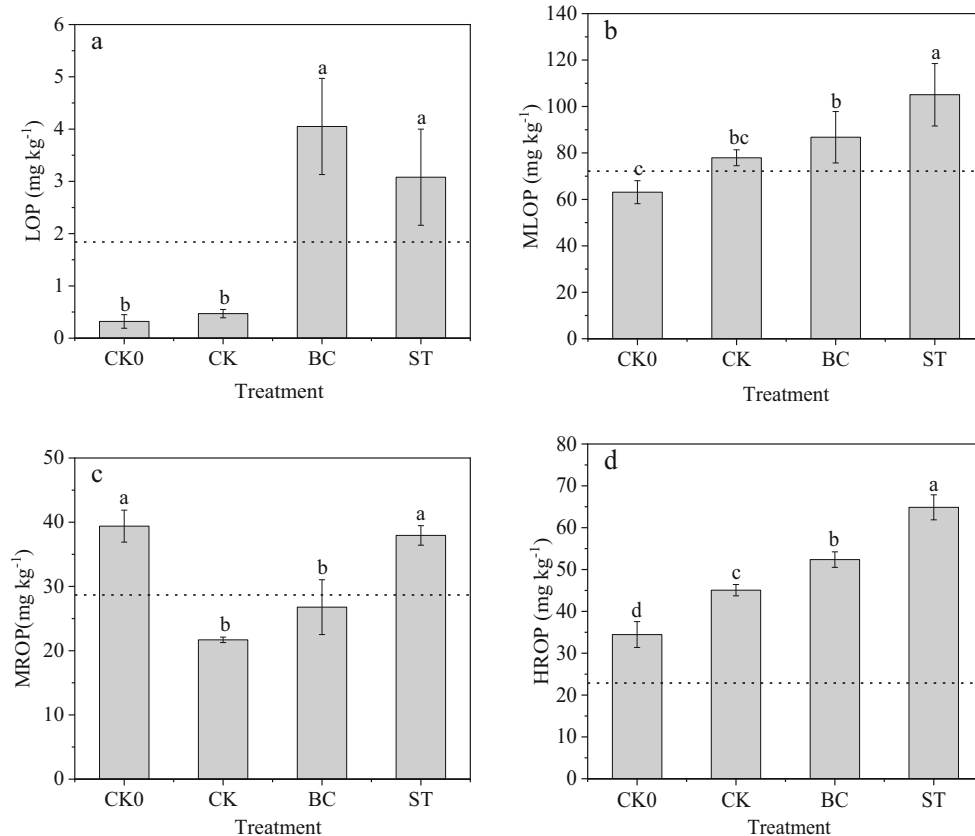
by 83% and 74%, respectively. In addition, in the BC and ST treatments, especially the BC treatment, the LOP values were higher in 2017 than in 2013, increasing by 124% and 71%, respectively.

MLOP was significantly affected by the different treatments. The MLOP contents ranged from 63.11 to 105.06 mg kg⁻¹ and followed the order ST > BC > CK > CK0. Relative to that in the CK treatment, MLOP in the BC and ST treatments were significantly increased by 11% and 35%, respectively. The MLOP/total P fraction ratio was significantly higher in the ST treatment than in the BC and CK treatments. The MLOP content in the ST treatment in 2017 was significantly higher than that in the initial soil in 2013.

MROP was higher in the BC and ST treatments than in the CK treatment, especially in the ST treatment. Among the treatments, the CK0 treatment yielded the highest MROP and the highest MROP/total P fraction ratio. In the CK treatment, MROP significantly decreased by 24% from 2013 to 2017. The MLOP values in the CK0 and ST treatments were significantly higher in 2017 than in 2013.

The pattern of HROP across the different treatments followed the order ST > BC > CK > CK0. The ST treatment yielded the highest HROP/total P fraction ratio. HROP in all treatments in 2017 was significantly higher than that in the initial soil in 2013.

Fig. 2 Organic P fractions in soils with maize stover and its biochar in 2017 and initial organic P fractions in 2013. The dotted lines represent the contents of different soil phosphorus fractions in 2013. Different lowercase letters indicate significant differences in the inorganic P concentration of each fraction among different maize stover incorporation practices ($p < 0.05$)



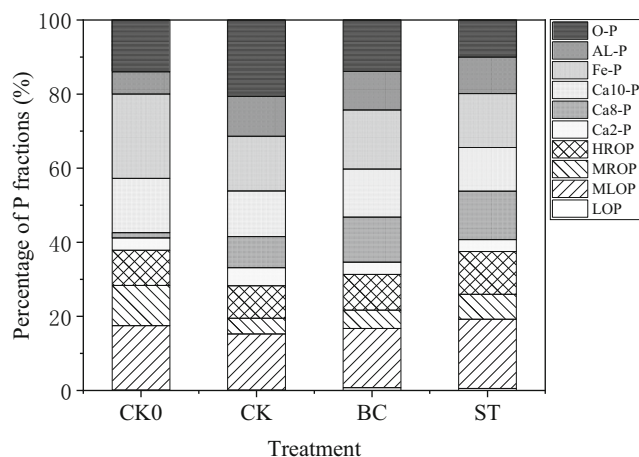


Fig. 3 Effects of maize stover and its biochar on the percentages of P fractions in soil

3.4 Comprehensive evaluation of soil P

3.4.1 Correlation and stepwise regression analysis of soil P

The Pearson’s correlation analysis results for total P, Olsen-P, and the P fractions are shown in Table 3. Total P was significantly and positively correlated with the contents of Ca₈-P, Ca₁₀-P, Al-P, LOP, MLOP, and HROP. Olsen-P was significantly ($p < 0.05$) and positively correlated with the Ca₂-P, Al-P, and O-P contents but significantly ($p < 0.05$) and negatively correlated with the Fe-P and MROP contents.

Stepwise regression analysis of total P and the different inorganic P and organic P fractions was performed (Table 3). Ca₈-P, Ca₁₀-P, HROP, and LOP were selected as the positive explanatory variables for total P, whereas MROP was selected as a negative explanatory variable. Using these selected organic and inorganic P fraction parameters showed that the inorganic P and organic P regression models explained 97% and 95% of the variation, respectively, in total P. Using the same procedure, Ca₂-P was selected as a positive explanatory

variable for Olsen-P. The multiple linear regression model including these variables explained 78% of the variation in Olsen-P. In another model, MROP was selected as a negative explanatory variable, and HROP, LOP, and MLOP were selected as positive explanatory variables. The multiple linear regression model including these variables explained 83% of the variation in Olsen-P.

3.4.2 PCA of soil P

The eigenvectors and the total variance interpretation of the 12 × 12 correlation matrix of P fraction indices were calculated based on the 12 P fraction indices. The results showed that the first three principal components (PCs) accounted for 94.36% of the variation, i.e., for more than 90% of the nutrient information provided by the raw data. These three PCs provided sufficient information to replace the original data. Total P, Ca₈-P, Ca₁₀-P, Al-P, LOP, MLOP, and HROP appeared to drive these differences along PC1. The fractions in PC2, which were associated with Olsen-P, Ca₂-P, O-P, and MROP, were the main drivers. Fe-P had the highest loading in PC3 (Fig. 4; Table 4).

The component score coefficient matrix was obtained by rotating the loading values of the three PCs. From the matrix, we calculated the comprehensive scores of the three PCs, and the linear equations of the comprehensive scores of the individual PCs were as follows:

$$F1 = 0.025 Ca_2P + 0.184 Ca_8P + 0.122 AlP - 0.056 FeP - 0.089 OP + 0.063 Ca_{10}P + 0.116 LOP + 0.255 MLOP + 0.116 MROP + 0.242 HROP + 0.035 OlsenP + 0.127 totalP$$

$$F2 = 0.176 Ca_2P - 0.02 Ca_8P + 0.095 AlP + 0.071 FeP + 0.294 OP + 0.153 Ca_{10}P - 0.006 LOP - 0.191 MLOP - 0.346 MROP - 0.155 HROP + 0.113 OlsenP + 0.072 TotalP$$

$$F3 = -0.123 Ca_2P - 0.029 Ca_8P - 0.019 AlP + 0.545 FeP + 0.091 OP + 0.255 Ca_{10}P + 0.233 LOP - 0.287 MLOP - 0.252 MROP - 0.211 HROP - 0.275 OlsenP + 0.129 TotalP$$

Table 3 Correlation coefficients (r values) and results of stepwise regressions of total P or Olsen-P and the inorganic P fractions

	Correlation coefficient					Regression analysis			
	Ca ₂ -P	Ca ₈ -P	Ca ₁₀ -P	Al-P	Fe-P	O-P	Regression equation	Adjusted R ²	p value
Total P	0.46	0.95*	0.92*	0.83*	0.23	0.09	$y = 156.149 + 2.438 Ca_8P + 9.879 Ca_{10}P$	0.947	< 0.001
Olsen-P	0.88*	0.34	0.23	0.57*	-0.68*	0.57*	$y = -0.186 + 1.618 Ca_2P$	0.783	< 0.001
Total P	0.74*	0.74*	-0.25	0.83*			$y = 482.568 + 4.198 HROP + 25.292 LOP + 4.665 MROP$	0.973	< 0.001
Olsen-P	-0.19	0.25	-0.60*	0.36			$y = 30.201 - 0.781 MROP + 0.250 HROP - 3.763 LOP + 0.241 MLOP$	0.834	< 0.001

*Significance at $p < 0.05$

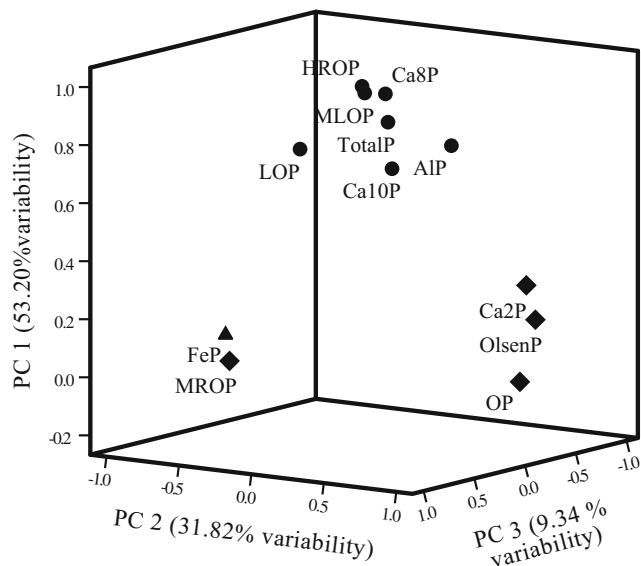


Fig. 4 PCA of the P fractionation data in 2017. Samples are represented by circle (PC1), diamond (PC2), and triangle (PC3). The percentages are the ratio of total variance explained by each principal component (PC). Text label abbreviations indicate the P fractions

The comprehensive score of each soil sample was calculated, and the specific model was $F = 0.5320 F_1 + 0.3182 F_2 + 0.0934 F_3$. The comprehensive scores of the four treatments calculated from the above equations were then described as general statistics as follows: $F_{CK0} = 64.38$, $F_{CK} = 92.12$, $F_{BC} = 103.65$, and $F_{ST} = 101.09$. These findings indicated that within the range of soil P indicators selected in this study, there was a significant difference in the scores of the PCs among the four treatments. Moreover, the biochar treatment yielded the highest score among the treatments.

Table 4 Principle component loadings for fractions of P in the soil

	PC1	PC2	PC3
Ca ₂ -P	0.025	0.176	-0.123
Ca ₈ -P	0.184	-0.020	-0.029
Ca ₁₀ -P	0.063	0.153	0.255
Al-P	0.122	0.095	-0.019
Fe-P	-0.056	0.071	0.545
O-P	-0.089	0.294	0.091
LOP	0.116	-0.006	0.233
MLOP	0.255	-0.191	-0.287
MROP	0.116	-0.346	-0.252
HROP	0.242	-0.155	-0.211
Olsen-P	0.035	0.113	-0.275
Total P	0.127	0.072	0.129
Eigenvalue	6.38	3.82	1.12
% variance explained	53.200	31.820	9.340
% cumulative variance	53.195	85.019	94.357

4 Discussion

4.1 Maize stover and biochar increased total P and Olsen-P contents

Studies have shown that P can be reused or recycled via the pyrolysis of organic feedstocks (Zheng et al. 2013; Robinson et al. 2018). Gul et al. (2015) indicated that the P content in 38 different types of biochar ranged from 0.13 to 42.79 g kg⁻¹. Compared with the initial soil in this research, the biochar in this study contained much higher total P (Table 1). Thus, the application of biochar was able to directly improve soil total P. The P adsorption capacity of biochar could be increased by its high specific surface area and abundant functional groups of biochar; thus, the application of biochar could increase soil total P (Dari et al. 2016). Biochar could increase soil total P by decreasing the runoff of soil P by its high P holding capacity (Xu et al. 2019).

The interactive effects between biochar and P fertilizer can reduce P availability in sodic acidic soils (Xu et al. 2016). The available P in the soil decreased significantly after 10 continuous years of straw retention in an Indian rice-wheat rotation cropping area (Bhandari et al. 2002). Biochar can act as a P sink and reduce the availability of soil P by adsorbing P from soil solutions (Zhang et al. 2016). P can be sorbed by biochar compounds because biochar contains Ca²⁺, Mg²⁺, Fe³⁺, or Al³⁺, which can serve as P sorption sites (Shepherd et al. 2017), potentially reducing the availability of P in the soil. The results of our long-term field experiment indicated that both biochar and stover retention reduced the available P concentration in the soil.

4.2 Maize stover and biochar influenced the inorganic P fractions

It is predicted that P speciation is dominated by Ca-bound phosphate for neutral to alkaline soils, while P is fixed by oxides and hydroxides of Al and Fe and consequently forms Al- and Fe-bound phosphate (Ngatia et al. 2017). There are large amounts of free ions in the soil solution, such as Ca²⁺, Mg²⁺, Fe³⁺, and Al³⁺. These free ions have highly active P sorption capacity, which fixes the phosphate in soil solution. Moreover, the precipitation of P with these ions greatly changes the chemical forms of P in the soil (Adhami et al. 2012). The application of biochar can affect the Al-P, Fe-P, and Ca-P contents in soils (Hong and Lu 2018) via changes in both pH and P sorption. The addition of biochar reduces soil acidity because biochar is highly alkaline and consequently decreases the P precipitation reactions with Fe³⁺ and Al³⁺ (Wang et al. 2012). The precipitation of P with Ca and Mg has been proposed by several authors and is one of the main mechanisms involved in P sorption to biochar (Karunanithi et al. 2017; Shepherd et al. 2017). The addition of biochar increases the Fe and Ca concentrations, which influence the stability of Fe-P and Ca-P (von Tucher

et al. 2018). O-P is generally difficult for plants to absorb and use. The addition of biochar to soils can reduce the fixation of P to soil phases (Farrell et al. 2014; Schmieder et al. 2018). Relative to the value in the CK treatment, O-P was decreased in the different stover incorporation treatments (Fig. 1f), suggesting that reductions in P fixation resulting from biochar and straw return may have occurred via reductions in soil O-P.

4.3 Maize stover and biochar influenced the organic P fractions

Organic P is an important part of total P. The levels of organic P species in the soil are shown in Fig. 2. In general, the application of maize stover and its biochar significantly increased the total organic P by 53.7% and 23.8%, respectively. LOP is highly active and easily degraded because it is sensitive to geochemical processes and biological transformation (Steffens et al. 2010). LOP can be absorbed by plants to meet the requirements of the plants, although it constitutes a small percentage of the total P (Fig. 3). LOP consists mainly of phospholipids and nucleic acids (Steffens et al. 2010). In this study, after 5 years of continuous maize cropping, the content of soil LOP was higher under the BC treatment than under the other treatments. According to previous research, biochar could affect phosphate-solubilizing bacteria (genera *Thiobacillus*, *Pseudomonas* and *Flavobacterium* in agricultural soils) (Figueiredo et al. 2019). Biochar containing a large amount of mineral nutrients was shown to increase the secretions of P-solubilizing secreted by microorganisms and consequently increase the amount of labile P in the soil (Gao and DeLuca 2018). MLOP is H_2SO_4 -extractable organic P that is related to monoester-P and some diester-P, which can easily be mineralized for absorption by plants (Zhu et al. 2017). The application of maize stover and its biochar increased the soil MROP. This result is consistent with the finding that MROP (as fulvic acid P) is easily affected by the iron-aluminum oxide and CEC in soils (Zhu et al. 2017). HROP (as humic acid P) is a component of organic P. In this study, the ST treatment yielded the highest HROP among the treatments. HROP is typically dominated by residual P, which is associated with highly stable organic constituents (Perkins and Underwood 2001). Although the direct return of stover to the field increased the total P content in the soil, the HROP/total P fraction ratio was the highest in the ST treatment. Thus, the direct application of maize stover limits the stover potential as a nutrient source for field ecosystems, although HROP can be converted into a form that plants can absorb and use.

5 Conclusions

The total P was significantly increased by the application of maize stover and its biochar, while Olsen-P was significantly decreased. The application of maize stover and its biochar

affected both organic and inorganic phosphorus fractions; biochar had a more advantageous effect on the soil inorganic P fractions, while stover had a greater effect on the content of organic P fractions.

This study investigated the characteristics and transformation of soil P fractions. Further research should take into account both phosphorus erosion and plant utilization of soil P to obtain a comprehensive understanding of P dynamics and the underlying mechanisms.

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