

# Effects of acidic phosphorus-rich biochar from halophyte species on P availability and fractions in alkaline soils

**Xuyang Wang**

Xinjiang Agricultural University

**Tao Sun**

Xinjiang Agricultural University

**Haigang Ma**

Xinjiang Agricultural University

**Guangmu Tang**

Xinjiang Academy of Agricultural Science

**Mo Chen**

Xinjiang Agricultural University

**Maidinuer Abulaizi**

Xinjiang Agricultural University

**Guangling Yu**

Xinjiang Agricultural University

**Hongtao Jia** (✉ [jht@xjau.edu.cn](mailto:jht@xjau.edu.cn))

Xinjiang Agricultural University

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## Research Article

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# Abstract

Conditioning alkaline soil with acidic phosphorus-rich biochar might contribute to achieving sustainable phosphorus (P) use and residue management. In this study, acidic phosphorus-rich biochar was prepared from halophyte species biochar (HBC) by the modification of  $\text{H}_3\text{PO}_4$  (P-HBC) and  $\text{H}_4\text{P}_2\text{O}_7$  (PA-HBC). The P combination method and fractions in biochars were characterized, and the effects of biochars on P fractions in different types of alkaline soil were examined with incubation experiments. The results showed that the pH values of P-HBC (3.31) and PA-HBC (2.17) decreased significantly, and the total P content increased to  $4.66 \text{ g}\cdot\text{kg}^{-1}$  and  $5.24 \text{ g}\cdot\text{kg}^{-1}$ , respectively. The spectral analysis confirmed the doping of P and acid groups in biochar. The addition of modified biochars in alkaline soils will make the soil tend to be neutral. Sequential extraction of soil P confirmed that biochar application facilitated the transformation of stable P into active fractions, with greater effects from modified biochars than HBC. Activation mechanism of biochar to soil P fractions varies from soil types. Overall, acidic phosphorus-rich biochars can be employed to improve alkaline soil properties and increase P activity.

## 1. Introduction

The alkaline soils are important agricultural soil resources [1, 2]. Due to the strong binding of phosphorus (P) with mineral elements in an alkaline environment and the formation of an insoluble compound, the utilization of phosphate fertilizer is low in alkaline soils [3]. Hence, in the farmland of Xinjiang, the utilization rate of P fertilizer is only 10%-25% [4]. Under the current socio-economic and environmental pressures for sustainability, it is necessary to improve P availability to plants and reduce its accumulation in alkaline soils.

The positive effects of biochar amendment on the growth of soil P availability and therefore, crop productivity, have been documented earlier [5]. Biochar has the potentials to enhance soil fertility through nutrient retention and changing the P content by partly replacing chemical fertilizers and promoting organic farming [6, 7]. However, when the biochar was added to soil, the nutrients available to plant provided by the biochar also vary with soil type. For example, the research by Chen et al [8] suggests that biochar application for acidic soils is considered as an effective way of reducing P leaching, increasing the retention of P by 16%-24%. In contrast, the P fixation due to the formation of precipitates between P and divalent ions ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) leads to the reduced availability of P in alkaline soil [9, 10]. Higher exchangeable cations and pH of the biochar result in more P retention in alkaline soils [11], limited the application of the biochar in the alkaline soil. Therefore, it is necessary to find effective biochar modification methods to prepare appropriate biochar for improving P availability in alkaline soils.

Plants that adapted to living in saline soils are called halophytes; they grow in large numbers in arid areas of Xinjiang. The halophytes can effectively improve the saline soil as they are well adjusted in the salt environment to remove the salt from different kinds of salt-affected problematic soils through salt excluding and excreting [12, 13]. These biomass wastes were conventionally treated via landfill disposal or incineration, leading to extra environmental pollution. Halophytes are valuable biomass resources rich

in cellulose and lignin, which can be utilized for biocar preparation [14, 15, 16]. Thus, the advantage of halophyte biochar can be reasonably adopted to produce tremendous environmental and economic benefits. The type of biomass, activating agents, and modification methods have a significant influence on biochar properties [17]. Phosphoric acid ( $H_3PO_4$ ) and pyrophosphoric acid ( $H_4P_2O_7$ ) are common activators. The two acids have been widely applied for the activation of biomass [18, 19]. Earlier studies have shown that biochar surface prepared by  $H_4P_2O_7$  activation biomass had the higher amount of total acidic groups than after  $H_3PO_4$  activation treatment, which resulted in a lower pH value (5.76), due to  $H_4P_2O_7$  is more acidic than  $H_3PO_4$  [5, 19, 20]. Nevertheless, no research till date systematically explored the application potential of biochar modified by  $H_3PO_4$  and  $H_4P_2O_7$  as soil amendments for simultaneous activation of P and improved soil properties in alkaline soil.

This study hypothesized that  $H_3PO_4$  and  $H_4P_2O_7$  modified could improve the structural characteristics and P binding form of halophyte biochar and P-rich biochar would facilitate the activation of P in alkaline soils. The main objectives of this study were to: (1) investigate the structure and properties on halophyte biochar before and after modification, (2) study the combination mode and fractions of P in halophyte biochar, and (3) explore the fractions and transformation of P in the soil after modified halophyte biochar enter the alkaline soil.

## 2. Materials And Methods

### 2.1 Soil and chemical reagents

Surface alkaline soil samples (0 to 20 cm) were collected from the fallow field at the research farm: aeolian sandy soils (AS) from the Soil Improvement Test Station, Xinjiang (86° 24' E, 45° 20' N), grey desert soils (GS) from the Experiment Station of Xinjiang Academy of Agricultural Sciences, Qitai (89° 12' E, 44° 13' N), brown desert soils (BS) and saline soils (SS) from the National Field Scientific Observation and Research Station of Farmland Ecosystem, Aksu (80° 45' E, 40° 37' N). The main properties of soil are shown in **Table S1**. Ultrapure water (18.2 M $\Omega$  cm, Millipore, USA) was used to prepare the desired solution. All the chemicals and reagents used in the present study were analytical grade.

### 2.2 Biochar production and characterization

The biomass precursors were *Salicornia angustifolia* (*Salicornia europaea* L.). The halophytes were air-dried at 60°C, washed with de-ionized water to remove dust and impurities, placed in a quartz reactor and then heated at 15°C·min<sup>-1</sup> in a muffle furnace in an N<sub>2</sub> environment at 400°C for 2 h (referred to hereafter HBC). After pyrolysis, the HBC was homogenized and ground through a 50-mesh sieve. HBC was provided by the Xinjiang Academy of Agricultural Sciences. Phosphoric acid-modified biochar (P-HBC) and pyrophosphoric acid-modified biochar (PA-HBC) were obtained by impregnated HBC, with  $H_3PO_4$  solution (70 wt.%) and  $H_4P_2O_7$  at a ratio of 20:1 (solution/g HBC).  $H_4P_2O_7$  can be obtained by the dehydration of phosphoric acid at 213°C. Mixed samples were shaken continuously for 24 h at 120 rpm on an orbital

shaker. After modification, the samples were washed with distilled water until the pH of the washed solution was steady.

The suspension was shaken for 30 min at 150 rpm and pH and electrical conductivity (EC) were determined at a solid: water ratio of 1:20 (w/v) using a pH meter (FE20 plus, Mettler Toledo, Switzerland) and an EC meter (BEC-6500A, Bell, America). The element compositions of the biochar were determined using an Elemental Analyzer (EA3000, Jena, Germany). The surface morphology was examined by field emission scanning electron microscopy energy dispersive spectroscopy (SEM-EDS) (S-4800, Hitachi, Japan). The specific surface area was determined by sorption of N<sub>2</sub> at 77 K, using a BELSORP-MAX analyzer, and applying the Brunauer Emmett Teller (BET) equation. For Fourier transform infrared (FTIR) of HBC before and after modification were obtained with FT/IR-4100 spectrometer (Jasco, Japan). HBC and spectroscopy grade KBr were dried at 105 °C for 4 h, then HBC was co-ground with KBr (1:100, wt/wt). The mixture was pressed to a disc under infrared lamp exposure. The spectroscopy was collected in the range of 4000 to 400 cm<sup>-1</sup> at a step of 4 cm<sup>-1</sup> resolution X-ray photoemission spectroscopy (XPS) measurements were carried out by the Thermo Fisher ESCALAB 250Xi system. The photoelectrons were excited by an Al K $\alpha$  X-ray (h $\nu$  = 1486.8 eV). The binding energy was scanned from 1200 eV to 0 eV. The full element spectrum and the survey scans C1s, O 1s and P2p spectrum were analyzed. XPS data were processed using XPSPEAK41 software. The content of elements was evaluated from the ratio of the areas under the corresponding core-level peaks of the survey spectrum.

## 2.3 Soil incubation experiments

Before starting the experiment, soil samples were air-dried and sieved through a 2-mm standard sieve. The 100 g of soil sample was weighed, put into 500 mL plastic culture bottle (12.8 cm depth, 7.9 cm diameter). Then the four soil (AS, BS, GS and SS) was respectively mixed with HBC, P-HBC and PA-HBC at a ratio of 1%. The blank control soil (CK) did not receive any biochar or amendment.

The incubation experiment included 16 treatments (including the control), and each bottle was regarded as a replicate, and 4 replicates (bottles) were used for each treatment. Total 64 bottles were incubated at 25°C for 60 d in an incubator, and deionized water was added on a weight basis to maintain the targeted water content (60% of Water Holding Capacity), every 2–3 d interval. Plastic films with 10 small holes were applied to cover the top of the bottles for ventilation and reduction of moisture losses. When the incubation was completed, mixed samples were air-dried and sieved (100 mesh) for later analysis.

## 2.4 Determination of chemical properties

Soil pH and EC were analyzed in a 1:2 soil-water extract using probes provided by pH meter FE20 plus and a BEC-6500A conductivity meter. Soil organic matter was measured using the external-heat potassium dichromate oxidation and titration method. Soil soluble sodium (Na<sup>+</sup>) and potassium (K<sup>+</sup>) were estimated with a flame photometry (FP6410, Jingke Analytical Instruments, China). The soluble calcium (Ca<sup>2+</sup>) and magnesium (Mg<sup>2+</sup>) contents of the soil samples were determined by atomic absorption spectrometry (RG3604, Hirp, China).

P fractions in both soil and biochar samples were analyzed through a sequential extraction process. For each sample, 0.5 g of sample was placed in a 50-mL centrifuge tube and extracted with 30 mL of H<sub>2</sub>O for 1 h, then sequentially with 0.5 M NaHCO<sub>3</sub> at pH 8.5 (16 h), 0.1 M NaOH at pH 13 (16 h), and 1.0 M HCl (16 h). After every addition of extractant, samples were centrifuged on an orbital shaker at 4000 rpm for 15 min. Total P (P<sub>t</sub>) content in biochar extracts was measured by digesting the extracts in a microwave at 140°C for 60 min. Inorganic P (P<sub>i</sub>) was analyzed by direct extraction. The organic P (P<sub>o</sub>) is the difference between P<sub>t</sub> and P<sub>i</sub> in extracts NaHCO<sub>3</sub> and NaOH. Lastly, the residue from HCl extraction was dissolved with 10 mL of H<sub>2</sub>SO<sub>4</sub>.H<sub>2</sub>O<sub>2</sub> and digested in a microwave at 300°C for 2 h [21]. Absorbance was measured at 880 nm by a molybdate-ascorbic acid method using spectrophotometer (Spectrumlab 22pc, LASPEC, China) to analyze of P.

## 2.5 Statistical analyses

All experiments were conducted in quadruplicate. Experimental data were listed as means ± standard deviation. One-way analysis of variance was carried out using SPSS 20.0 and Origin Pro 2021 was used to draw the data. Multiple comparisons were made by the least significant difference test ( $p < 0.05$ ). Pearson's correlation analysis with a significance level of  $p < 0.05$  and  $p < 0.01$  was used to quantify the correlation between variables.

## 3. Results

### 3.1 Characterization of biochars

The element compositions of the biochars are listed in Table 1. Compared with the HBC, the C content decreased significantly by 14.17% and 27.34% while the O content increased by 11.83% and 27.93% in P-HBC and PA-HBC samples, respectively. Moreover, the O/C atomic ratio in HBC was  $< 0.2$ , suggesting longer stability and half-life of HBC [22]. The O/C, as well as H/C ratios of P-HBC and PA-HBC, increased relative to those of HBC. This increase indicated that the biochars modified by H<sub>3</sub>PO<sub>4</sub> and H<sub>4</sub>P<sub>2</sub>O<sub>7</sub> became strongly hydrophilic. The ash content was significantly increased in P-HBC and PA-HBC relative to that in HBC.

Table 1  
Element compositions of halophyte biochar (HBC), H<sub>3</sub>PO<sub>4</sub> modified biochar (P-HBC), and H<sub>4</sub>P<sub>2</sub>O<sub>7</sub> modified biochar (PA-HBC).

Property	Treatment		
	HBC	P-HBC	PA-HBC
C (%)	59.79	45.62	32.45
N (%)	1.07	0.56	0.84
H (%)	2.96	3.13	1.85
O (%)	11.81	23.64	39.74
Atomic ratio O/C	0.15	0.39	0.92
Atomic ratio H/C	0.59	0.82	0.68
Ash (%)	24.37	27.06	26.12
O% = 100% - (C% + N% + H% + Ash%).			

### 3.2 Textural structure analysis of biochars

The pore size distribution and N<sub>2</sub> adsorption–desorption isotherms at 77K of the biochars are shown in Fig. 1. The modification methods seemed to have a remarkable influence on the classification of the N<sub>2</sub> adsorption-desorption isotherms. HBC possessed a typical Type IV adsorption isotherm, indicating a mesoporous structure for HBC. The adsorption-desorption isotherms of P-HBC and PA-HBC presented a Type I curve, which suggested that P-HBC and PA-HBC possessed a narrow pore size distribution in the micropore range.

Surface area and pore structural parameters of biochars are listed in Table 2. The surface area and pore volume were significantly decreased in the order of PA-HBC (0.71 m<sup>2</sup>·g<sup>-1</sup>) < P-HBC (1.00 m<sup>2</sup>·g<sup>-1</sup>) < HBC (11.89 m<sup>2</sup>·g<sup>-1</sup>). The three biochars were mainly mesoporous (2–50 nm). The average pore diameter of HBC, P-HBC, and PA-HBC obtained 7.17, 3.78, and 2.43 nm, respectively.

Table 2  
BET of halophyte biochar (HBC), H<sub>3</sub>PO<sub>4</sub> modified biochar (P-HBC), and H<sub>4</sub>P<sub>2</sub>O<sub>7</sub> modified biochar (PA-HBC).

Property	Treatment		
	HBC	P-HBC	PA-HBC
BET surface area (m <sup>2</sup> ·g <sup>-1</sup> )	11.89	1.00	0.71
Average pore diameter (nm)	7.17	3.78	2.43
Total pore volume (cm <sup>3</sup> ·g <sup>-1</sup> )	0.0291	0.0010	0.0007

The differences in the surface morphology and P distribution of HBC before and after modification were observed through SEM-EDS imaging (Fig. 2). HBC exhibited fragments that appeared mainly due to the thermal decomposition of cellulose and residues of salts [23]. The granular structure with high P content was formed on the surface of modified biochar. The P content on the surface of P-HBC and PA-HBC was significantly increased compared to that on the surface of HBC by 9.16% and 11.55%, respectively (Table S2).

### 3.3 Chemical properties and P morphology analysis of biochar

The existence of functional groups of P in all samples was investigated via FT-IR spectroscopy within a scanning range of  $4000 - 400 \text{ cm}^{-1}$  (Fig. 3). The multiple signals were superpositioned at  $490 \text{ cm}^{-1}$ ,  $799 \text{ cm}^{-1}$ ,  $1085 \text{ cm}^{-1}$ ,  $1420 \text{ cm}^{-1}$ , and  $2416 \text{ cm}^{-1}$ . After modification, the absorption peak intensity of the biochar was observed to increase significantly at  $490 \text{ cm}^{-1}$ , proving that the modified process can effectively promote the formation and stabilization of the  $\text{P}(\text{OH})_3$  bond. The peak of C - P stretching at  $799 \text{ cm}^{-1}$  disappeared, as reported earlier [24], indicating that  $\text{H}_3\text{PO}_4$  and  $\text{H}_4\text{P}_2\text{O}_7$  destroy the P-C present in the original biochar. Within this range, the peak at  $1085 \text{ cm}^{-1}$  can be attributed to the ionized P-O linkage and the symmetrical vibration of P - O-P in polyphosphate chains [25]. The peaks in the region of  $1420 \text{ cm}^{-1}$  were assigned to the carboxylic (-COOH) stretching vibration. P-HBC and PA-HBC exhibited new absorption peaks at  $2416 \text{ cm}^{-1}$ , which is attributed to  $\text{PH}_3$  or P-H, and may also be assigned to the superposition of two signals. Results revealed fresh P-containing and acidic functional groups are formed in P-HBC and PA-HBC, which are essential for application in alkaline soils.

The HBC samples were alkaline with a pH of 10.18. After being modified by  $\text{H}_3\text{PO}_4$  and  $\text{H}_4\text{P}_2\text{O}_7$ , their pH reduced significantly (3.31 and 2.17, respectively) and they became acidic (Fig. 4a). The EC of HBC was  $3.35 \text{ ds}\cdot\text{m}^{-1}$ , which was not significantly different from that of P-HBC and PA-HBC (Fig. 4b). The total P of modified samples increased significantly in the order of PA-HBC ( $5.24 \text{ g}\cdot\text{kg}^{-1}$ ) > P-HBC ( $4.66 \text{ g}\cdot\text{kg}^{-1}$ ) > HBC ( $0.51 \text{ g}\cdot\text{kg}^{-1}$ ), which indicated that P was loaded by biochar (Fig. 4c). The proportions occupied of P fractions in each treatments are presented in Fig. 4d. The modification treatment showed a significant influence on all the biochar P fractions. In particular, the  $\text{H}_3\text{PO}_4$  and  $\text{H}_4\text{P}_2\text{O}_7$  increased the proportion of  $\text{H}_2\text{O}$ -extractable P by 70.10% and 61.60% in biochars, as compared to the HBC. The concentration of HCl-P decreased by 30.16% and 30.25% in P-HBC and PA-HBC, in contrast to the HBC. Furthermore, the concentration of Rs-P decreased by 32.12% and 30.40%, respectively.

The chemical composition and bonding configurations of P on the biochar were further analyzed by XPS and the results are presented in Fig. 4e. Three characteristic peaks appeared at approximately 132 eV, 286 eV, and 534 eV corresponding to the P2p, C1s, and O1s peaks in the samples (P-HBC and PA-HBC). Particularly, the P2p peak was not observed in HBC, further illustrating the successful loading of P atoms into the modified samples. With the help of the XPS analysis, the C, O, and P on the surface of modified

samples were semi-quantitatively estimated (**Table S3**). After modification, the percent C content tended to decrease. The data also indicate that the values of O increased after modification.

To further understand the chemical bond configuration of P in the activated biochar, the high-resolution P2p and O1s peaks of both P-HBC and PA-HBC were deconvoluted, and the components were semi-quantitatively analyzed peak areas as shown in Fig. 4f, g and **Table S4**. Three major peaks at approximately 133.1 eV (C-P-O), 134.0 eV (C-O-P), and 135.0 eV (O = P-O) appeared for the P2p peak for both P-HBC and PA-HBC, of which the peak at 135.0 eV was assigned to pyrophosphate [26]. The O1s spectrum of P-HBC and PA-HBC was deconvoluted into three peaks assigned to C = O and/or P = O (approximately 531.0 eV), P-O-C and/or C-O-C (approximately 532.2 eV), and P-O-P (approximately 533.5 eV) [27]. Compared with P-HBC, the percent C-O-P of PA-HBC increased from 34.79–37.24%, and the relative contents of C-P-O and O = P-O decreased by 2.09% and 0.36% respectively (**Table S4**). After modification, the deconvolution result of O1s showed an increase in the proportion of P-O-C and/or C-O-C from 35.40–43.91% and 42.10%, as well as in the proportion of P-O-P from 4.94–24.05% and 22.61%, which also suggested that the modification of biochar promotes the formation and accumulation of P species (**Table S4**). The binding energy of the C = O and/or P = O, as well as C-O-C and/or P-O-C bonding shifted positively by P doping, inducing the higher binding energy. This could be because the charge is transferred from the C atom to the P atom, forming a chemical bond related to P [28]. Thus it can be seen, P was mainly bound on the surface of biochar by directly bonding with C atoms or bridged by O atoms.

### 3.4 Effects of biochars on soil

The pH, EC and total P of the soil differed depending on the type of biochar that was added (Fig. 5). HBC is strongly alkaline, therefore, the pH of the soil increased after adding HBC, although the increase was not significant. Both P-HBC and PA-HBC led to a significant drop in soil pH to 7.16–7.45. The addition of HBC also increased the EC value of BS and GS to  $5.13 \text{ ds}\cdot\text{m}^{-1}$  and  $1.50 \text{ ds}\cdot\text{m}^{-1}$ , respectively, while neither P-HBC nor PA-HBC had a significant impact on soil EC value. The application of biochars showed an insignificant impact on total P in the soils. The addition of modified biochars with quite low pH value in alkaline soils will makes the soil tend to be neutral, which will have a positive impact on seed germination and plant growth. In contrast, original biochar increased the EC values of some soil types to excessively high levels.

Figure 6 shows the results of sequential extraction of the different soils after 60 days of incubation. The effect of HBC on soil P fractions depending on the type of alkaline soils. After the application of HBC, organic P ( $\text{NaHCO}_3\text{-Po}$  and  $\text{NaOH-Po}$ ) of AS and BS soils increased by 4.19% – 10.96%. Inorganic P ( $\text{NaHCO}_3\text{-Pi}$  and  $\text{NaOH-Pi}$ ) was decreased in GS soil and increased in SS soil. Regardless of the status of P fractions of the contral experimental soils (CK),  $\text{H}_2\text{O-P}$  increased significantly in soils with the application of the P-HBC and PA-HBC to alkaline soils. Compared with contral soils,  $\text{H}_2\text{O-P}$  content increased by 2.13% – 26.02%. Application of modified biochars sources (P-HBC and PA-HBC) increased inorganic P ( $\text{NaHCO}_3\text{-Pi}$  and  $\text{NaOH-Pi}$ ) content by 1.28% – 29.01%. In addition, the concentrate of organic P ( $\text{NaHCO}_3\text{-Po}$  and  $\text{NaOH-Po}$ ) reduced by 0.40% -20.45% in modified biochars-treated soils was observed.



It must also be mentioned that HCl-P of each treatments only increased in SS soil, as compared to the control. The biochars in the soils enhanced the transformation ability of Rs-P. The Rs-P decreased by 2.35% – 40.62% due to biochars application. This phenomenon is weaker in HBC treatments, stronger in P-HBC treatments and PA-HBC treatments. This is evident, biochars has a beneficial impact on P in alkaline soils, modified biochars is more beneficial to soil P, it brings more usable P fractions.

In correlating the P fractions of biochars versus the soil characteristics, it was observed that the interaction between these factors changed completely depending on the different analysed alkaline soil types (Fig. 7). The contents of biochars H<sub>2</sub>O-P and Rs-P were negative correlated to soil pH in all alkaline soil treatments. The inorganic P involved NaHCO<sub>3</sub>-Pi and NaOH-Pi in biochars had a negative relationships to the organic P (NaHCO<sub>3</sub>-Po and NaOH-Po) in soils, respectively. The inorganic P (NaHCO<sub>3</sub>-Pi and NaOH-Pi) and Rs-P in biochars had a negative correlation with soils pH. Additionally, It is only observed in SS soil that biochars NaOH-Po was positive correlated with soil HCl-P, whereas it was negatively correlated with soil Rs-P. Finally, it was found that biochars can change the availability of P by indirectly transforming P fractions through the changes in soil properties.

## 4. Discussion

The properties of biochars are known to exhibit deviation over a wide range due to differences in halophytes and acids (here, H<sub>3</sub>PO<sub>4</sub> and H<sub>4</sub>P<sub>2</sub>O<sub>7</sub>). The content of cations such as Ca, K, Mg, and Na is rich in halophytes. After pyrolysis, these form carbonates and oxides, increasing the pH of HBC [15, 29]. Both H<sub>3</sub>PO<sub>4</sub> and H<sub>4</sub>P<sub>2</sub>O<sub>7</sub> are oxygen-rich phosphoric acids that are easy to react with soluble minerals of halophytes forming insoluble phosphate salts [30]. Due to the formation and accumulation of mineral elements in modified biochars, the ash content increased significantly. The pores of the biochar were blocked by phosphate salts, resulted in a decrease in pore volume, which corroborates the finding of Liu et al. [23]. The spectral and elemental analysis showed that the values of O increased after modification, which could be attributed to the formation of -COOH and oxygen-containing phosphate groups after modification by oxygen-rich acid [15]. The formation of these acid groups is the primary cause for the change in the chemical properties of biochars. Furthermore, the C content of biochar decreased after H<sub>3</sub>PO<sub>4</sub> and H<sub>4</sub>P<sub>2</sub>O<sub>7</sub> modification. This may be due to the instability of the edge of the biochar, whereby, C is easily replaced by O or P, or is lost in the form of CO or CO<sub>2</sub> generated by the reaction of biochar with acid [28]. H<sub>4</sub>P<sub>2</sub>O<sub>7</sub> has a higher acidity and more oxygen content than H<sub>3</sub>PO<sub>4</sub>. Therefore, the content of the O atom with the higher electronegativity increased owing to the partial oxidization of biochar by H<sub>4</sub>P<sub>2</sub>O<sub>7</sub> [28]. It facilitated the formation of more C-O-P in PA-HBC. We observed that more oxidized P was covalently bonded with C in PA-HBC than in P-HBC. Based on molecular orbital calculations, the O-P bond is the weakest and the C-P bond might be more stable than the C-O-P bond [27]. Through the modification by H<sub>3</sub>PO<sub>4</sub> and H<sub>4</sub>P<sub>2</sub>O<sub>7</sub>, the association of P with C bridged by O in biochars increased, and it was the highest in the H<sub>4</sub>P<sub>2</sub>O<sub>7</sub> treated samples. Therefore, the effectiveness of P might be relatively high in PA-HBC, followed by P-HBC. This conjecture was proved by sequential extraction of P.

The sequential fraction method considers that the effectiveness of the extraction of P species gradually decreases in the order of water,  $\text{NaHCO}_3$ ,  $\text{NaOH}$ , and  $\text{HCl}$ , and the remaining P in the residue is considered to be the least effective form [31]. The pyrolysis process of biochars can lead to the conversion of P to more recalcitrant forms. As a result, a higher proportion of HCL-P and Rs-P accumulate in HBC [5, 32]. Adhikari et al. [33] reported a somewhat higher proportion of HCL-P (57.60%) in the biochar prepared at 400 °C. However, in this study, the proportion of HCL-P (33.43%) was similar to that of Rs-P (39.29%) and it could be attributed to the high mineral components in halophytes [15]. HCL-P and Rs-P represent occluded P, with slow turnover and consist of P bound to calcium (Ca) and other cations [33]. The pH also showed a positive correlation to Rs-P fraction, indicating that higher pH is related to higher amounts of Rs-P [21]. HBC is rich in cations such as Ca and magnesium (Mg), and has a higher pH (10.24), which promotes the formation of HCL-P and Rs-P in HBC. Compared with HBC, the content of HCL-P was reduced after modification. This discrepancy might be because HCL-P transforms to other forms of P. Acidic groups such as  $-\text{COOH}$  and phosphoric acid groups on the surface of the biochar were enriched by  $\text{H}_3\text{PO}_4$  and  $\text{H}_4\text{P}_2\text{O}_7$  modification. In an acidic environment, the  $-\text{COOH}$  groups react with Ca and Mg and inhibit the formation of insoluble P forms. While desorption of P in the original biochar occurred due to the addition of acid, it resulted in a reduction in the HCL-P fraction [34].

The P availability in the soil is mainly affected by the adsorption of pH and metal oxides. Along with HBC, the metal cations in HBC also entered the soil. Higher pH increases the precipitation of P to stable forms. In alkaline soils and HBC, the large number of free cation oxides could be the sites for P sorption [5, 12, 35]. This leads to the increase in the organic P ( $\text{NaHCO}_3\text{-Po}$  and  $\text{NaOH-Po}$ ) content in the soil after applying HBC. The alkaline soils observed in the application of modified biochars with acidity tend to be neutral, due to the high buffering capacity of soils. After the application of P-HBC and PA-HBC, conversion of organic P ( $\text{NaHCO}_3\text{-Po}$  and  $\text{NaOH-Po}$ ) in the soil also occurred due to the changes in pH and other soil reactions, leading to higher P availability [36]. This is because organic acids bound in modified biochars can provide organic anions, and the bonds between organic anion and cation are stronger than those between phosphate and cations [34, 37]. The change in P fractions was also affected by several processes like adsorption of P to cation and metal oxides, mineralization, dissolution, and precipitation to mineral pools. The application of P-HBC and PA-HBC reduced the pH of the soil, thus causing an increase in amounts of free cation oxides in the soil than in biochars. Application of acidic biochars can greatly increase available P fractions ( $\text{H}_2\text{O-P}$  and  $\text{NaHCO}_3\text{-Pi}$ ) content in the alkaline soil due to the competition between free cations in the soil with biochar surface for adsorption sites on phosphate [11, 38]. Therefore, when incorporated into the soil, modified biochars can change the availability of P by indirectly transforming P fractions through the changes in soil properties, as suggest by Glaser et al. [7] and Figueiredo et al. [39].

The effects of biochars on diverse alkaline soils were also different. Compared to other soils, the more metal cation in SS soil provides more substrates for the reaction, although AS, BS and GS also contains cation. Increased concentrations for HCL-P only in the SS soil treatments might be ascribed to the sorption/precipitation of P with excess cations in SS soil (Hafeez et al. 2019). Furthermore, a significant

correlation between stable P forms (HCl-P and Rs-P) and NaOH-Po was noted only in SS soil, which could be attributed to two reasons: (i) Dissolved organic matter released from biochar in the form of organic ligands can form organo-metal. The SS soil contained more metal ion content than other soils, the response of Rs-P to organic P fractions is more obvious, and thus increased Rs-P transformation rate caused by NaOH-Po [40]. (ii) The excessive metal ion in SS can form HCl-P in soil due to mineralization between organic P and cation, and thus HCl-P of SS soil are strongly controlled by factors such as organic P fractions (NaHCO<sub>3</sub>-Po and NaOH-Po) [41].

## 5. Conclusions

In conclusion, these results indicate that H<sub>3</sub>PO<sub>4</sub> and H<sub>4</sub>P<sub>2</sub>O<sub>7</sub> modifications are a feasible option for enhancing the sustainable use of P in alkaline soils. The H<sub>3</sub>PO<sub>4</sub> and H<sub>4</sub>P<sub>2</sub>O<sub>7</sub> modifications were effective in decreasing soil pH, specific surface area, and pore volume. Although C were partially lost in the process of modification, mineral nutrients, especially P, were concentrated in biochars and form granular structures with a high P content. The spectral analyses performed in this study revealed the association of P directly with C or indirectly with C through O increased phosphate content in biochar. The effect of H<sub>3</sub>PO<sub>4</sub> and H<sub>4</sub>P<sub>2</sub>O<sub>7</sub> with an increase in the proportion of H<sub>2</sub>O-P and NaHCO<sub>3</sub>-Pi rendered P-HBC and PA-HBC richer in total P and active P compared to that in HBC. In addition, biochars enhanced the available concentration of P in soil through improvement of soil properties and transformed soil P fractions. In particular, the modified biochar was found to be more efficient in increasing available P fractions than the original biochar. However, specific alkaline soil type also brought potential negative effects on P fractions. In summary, HBC modified with H<sub>3</sub>PO<sub>4</sub> and H<sub>4</sub>P<sub>2</sub>O<sub>7</sub> could be a effective candidate for a positively impacting on alkaline soil properties and P availability.

## Abbreviations

HBC  
halophyte biochar  
P-HBC  
H<sub>3</sub>PO<sub>4</sub> modified biochar  
PA-HBC  
H<sub>4</sub>P<sub>2</sub>O<sub>7</sub> modified biochar  
AS  
aeolian sandy soils  
BS  
brown desert soils  
GS  
grey desert soils  
SS  
saline soils

CK

untreated soil.

## Declarations

### Availability of data and material

All data generated or analysed during this study are included in this published article.

### Competing interests

The authors declare that there are no conflicts of interest to declare.

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### Author contribution

Xuyang Wang, Tao Sun and Guangmu Tang conceived and designed the study, and wrote the manuscript. Guangmu Tang, Maidinuer Abulaizi, Haigang Ma, Mo Chen, Guangling Yu, and Hongtao Jia were responsible for performing the field and laboratory work. Xuyang Wang and Hongtao Jia analyzed the data. All authors discussed the results, critically reviewed the manuscript, and approved its publication.

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### Ethics approval and consent to participate

Not applicable.

### Consent for publication

Not applicable.

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## Figures

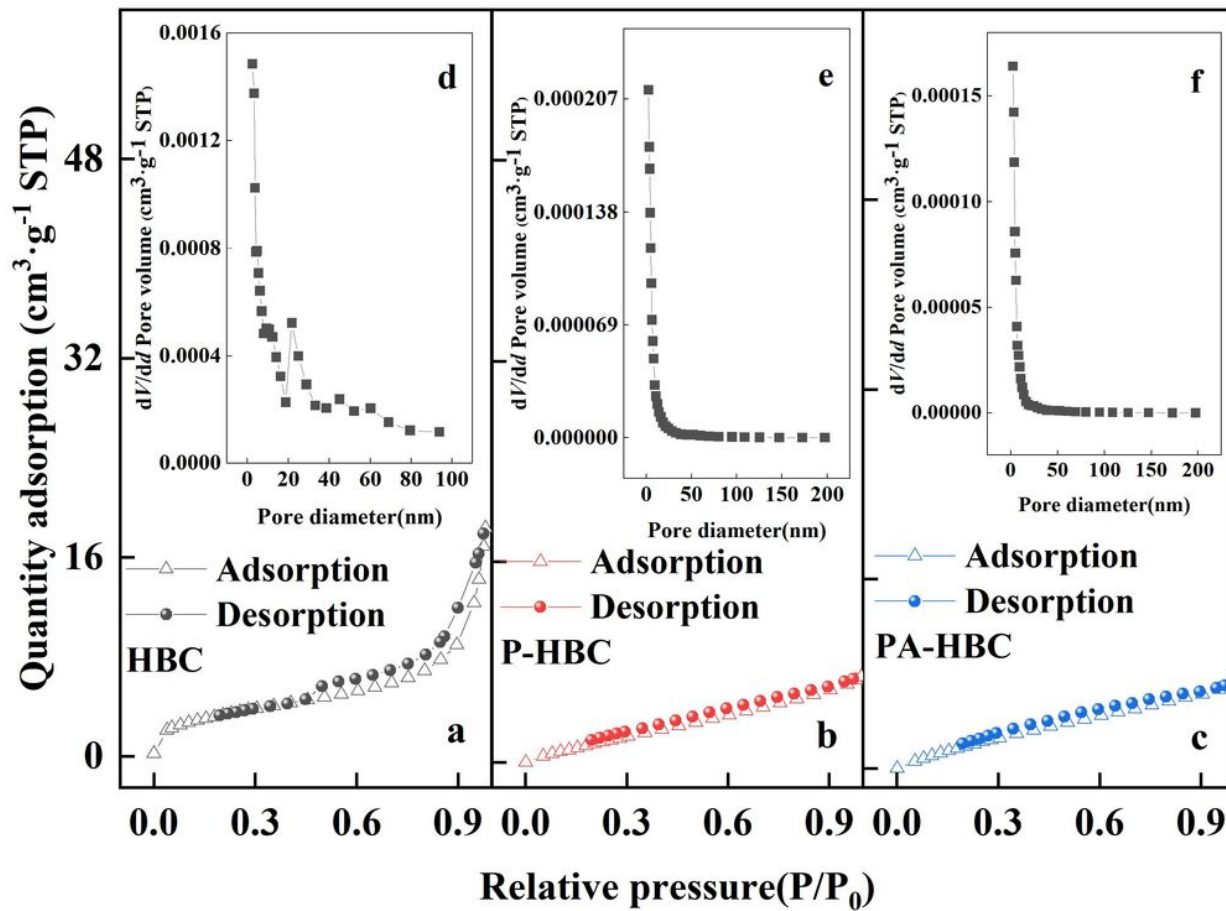
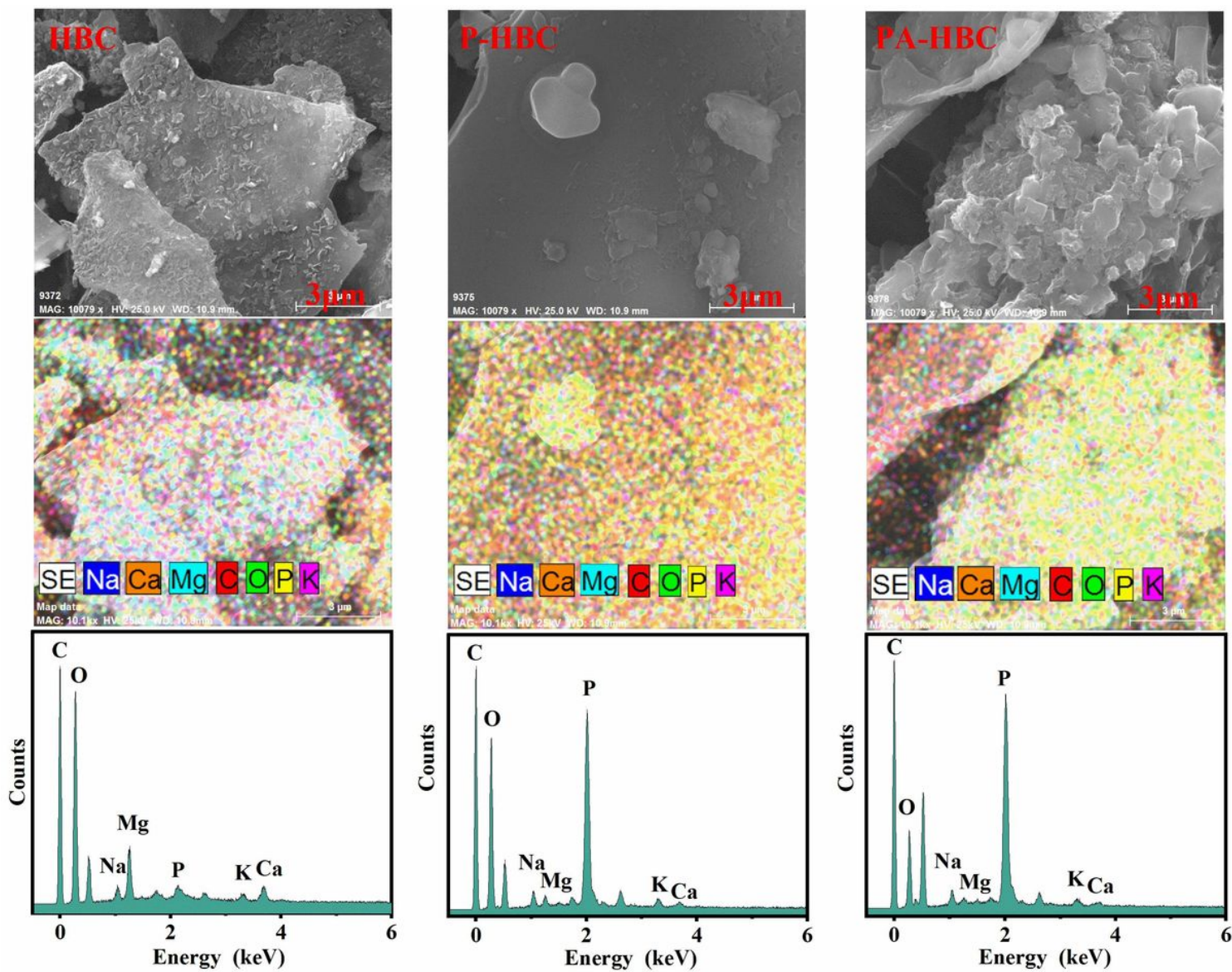


Figure 1

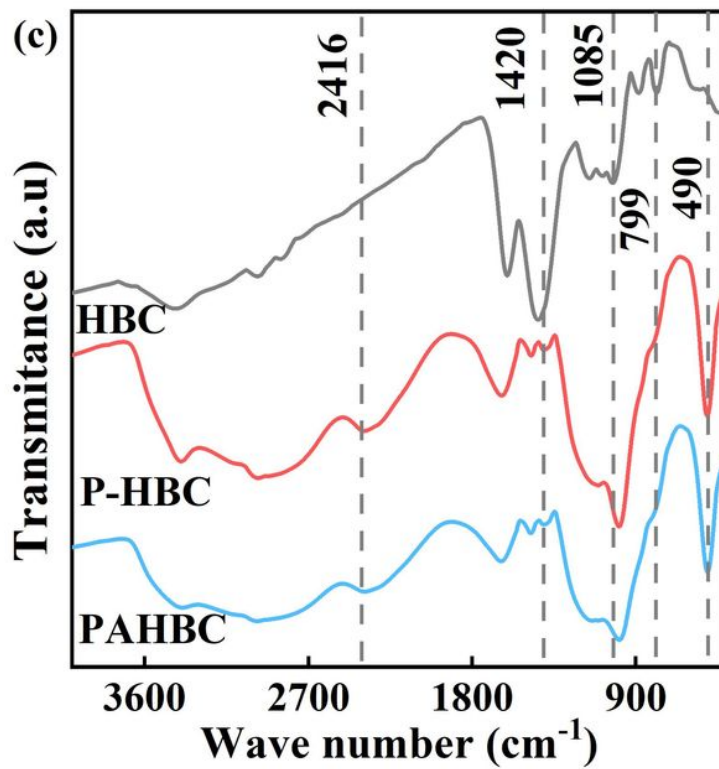
The  $N_2$  adsorption-desorption isotherms (a, b, c) and pore size distribution (d, e, f) of HBC,  $H_3PO_4$  modified biochar (P-HBC), and  $H_4P_2O_7$  modified biochar (PA-HBC).





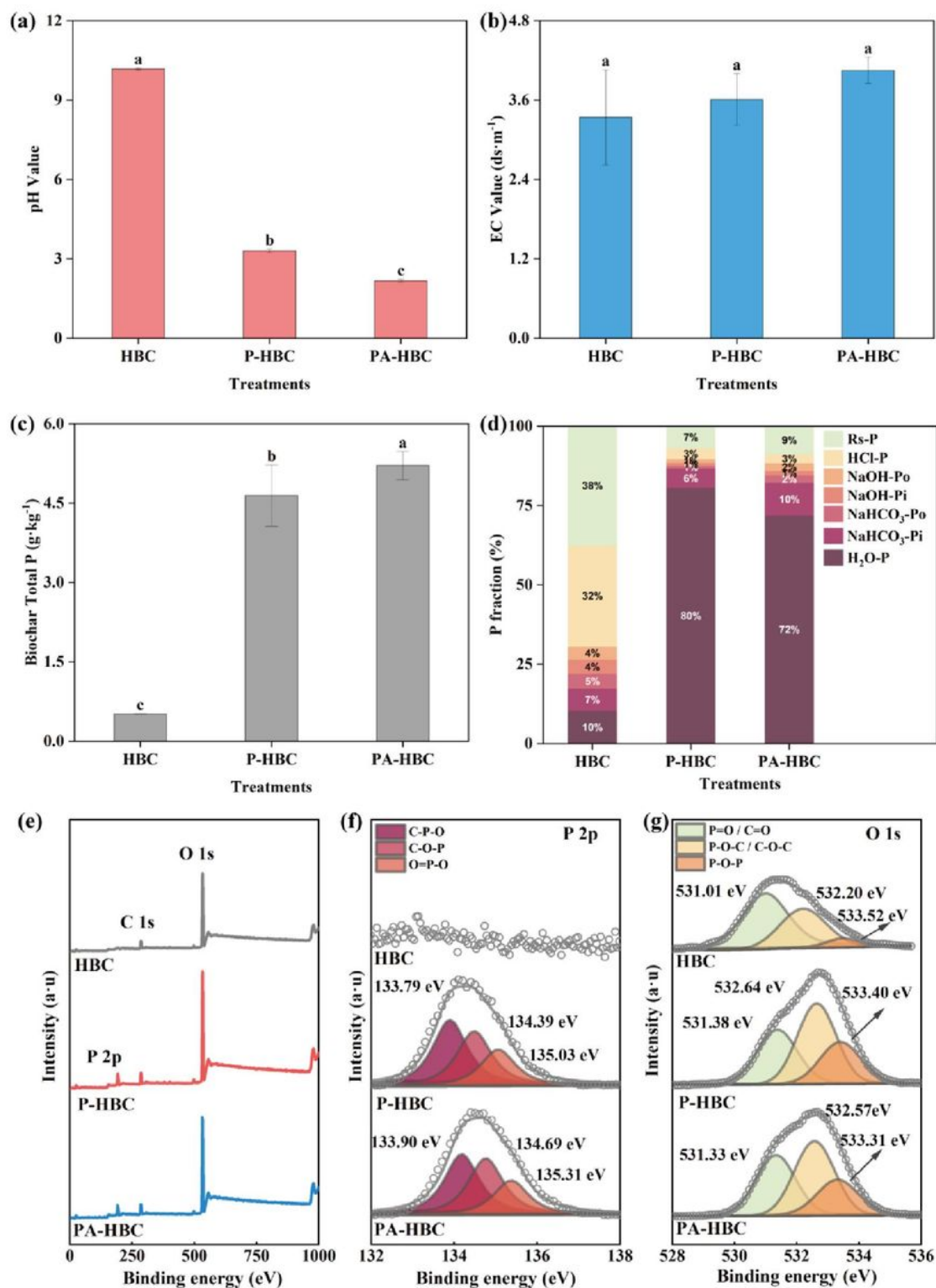
**Figure 2**

Scanning electron microscopy energy dispersive spectroscopy (SEM-EDS) imaging of the halophyte biochar (HBC),  $\text{H}_3\text{PO}_4$  modified biochar (P-HBC), and  $\text{H}_4\text{P}_2\text{O}_7$  modified biochar (PA-HBC).



**Figure 3**

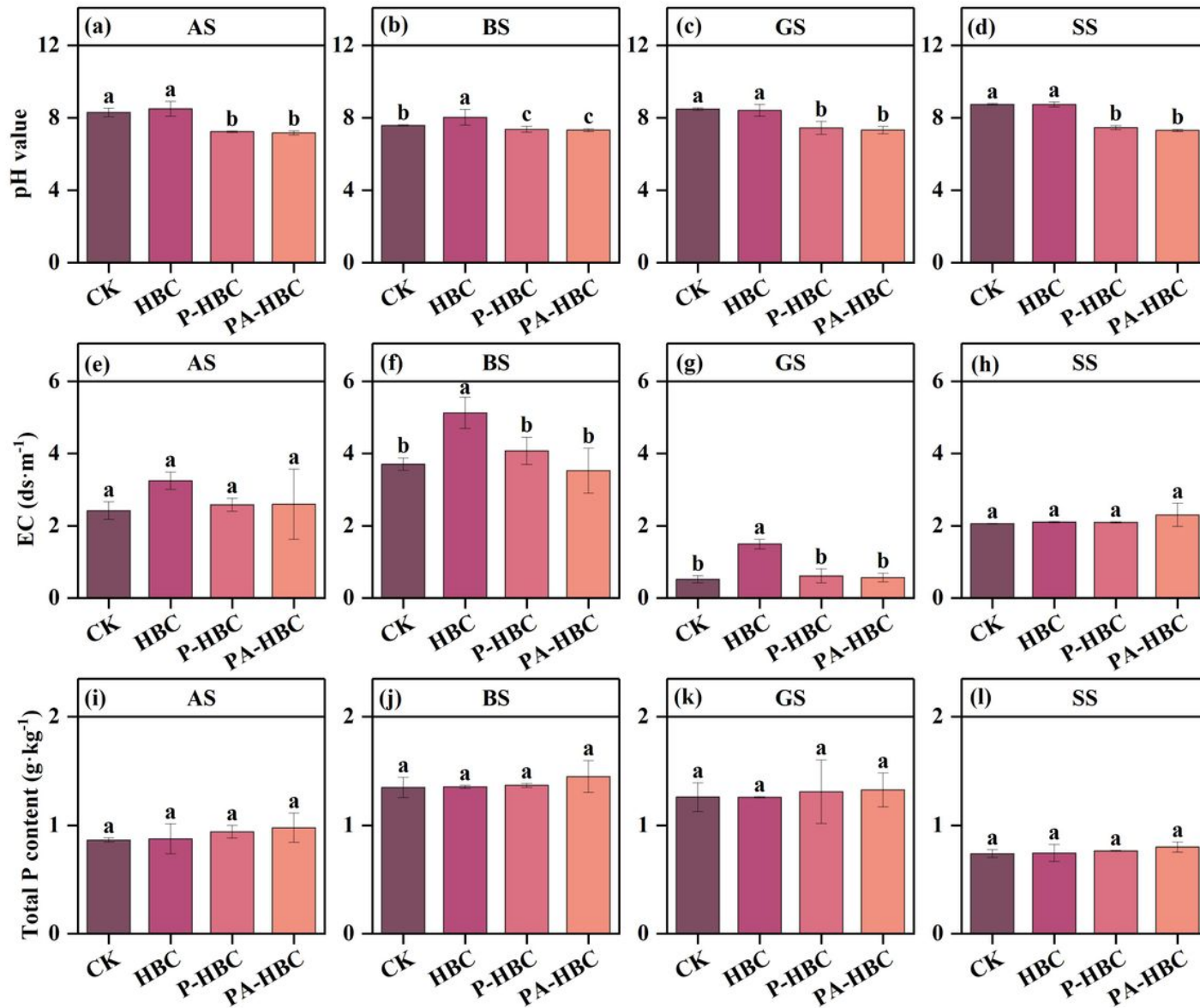
The Fourier transform infrared spectra (FT-IR) of the halophyte biochar (HBC),  $\text{H}_3\text{PO}_4$  modified biochar (P-HBC), and  $\text{H}_4\text{P}_2\text{O}_7$  modified biochar (PA-HBC).



**Figure 4**

Influence of  $\text{H}_3\text{PO}_4$  and  $\text{H}_4\text{P}_2\text{O}_7$  modified on pH (a), electrical conductivity (EC) (b), total P (c), and relative proportion of each P fractions in the biochars (d); X-ray photoelectron spectroscopy (XPS) spectrum of the halophyte biochar (HBC),  $\text{H}_3\text{PO}_4$  modified biochar (P-HBC), and  $\text{H}_4\text{P}_2\text{O}_7$  modified biochar (PA-HBC) (e); high-resolution XPS spectrum of P2p (f); and high-resolution XPS spectrum of O1s (g). Error bars are

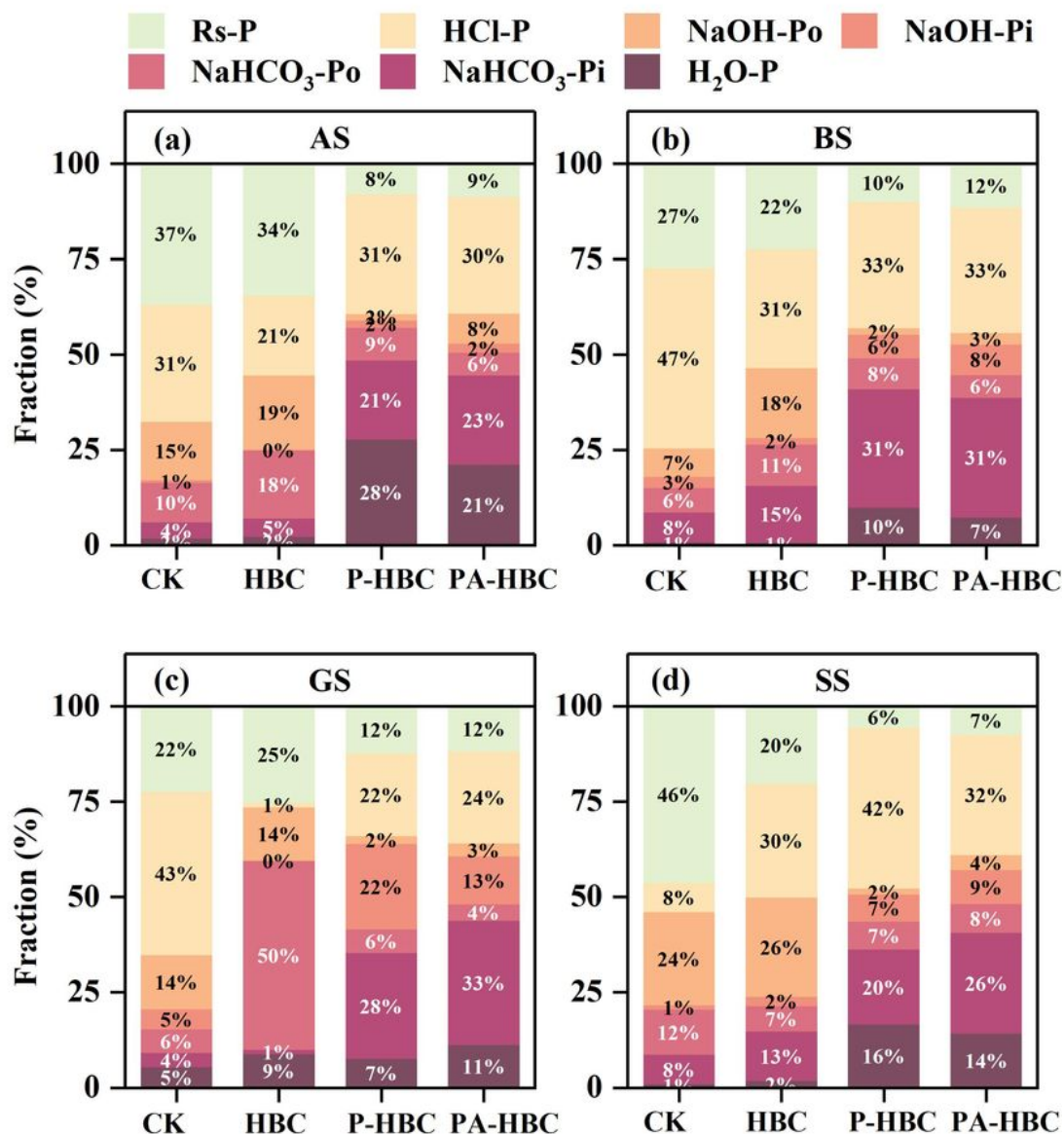
standard deviation of the means ( $n = 4$ ). Different letters above the bars indicate significant ( $p < 0.05$ ) difference between treatments.



**Figure 5**

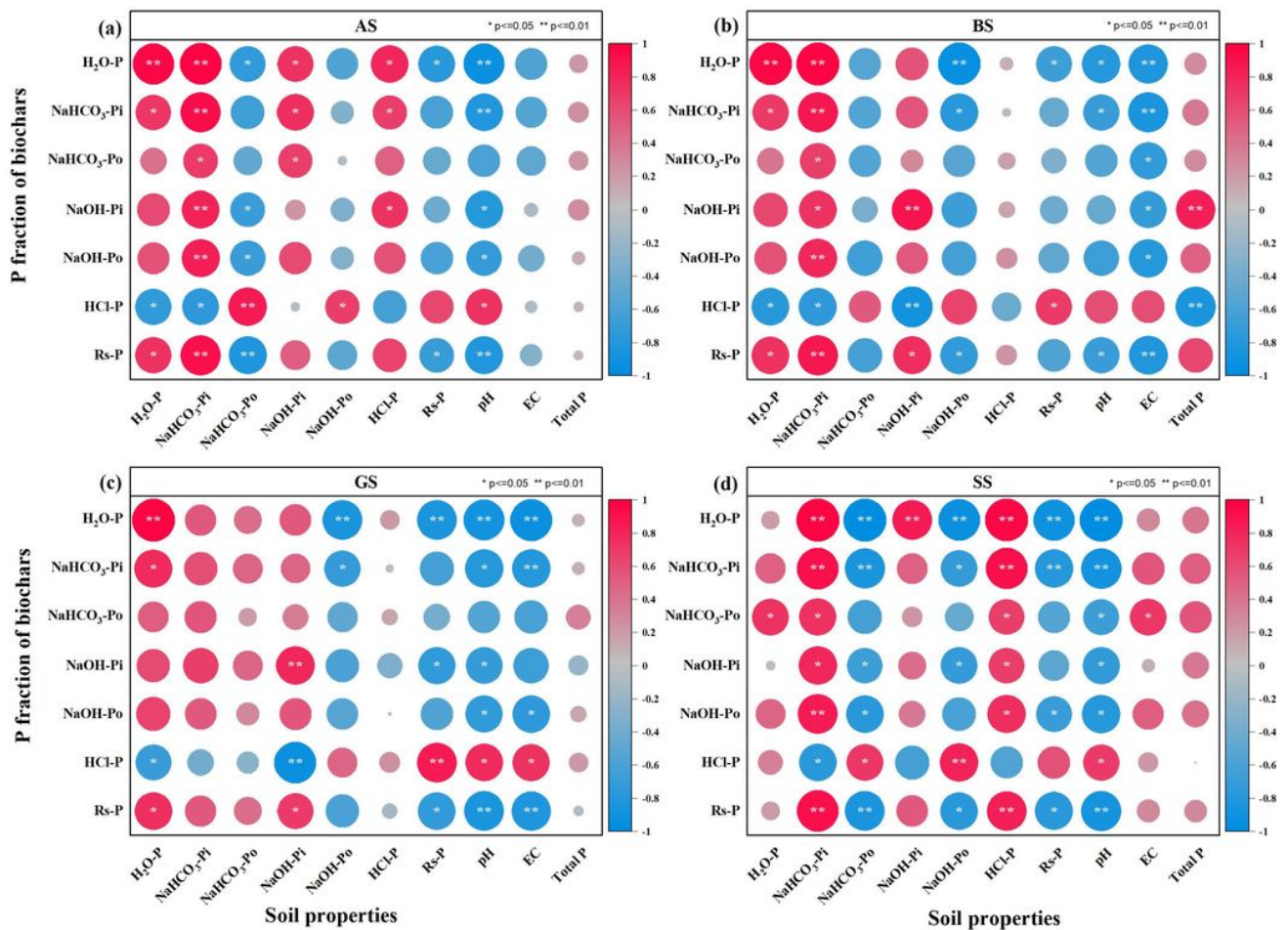
Influence of halophyte biochar (HBC),  $\text{H}_3\text{PO}_4$  modified biochar (P-HBC), and  $\text{H}_4\text{P}_2\text{O}_7$  modified biochar (PA-HBC) on pH (a, b, c and d), electrical conductivity (EC) (e, f, g and h) and total P (i, j, k and l) in the soils. Control: untreated soil (CK); AS: aeolian sandy soils; BS: brown desert soils; GS: grey desert soils; SS: saline soils. Error bars are standard deviation of the means ( $n = 4$ ). Different letters above the bars indicate significant ( $p < 0.05$ ) difference between treatments.





**Figure 6**

Influence of halophyte biochar (HBC), H<sub>3</sub>PO<sub>4</sub> modified biochar (P-HBC), and H<sub>4</sub>P<sub>2</sub>O<sub>7</sub> modified biochar (PA-HBC) on relative proportion of each P fractions in the AS (a), BS (b), GS (c) and SS (d). Control: untreated soil (CK); AS: aeolian sandy soils; BS: brown desert soils; GS: grey desert soils; SS: saline soils.



**Figure 7**

Pearson correlation matrix featuring relationships between soil properties and biochar P fractions. AS: aeolian sandy soils (a); BS: brown desert soils (b); GS: grey desert soils (c); SS: saline soils (d). Correlation significance was set at \*  $p < 0.05$ , \*\*  $p < 0.01$ .

## Supplementary Files

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