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Industrial and agricultural waste amendments interact with microorganism activities to enhance P availability in rice-paddy soils

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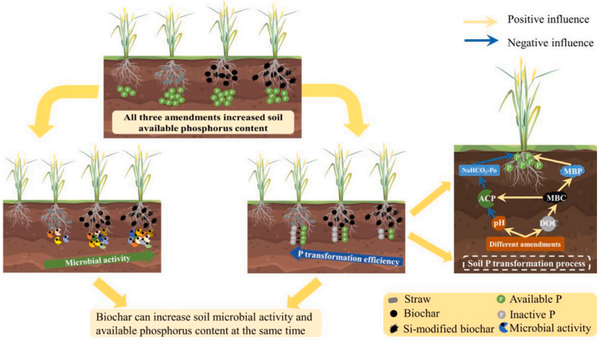
HIGHLIGHTS

- Straw, biochar and Si-modified biochar applications promoted soil P transformation.
- All three amendments promoted soil P availability by altering soil pH and DOC.
- Biochar was the amendment that most improved the soil P transformation efficiency.
- Biochar can simultaneously improve soil microbial activity and available P.

GRAPHICAL ABSTRACT



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ABSTRACT

Adding industrial and agricultural wastes to farmland can increase soil available phosphorus (P) pool and boost crop production, but the process affecting soil P transformation and bioavailability is still poorly understood. We studied the effects of straw (ST), biochar (BC) and Si-modified biochar (Si-BC) amendments on the available-P content and its fraction transformation in rice-paddy soils. Our results showed that these three soil amendments significantly increased the concentrations of both microbial biomass carbon (MBC) and microbial biomass-P (MBP) during the first rice season; by contrast, the effects of ST and BC application were relatively poor on acid-phosphatase (ACP) activity, which was increased by 24 % under ST and 14 % under BC. Soil total P concentrations did not differ significantly, although the concentration and percentage of each P-fraction were altered significantly among treatments. Although all three applications increase soil available-P concentration by

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promoting the transformation of organic-P (Po) components to inorganic-P (Pi), there are differences in the transformation efficiency of the soil P fraction between these amendments. Redundancy analysis results also showed significant clustering of soil P-fraction transformations after ST and BC treatments. Structural equation model analysis further indicated that all amendments regulated microbial processes by changing soil pH and dissolved organic carbon (DOC), thereby promoting soil P transformation and improving P efficiency. Sodium bicarbonate-extractable Po ($NaHCO_3$-Po) contributed most to soil available-P under the different amendments. Compared to ST and Si-BC, BC application improved more soil microbial status and the transformation of soil unavailable-P into available-P, therefore the application of BC in rice fields is the most beneficial method to promote phosphorus use and production sustainability in rice. These findings helped to understand the effects of using industrial and agricultural waste (e.g. straw, biochar and Si-modified biochar) on soil P-fractions and so provided a reference for sustainable resource use and green production in rice-paddy ecosystems.

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1. Introduction

Phosphorus (P) is an essential nutrient for life and directly affects plant growth and ecosystem function (Vitousek et al., 2010). Indeed, the use of chemical phosphate fertilisers has increased significantly in recent decades and today ensures that agricultural output meets the demand for food from the growing global populations (Tian et al., 2021). Between 1961 and 2019, global consumption of phosphate fertilisers (P_2O_5) is estimated to have increased by 34.5 million tonnes (Mt) (IFASTAT, 2021). Yet, P fertiliser use efficiency (PFUE) globally declined from 68 % to 18–20 % in 2004–2014 and grain and above-ground PFUE reached only 9.1 % and 12.4 %, respectively, in that period (Zhang et al., 2019; Yuan et al., 2018; Umar et al., 2020; Yu et al., 2021). This decline is attributed to the large amounts of P in fertilisers not taken up by vegetation and soils that accumulate in not directly plant available forms due to soil transformation (Peñuelas et al., 2020), which thus can increase the risk of soil P loss to water bodies (Li et al., 2016).

Soil P exists in the forms of organic P (Po) and inorganic P (Pi). The sequential extraction method proposed by Hedley et al. (1982) has been widely used in the study of soil P fractions. According to the availability of P to plants, soil P can be divided into active P fractions (Resin-P, $NaHCO_3$-Pi, $NaHCO_3$-Po), moderately active P fractions (NaOH-Pi, NaOH-Po), and inactive P fractions (HCl-Pi, HCl-Po, Residual-P). Resin-P – that is, plant available P – is the most easily absorbed and used form in plant uptake (Hedley et al., 1982; Zhang et al., 2021). The transformation of soil P fractions and the release of available P from less active P fractions are affected by abiotic and biotic factors and, for example, under anoxic conditions moderately active P fractions binding to iron-aluminium oxides can be reduced and dissolved to become plant available P (Cui et al., 2019). Inactive P fractions can release available P through microbial mineralisation or by altering the charge transfer of soil ions (Mengmeng et al., 2021). Soil microorganisms compete with plants for P acquisition. After microbial death, the captured P is returned to the soil as a source of active P that can be used by plants (Turner and Blackwell, 2013). In addition, phosphatases secreted by microorganisms and plant roots can accelerate the rate of soil P mineralisation as the organic P is transformed into inorganic phosphate, thereby promoting the production of soil available P (Pu et al., 2023).

Waste amendments originating from industry and agriculture such as straw, biochar and Si-modified biochar – all rich in P and other elements (Si, Fe, N and C) – can improve soil nutrient levels and crop productivity in a relatively short period of time (Wang et al., 2015; Lin et al., 2022; Yang et al., 2022). For example, the total P contained in crop straw can reduce phosphate fertiliser use by 24 % (Li et al., 2018). Moreover, straw amendment may increase not only the transformation of inorganic P to active P (Li et al., 2019a, 2019b) but also conserve soil P by reducing runoff or losses via leaching (Wang et al., 2019; Soltangheisi et al., 2018). Biochar is a highly aromatic, refractory, solid carbon-rich substance produced by pyrolysis under anoxic conditions (Zhao et al., 2021). The application of biochar amendments to rice soils promotes rice growth, increases grain yield, and improves the use of phosphate fertiliser and soil quality (Zhang et al., 2020; Korai et al., 2021). P carried by biochar is one of the best ways of increasing soil available P content (Glaser and Lehr, 2019). Limwikran et al. (2018) found that when biochar with a P concentration of 1.3 % was applied to cropland at 10 t ha^{-1}, the amount of P applied was equivalent to 200 kg ha^{-1} of $Ca_3(PO_4)_2$, which is much higher than the normal application rate of chemical P fertiliser. Furthermore, biochar changes the state of P in the soil and its migration and transformation by chemical and biological methods (Yang et al., 2021; Zhang et al., 2020). Biochar can affect soil available P by interacting with organic and inorganic soil components and altering the sorption and desorption characteristics of soil P (Xu et al., 2014). At the same time, biochar increases soil P availability by activating phosphatase activity and accelerating the hydrolysis of catalysed organically bound P (Dai et al., 2020; Kageyama et al., 2011). Although the effects of straw and biochar on soil P effectiveness have been extensively studied, few studies have ever compared the effects of straw and its biochar counterpart on P effectiveness.

With the increase in steel production, the accumulation of large amounts of by-product (slag) causes significant environmental stress (Das et al., 2020). However, in recent years numerous studies have shown that slag provides dissolved Si (DSi) and also improves soil physical, chemical and biological conditions that can increase crop yields (Wang et al., 2015; Wang et al., 2017; Wang et al., 2018a; Das et al., 2020). As well, DSi released from Si-rich substances can replace Fe/Al-associated P and make P available for plants (Etesami et al., 2021; Alam et al., 2022). However, a large amount of Ca, Fe and Al oxides in Si-rich slag may immobilize P and have a negative impact on soil P availability via P transformation from labile to more occluded fractions (Brady and Weil, 2008; Iwama et al., 2020). Interestingly, this adverse effect of Ca, Fe and Al oxides in Si-rich slag on available P can be reduced if Si-rich slag is blended with biochar to form a Si-modified biochar, probably because the biochar carbon interacts with these metallic oxides through adsorption or co-precipitation (Wang et al., 2018a; Han et al., 2020; Bi et al., 2021; Chen et al., 2021). Many of the above-mentioned studies have shown how straw, biochar and Si-modified biochar application significantly alter soil available P and P transformation, and most agree that these amendments affect soil P status via chemical reactions. Nevertheless, it is still unclear how these amendments affect soil P by regulating soil microbial activity. Therefore, a comprehensive understanding of the effects of these amendments on soil P is essential for more rational use of waste and for better scientific guidance in farmland fertiliser management.

Annually, around 750 million tons of rice, grown in >100 countries to feed >50 % of the world's population, are harvested worldwide (FAO, 2020). China is the world's largest rice producer and accounts for about 25 % of the world's rice production (FAO, 2020), and about 90 % of its rice fields are found in the subtropical regions of Fujian, Jiangxi and Hunan provinces (Wang et al., 2018b). The soils of the paddy fields in these regions are mostly acidic and highly weathered and a large amount of soil P is fixed by Fe and Al oxides. Rather less P can be directly absorbed and used by crops, thereby resulting in soil P deficiency (Yuan et al., 2022). We carried out field trials in Fujian province, a typical subtropical rice growing region, to (i) compare the extent to which the application of industrial and agricultural waste such as straw, biochar and Si-modified biochar affects available P and P transformation in distinct P fractions in paddy soils, and (ii) determine which amendment application is most beneficial for sustainable rice production. We further assessed the intrinsic regulatory factors of available P and P transformation in paddy-field soils under the application of these amendments.

2. Materials and methods

2.1. Study site

The study site is located in Wufeng Comprehensive Experimental Base of the Fujian Rice Research Institute, Fuzhou City, Fujian Province (26.1° N, 119.3° E) (Yin et al., 2021). This region enjoys a subtropical marine monsoon climate, with annual average temperature of 19.6 °C, precipitation of 1392.5 mm, evaporation of 1413.7 mm and relative humidity of 77.6 %. The soil in the study site consists of 28 % sand, 60 % silt and 12 % clay (Wang et al., 2016).

Rice was transplanted mechanically on 18 April 2018 and harvested on 6 July 2018. Shallow water irrigation was carried out during the tillering stage, followed by dry-wet alternation to regulate soil temperature and increase root respiration. The main fertiliser types applied to the paddy fields were compound fertiliser (N: P_2O_5: K_2O = 16 %:16 %:16 %) and urea (46 % N). Base fertiliser (N, P_2O_5 and K_2O applied at 42, 40 and 40 kg ha^{-1}, respectively), tillering fertiliser (N, P_2O_5 and K_2O applied at 35, 20 and 20 kg ha^{-1}, respectively) and panicle fertiliser (N, P_2O_5 and K_2O applied at 18, 10 and 10 kg ha^{-1}, respectively) were applied one day before, and one week and eight weeks after transplanting, respectively (Yin et al., 2021).

2.2. Experimental designs

A randomized group design was used to create four treatments: control (CK), straw (ST), biochar (BC) and Si-modified biochar (Si-BC) treatments, with three replications for each treatment to give a total of 12 plots. The surface area of each plot was 10 m^2. In order to prevent the exchange of water and nutrients, plots were separated by PVC waterproof boards (0.5-cm thick and 30-cm high). The minimum distance between plots was about 1 m (Wang et al., 2018a). The control group was a blank treatment, straw (4 t ha^{-1}), biochar (4 t ha^{-1}) and Si-modified biochar (4 t ha^{-1}) were applied according to the principle of equal substance weight, and the application amount of 4 t ha^{-1} in each treatment was formulated according to the actual amount of biofertilizer applied by local farmers and the previous experimental results in this study area (Hei et al., 2023; Yin et al., 2021; Yang et al., 2022). The raw material of straw was corn straw and the raw material of biochar was corncob with a particle size of 3–5 cm. Both were from Liao Ning Golden Future Agriculture Technology Co., Ltd., Liaoning China. Biochar was prepared by anoxic retorting carbonization technology, and was slowly pyrolyzed at a heating rate of 3–5 °C min^{-1}. The residence time was 2–3 h when the temperature rose up to 500 °C. After the pyrolysis was completed, the biochar was collected when the furnace temperature was naturally cooled to below 50 °C, and the biochar particle size was 0.8–1.0 mm (Liu et al., 2023a, 2023b; Malghani et al., 2013). Si-modified biochar was prepared by uniformly mixing the biochar obtained using the above method and Si-rich slag (TISCO & HARSCO Technology Co., Ltd., Taiyuan China) at a ratio of 1:1. The preparation method was as follows: (i) The Si-rich slag was crushed into particles so that the particle size was <2 mm. (ii) The prepared biochar and slag particles were put into a container, some suitable adhesives were added, and the mixture was thoroughly mixed by stirring. (iii) The mixture was then compacted and granulated by a granulator, with the final particle size of 1–4 mm through edging-drying-screening. Considering the long and slow effect of biochar, it is also necessary to make the application more evenly mixed with the soil to achieve long-term soil health effects (Da Silva Carneiro et al., 2021). Before rice transplanting, a soil depth of 15 cm was plowed with a plow board, and straw, biochar and Si-modified biochar were mixed with the plowed soil thoroughly, respectively. The mixture of application and soil was then levelled (Wang et al., 2015). The main nutrient elements of each application are shown in Table 1.

2.3. Soil sampling and analysis

When the rice was mature, we stratified the soil according to the depth of the tillage layer and the plowed subsoil, and sampled the topsoil (0–15 cm) and subsoil (15–30 cm) of the paddy field with a soil extractor. During transport, samples were stored in a portable incubator with ice. After removing the gravel and roots, the soils were gently ground and passed through a 2-mm soil sieve. The pre-treated soil samples were divided into two parts: one part was stored at 4 °C to determine the phosphatase activity, the microbial biomass carbon and P, while the other was dried under natural conditions to determine its soil basic physicochemical properties and P fractions.

Soil temperature and electrical conductivity (EC) were measured using a portable instrument (2265FS, USA) and soil pH using a portable pH meter (Starter 300, USA). Total carbon (TC) and total nitrogen (TN) concentrations in the two soil layers were determined using an elemental analyser (Elementar Vario Max CN, Germany), while soil acid phosphatase (ACP) and alkaline phosphatase (ALP) activity were determined with the *p*-nitrophenyl phosphate method (Acosta-Martínez and Tabatabai, 2000). Soil DOC was extracted with deionized water (Dong et al., 2023). Specifically, fresh soil (5 g) was suspended in deionized water (w:v = 1:10), shaken for 30 min (250 rpm), and then centrifuged for 20 min (4000 rpm). The supernatants were then filtered through a 0.45-μm filter and determined using a total organic carbon analyser (TOC-V_{CPH} Shimadzu Scientific Instruments, Japan). Soil microbial biomass carbon (MBC) was measured by fumigation-K_2SO_4 extraction (Vance et al., 1987), while soil microbial biomass P (MBP) was calculated by chloroform fumigation-$NaHCO_3$ extraction (Brookes et al., 1982) using a continuous flow analyser (Skalar Analysis San ++, Netherlands).

According to the Hedley et al. (1982) continuous leaching method modified by Tiessen and Moir (1993), soil P can be separated into Resin-P, $NaHCO_3$-Pi, $NaHCO_3$-Po, NaOH-Pi, NaOH-Po, HCl-Pi, HCl-Po and Residual-P. Depending on the uptake and use of different forms of P by plants, soil P can be divided into the following categories (Fan et al., 2019): Resin-P represents available P, an inorganic form of P that can be directly absorbed and used by plants; $NaHCO_3$-Pi/Po represents active P, which is readily converted into available P and is a direct source of available P; NaOH-Pi/Po is a moderately active P, a form of P that is closely bound to Fe and Al oxides in the soil; and HCl-Pi/Po and Residual-P represent inactive P, a form of P that is fixed in the soil for a long time and is difficult for plants to use. In short, the dry soil was sequentially extracted at a 1:60 solid-to-liquid ratio (w-to-v) with deionized water, 0.5 mol/L $NaHCO_3$, 0.1 mol/L NaOH and 1 mol/L HCl, the residual sample being digested with H_2SO_4–H_2O_2. After extraction lasting 16 h at 150 rpm on a shaker, suspensions were then spun for 15 min at 10,000 ×*g* and filtered using a 0.45-μm filter membrane for P determination. The $NaHCO_3$, NaOH and HCl soil extracts were separated into two proportions, of which one was digested with H_2SO_4–H_2O_2 for total P (Pi + Po) and the other analysed for inorganic P (Pi). The total and inorganic P concentrations in the extracts were determined using a continuous flow analyser (Skalar Analysis San ++, Netherlands). $NaHCO_3$-Po, NaOH-Po and HCl-Po were measured by calculating the P difference between the digested and undigested relevant extracts. Residual P was calculated as the difference between the total P content of the soil and the total P content of each of the above forms.

2.4. Data processing and analysis

SPSS 22.0 statistical software was used to test the normality and chi-square of the data, if the test was not passed, before proceeding any

Table 1
Main nutrient elements of the amendments.

Treatment	C	N	P	Si	Ca	Fe	K	Mg	S
	g kg^{-1}								
Straw	359.6	20.1	0.31	40.2	6.59	3.82	10.07	3.90	1.90
Biochar	422.5	10.5	1.56	105.8	19.09	4.82	18.01	8.52	1.68
Si-modified biochar	386.1	17.8	3.37	152.4	95.11	8.18	15.84	16.92	1.87

further all the original data were log-transformed until the conditions were met. One-way ANOVA analysis was used to compare the inter-treatment differences in rice soil physicochemical, TC, TN and TP concentrations, and their stoichiometric characteristics, as well as the soil P fraction content, phosphatase activity, MBC and MBP under different treatments. Significant differences were considered at $p < 0.05$. Pearson correlation analysis and redundancy analysis were performed using the Correlation Plot plug-in in *Origin2021b* and *Canoco5* to investigate the effects of the different treatments on soil P content, soil biological factors and non-biological factors. The method proposed by Hou et al. (2016) was used to construct a structural equation model (SEM) using *Amos* to investigate further how different treatments affected soil available P concentrations and P transformation between distinct fractions.

3. Results

3.1. Effects of different waste amendments on the physicochemical properties and nutrients of paddy-field soil

Compared to the control, straw application significantly increased soil EC and water content but lowered its pH; biochar application significantly increased soil temperature ($p < 0.05$); and Si-modified biochar application significantly increased soil pH but decreased soil temperature, EC and water content (Table 2).

None of the waste amendments had a significant effect on topsoil TC, TN or TP concentrations or on their metrological characteristics, although DOC increased by 130–140 % under BC and Si-BC ($p < 0.05$). In the subsoil, straw decreased TP by 30 % but increased DOC by 90 %; biochar increased C/P, N/P and DOC by 94 % (20.68 to 10.66), 91 % (1.91 to 0.99) and 64 %, respectively, but decreased TP by 50 %; Si-modified biochar increased DOC concentrations by 110 % (Fig. 1).

3.2. Effects of different waste amendments on microbial factors in paddy-field soil

Soil microbial factors varied significantly between soil layers, with the topsoil having significantly higher values than the subsoil. In the topsoil, the three amendments increased the MBC content by 26 %, 63 % and 60 % and MBP by 48 %, 53 % and 47 %, respectively. ACP increased by 24 % and 14 % under straw and Si-modified biochar, respectively. ALP increased by 22 % under straw and decreased by 9 % and 19 % under biochar and Si-modified biochar, respectively. The MBP, MBC/MBP, ACP and ALP of the subsoil did not change significantly under any of the treatments. The change in the trend in MBC was similar to that in the topsoil (Si-BC > BC > ST > CK, Fig. 2).

Table 2
Physical and chemical properties of topsoil (0–15 cm) under different waste amendments. Data represent means and standard errors (n = 4). Different lowercase letters indicate significant differences between treatments ($p < 0.05$).

Treatment	T (°C)	EC (mS cm^{-1})	pH	SWC (%)
Control	29.63 ± 0.09ab	0.45 ± 0.02ab	6.17 ± 0.05b	0.40 ± 0.01ab
Straw	29.60 ± 0.06ab	0.71 ± 0.10a	6.04 ± 0.04c	0.42 ± 0.01a
Biochar	29.80 ± 0.06a	0.66 ± 0.11ab	6.20 ± 0.04ab	0.37 ± 0.01bc
Si-modified biochar	29.53 ± 0.07b	0.42 ± 0.06b	6.31 ± 0.02a	0.36 ± 0.02c

Note: T, EC and SWC represent Soil temperature, soil electrical conductivity and soil water content.

3.3. Effects of different waste amendments on soil P fractions

Except for the subsoil amended with biochar, the proportion of moderately active soil P (44 %–50 % of total P) was the largest, followed by inactive P (21 %–40 %), active P (12 %–18 %) and available P (<6 %) in the different treatments and layers. All waste amendments significantly increased the ratio of active P to available P in the soil. In addition, the proportion of inactive P in the subsoil was significantly higher than in the topsoil (Fig. 4).

None of the waste amendments significantly affected the $NaHCO_3$-Pi, HCl-Pi, HCl-Po or Residual-P fractions in the topsoil. However, Resin-P significantly increased by 85 %, 91 % and 42 %, and inorganic P by 13 %, 15 % and 9 %, respectively, and $NaHCO_3$-Po significantly decreased by 28 %, 34 % and 25 %, in straw, biochar and Si-modified biochar, respectively with respect to control. ($p < 0.05$). In addition, biochar significantly increased NaOH-Pi and NaOH-Po. In the subsoil, Resin-P showed a completely opposite trend to the topsoil (CK > ST > BC > Si-BC). All three waste amendments significantly increased Residual-P. Straw and biochar significantly decreased NaOH-Pi, NaOH-Po, HCl-Pi, HCl-Po, inorganic P and organic P, while Si-modified biochar significantly increased $NaHCO_3$-Pi by 45 % and decreased HCl-Pi and HCl-Po by 13 % and 46 %, respectively (Fig. 3).

3.4. Factors driving soil available P and P fraction transformation under different waste amendments

Soil MBC was positively correlated ($p < 0.05$) with soil nutrient factors (TC, TN, TP and DOC concentrations), Resin-P, NaOH-Po and NaOH-Pi but negatively correlated with SWC and $NaHCO_3$-Po under the different waste amendments. MBP was positively correlated with soil TN, TP and MBC concentrations, Resin-P, HCl-Pi, inorganic P and organic P, while MBC/MBP was positively correlated with pH, TC, C/N and C/P but negatively correlated with ACP and ALP. ACP was positively correlated with EC, TP, ALP, resin-P and inorganic P but negatively correlated with pH, C/P, N/P, MBC/MBP and $NaHCO_3$-Po. ALP was positively correlated with EC, SWC and ACP but negatively correlated with pH, TC and MBC/MBP. Resin-P was positively correlated with TP, MBC, MBP and ACP but negatively correlated with N/P and $NaHCO_3$-Po (Fig. 5).

To further investigate the effects of the different applications on the transformation of soil available P and P fractions, RDA and structural equation modelling (SEM) analyses were performed to link P fractions to soil environmental factors. The RDA results showed (Fig. 6) that axis 1 explained 54 % of the variance while axis 2 explained 21 % of the variance. Except for the Si-modified biochar treatment, there were significant clusters in all the other treatments indicating that straw and biochar application could significantly alter soil P fractions and promote the transformation of P fractions. The highest percentages of P fraction (28 % and 15 %; $p < 0.05$) were explained by soil MBP and MBC concentrations, respectively, followed by pH, ACP and DOC (15 %, 7 % and

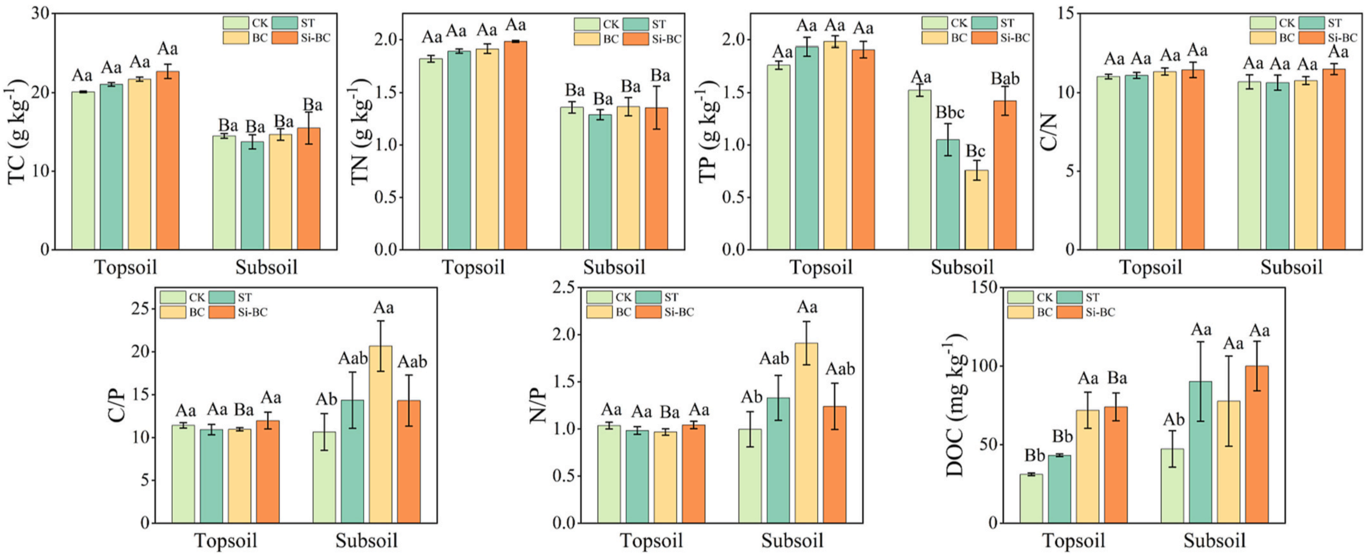

Fig. 1. Analysis of the effect of different waste amendments on soil nutrient content. Data represent means and standard errors ($n = 4$). Lowercase letters indicate significant differences between treatments in the same soil layer ($p < 0.05$); uppercase letters indicate that the same treatment was significantly different between the different soil layers ($p < 0.05$). CK = control, ST = Straw treatment, BC = biochar treatment, Si-BC = Si-modified biochar.

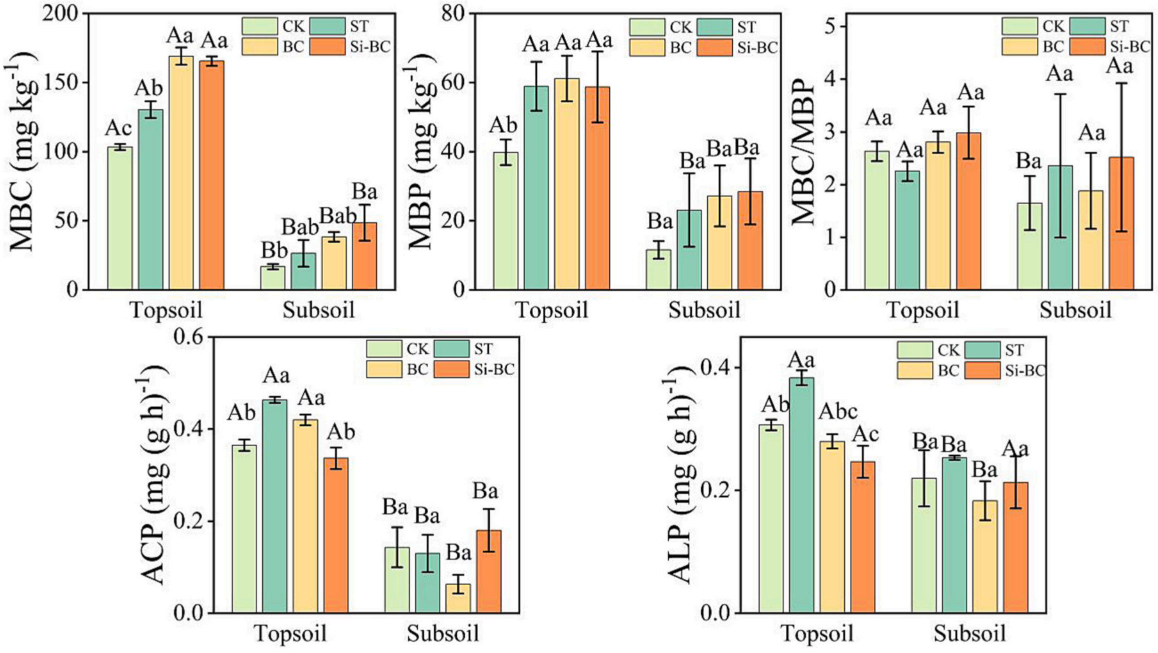

Fig. 2. Analysis of the effects of different waste amendments on soil microbial factors. Data represent means and standard errors (n = 4). Lowercase letters indicate significant differences between treatments in the same soil layer ($p < 0.05$); uppercase letters indicate that the same treatment was significantly different between the different soil layers ($p < 0.05$). CK = control, ST = Straw treatment, BC = biochar treatment, Si-BC = Si-modified biochar.

5 %; $p < 0.05$).

The structural equation model (SEM) analysis (Fig. 7) showed how all the amendments regulated soil microbial processes by changing soil pH and DOC (path coefficients = 0.588 and 0.833), thereby affecting soil available P content. In addition, only $NaHCO_3$-Po had a direct effect on available P (path coefficient = −0.586), which indicates that $NaHCO_3$-Po was the main contributor to soil available P.

4. Discussion

4.1. *Effects of different waste amendments on microbial factors in paddy-field soil*

Soil microorganisms are the main active driving force of soil nutrient and material transformation in soils. Changes in microbial biomass carbon and P content indicate changes in soil microbial population, quantity and activity, which is closely linked with soil available nutrients (Shourie and Singh, 2021). In this study, all amendments significantly increased soil MBC and MBP concentrations, albeit only modestly after the straw application. The porous structure of biochar and

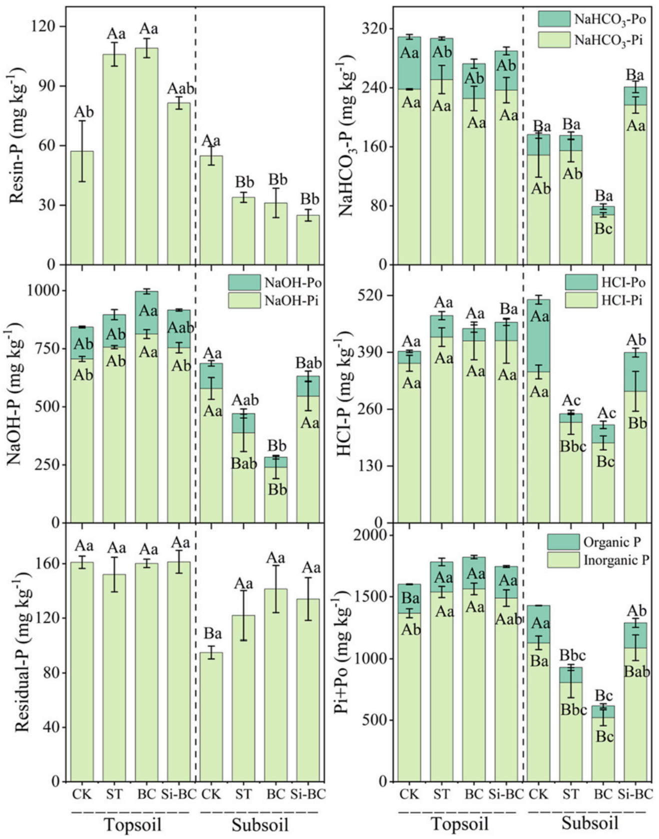

Fig. 3. Effects of different waste amendments on soil P fractions. Data represent means and standard errors (n = 4). Lowercase letters indicate significant differences between treatments in the same soil layer ($p < 0.05$); uppercase letters indicate that the same treatment was significantly different between the different soil layers ($p < 0.05$). CK = control, ST = Straw treatment, BC = biochar treatment, Si-BC = Si-modified biochar.

abundant oxygen-containing functional groups such as —COOH, —OH and C=O provide habitat for soil microbial growth (Bornø et al., 2018) resulting in more significant increases in soil MBC and MBP concentrations after biochar application. This indicates that biochar application stimulates greater microbial activity and more biological storage and use in soils, which in the long term will be highly beneficial for the sustainable development of paddy fields.

In the process of soil phosphorus transformation, microorganisms play a complex role. Previous studies have consistently demonstrated that phosphatase is a key metabolic product in the microbial-influenced soil phosphorus transformation process. Phosphatase promotes the hydrolysis of soil organophosphates into plant- and microorganism-accessible forms of phosphorus (Nannipieri et al., 2011; Nash et al., 2014). Additionally, phosphatase activity serves as an indicator of microbial status, including the presence of phosphate-solubilizing microorganisms that directly secrete phosphatases (Liu et al., 2023a, 2023b) and the influence of arbuscular mycorrhizal fungi on phosphatases and phosphate-solubilizing organic acids (Yu et al., 2022; Liu et al., 2021). It has been documented that phosphatase hydrolysis is a crucial mechanism employed by plants and microorganisms to obtain P under low P availability (Yadav and Tarafdar, 2001). When soils contain high levels of available phosphorus, plants primarily utilize this fraction of phosphorus, leading to reduced phosphatase synthesis and activity (Sinsabaugh and Follstad, 2012).

Comparatively, Si-modified biochar, with its higher phosphorus content, increases the concentration of available P in the soil, potentially alleviating P stress in rice and microorganisms. As a result, the application of Si-modified biochar was associated with relatively low soil phosphatase activity. Notably, in acidic soils, ACP exhibited a more pronounced correlation with soil P fractions than ALP, emphasizing the significance of ACP in these acidic conditions (Yu et al., 2022). ACP showed a significant negative correlation with soil pH ($p < 0.05$). Under straw application, ACP increased by 24 %, consistent with the lower soil pH observed under this treatment. Conversely, ACP decreased by 19 % following Si-modified biochar application, aligning with the higher soil pH observed under this treatment. These findings align with the established role of soil pH as a critical regulator of acid phosphatase activity (Liu et al., 2017). pH variations influence the conformation of the peptide chain and the microenvironment of amino acid residues in acid phosphatase (Herbien and Neal, 1990), creating an optimal environment at pH < 6. Higher pH values may reduce acid phosphatase activity. pH also impacts the adsorption behavior of acid phosphatase and humus or clay, thereby affecting the enzyme's dissociation state and subsequent changes in its activity (Yuan et al., 2022).

Furthermore, an intriguing observation emerged in this study: both

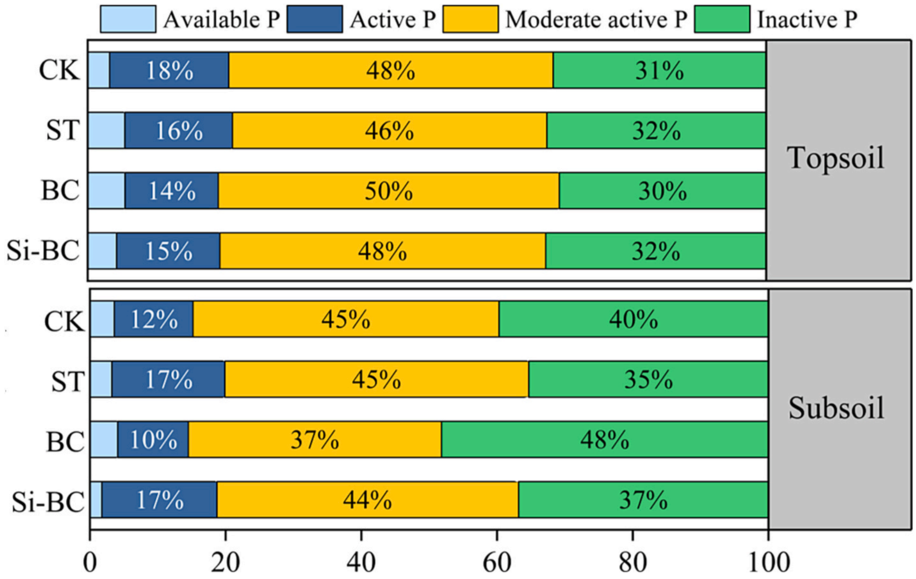

Fig. 4. Effects of different waste amendments on the proportion of soil P components. CK = control, ST = Straw treatment, BC = biochar treatment, Si-BC = Si-modified biochar.

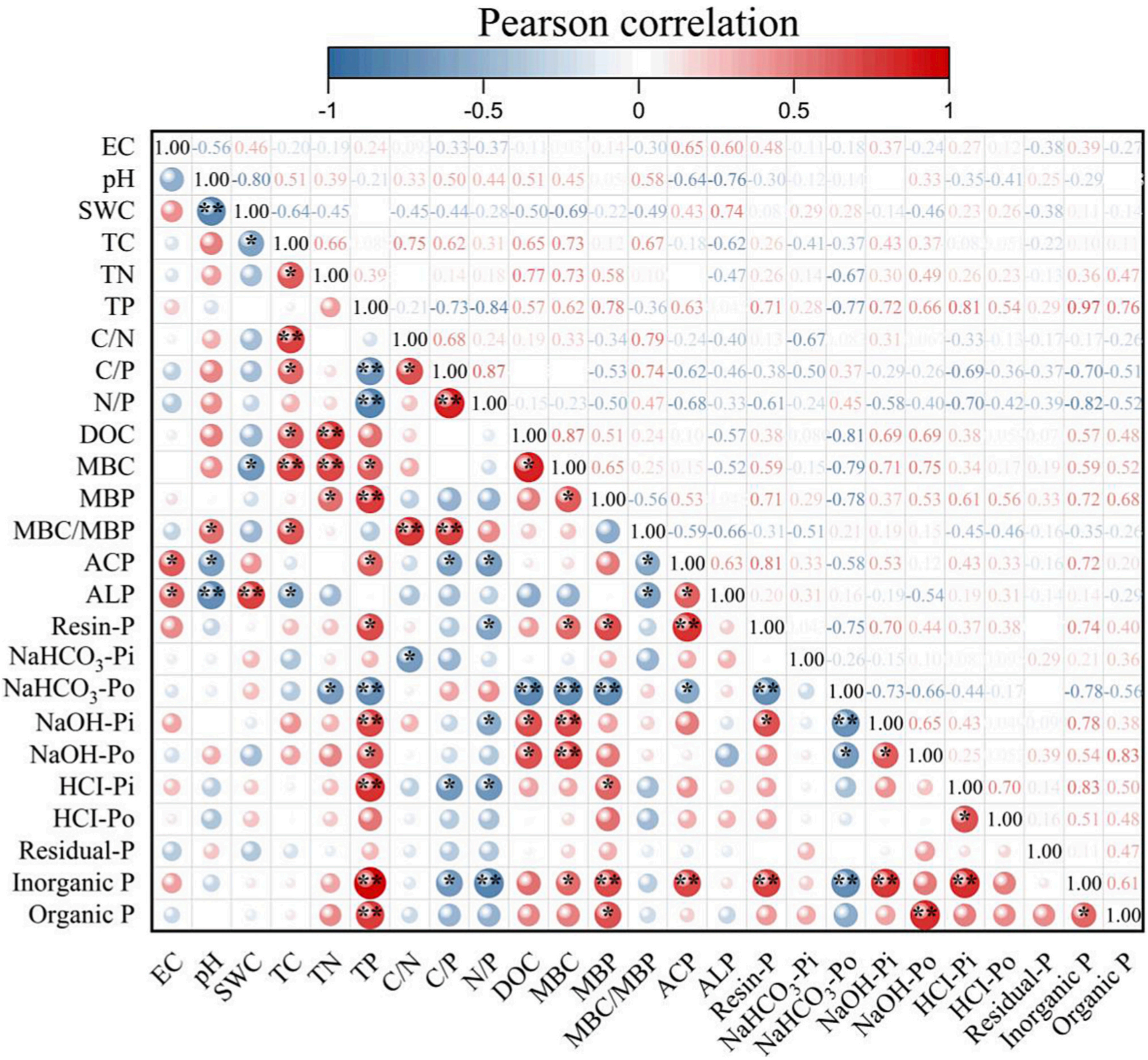

Fig. 5. Pearson correlation analysis between environmental factors and P fractions in the topsoil (0–15 cm). * significant, *$p < 0.05$, **$p < 0.01$.

ACP and ALP, secreted by phosphorus-solubilizing microorganisms, exhibited the highest levels following straw application. This suggests that straw application may promote the growth of phosphorus-solubilizing microorganisms. Concurrently, soil pH significantly decreased after straw application, indicating that straw application partly stimulates the growth of phosphorus-solubilizing microorganisms, leading to the secretion of organic and inorganic acids that reduce soil pH (Yadav et al., 2015; Liu et al., 2014).

4.2. *Effects of different waste amendment applications on available P and P fraction transformation in paddy-field soils*

The transformation of total P and P fractions in soil is crucial for a balanced supply of regional soil available P. In this study, we found that under the application of different waste amendments soil TP concentrations increased and were significantly positively correlated with Resin-P, NaOH-Po, NaOH-Pi and other P fractions ($p < 0.05$). The applied straw, biochar and Si-modified biochar contained 1.24, 6.24 and 13.48 kg P ha^{-1}, respectively, which indicates that the application of different waste amendments directly adds P to the soil and alleviates soil P limitation. This conclusion is similar to that of Glaser and Lehr (2019), who analysed the effects of biochar on agricultural soil available P concentrations throughout the world. More available P was directly imported into the soil by biochar with higher P concentrations.

Together with the direct input from exogenous sources, the internal transformation of soil P was another key source of available soil P (Yang et al., 2021). The application of different waste amendments significantly changed the concentrations of distinct soil P fractions and the proportion of each fraction in TP. The response of soil P to different amendments was related to the stability of the different P fractions. In this study, the concentrations and proportions of moderately active P (NaOH-Pi and NaOH-Po) strongly bound to soil Fe and Al oxides were the highest, followed by inactive P (HCl-Pi, HCl-P and Residual-P) mainly in Ca-P form. The active P fractions (NaHCO$_3$-Pi and NaHCO$_3$-Po) had the lowest concentrations and proportions and changed the most. Of them, NaHCO$_3$-Po decreased significantly and was significantly negatively correlated with available P ($p < 0.05$), strongly suggesting that the application of waste amendments to paddy-field soils may promote the transformation of NaHCO$_3$-Po into available P. Both Pearson's correlation and path analysis showed a highly significant

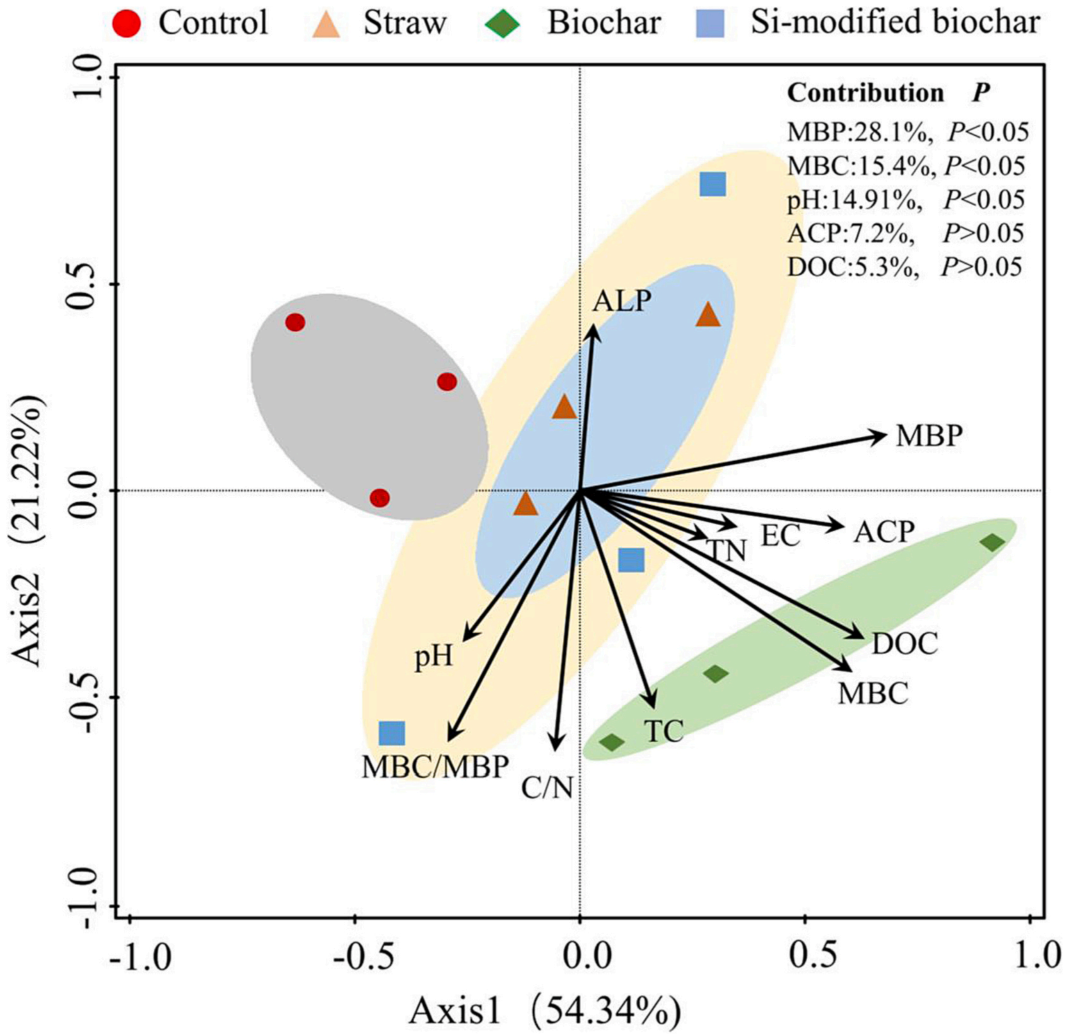

Fig. 6. RDA analysis of environmental factors and P fractions in the topsoil (0–15 cm). The angles between the response and explanatory variables represent their correlations, and the acute and obtuse angles represent positive and negative correlations, respectively. The amounts of variance explained for axes 1 and 2 are in brackets.

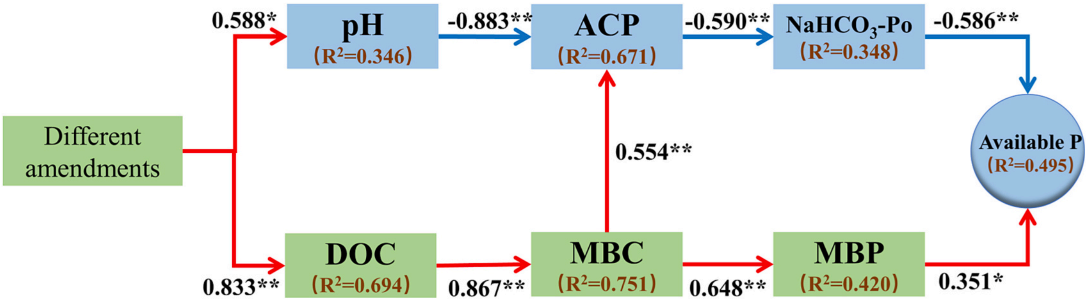

Fig. 7. Structural equation model (SEM) analysis of environmental factors on the transformation of available P in the topsoil (0–15 cm). The red arrow indicates a positive impact and the blue arrow a negative impact; the number below the arrow represents the degree of influence: the more the absolute value tends to 1, the greater its degree of influence; * significant, *$p < 0.05$, **$p < 0.01$; R^2 is the explanation of a factor.

correlation between $NaHCO_3$-Po and available P (Resin-P) fractions, suggesting that $NaHCO_3$-Po is a sensitive P source for soil P effectiveness and that other P fractions may be indirectly affecting available P through $NaHCO_3$-Po. In addition, we found that the effects of different applications on available P and P fractions differed between soil depths and were more pronounced in the topsoil than in the subsoil, which may be due to the role of abundant exogenous P inputs and root secretions that stimulate soil microorganism activity and the P mineralisation in the topsoil (Lu et al., 2023).

We observed no significant differences in the effects of the different waste amendments on soil TP, although there were significant differences in the P concentrations of the different soil forms and a significant positive correlation between total soil inorganic P and ACP. This indicates that, although different waste amendments do directly input available P into soil, this is not the dominant path and the effects of these amendments on soil available P depend mainly on promoting the

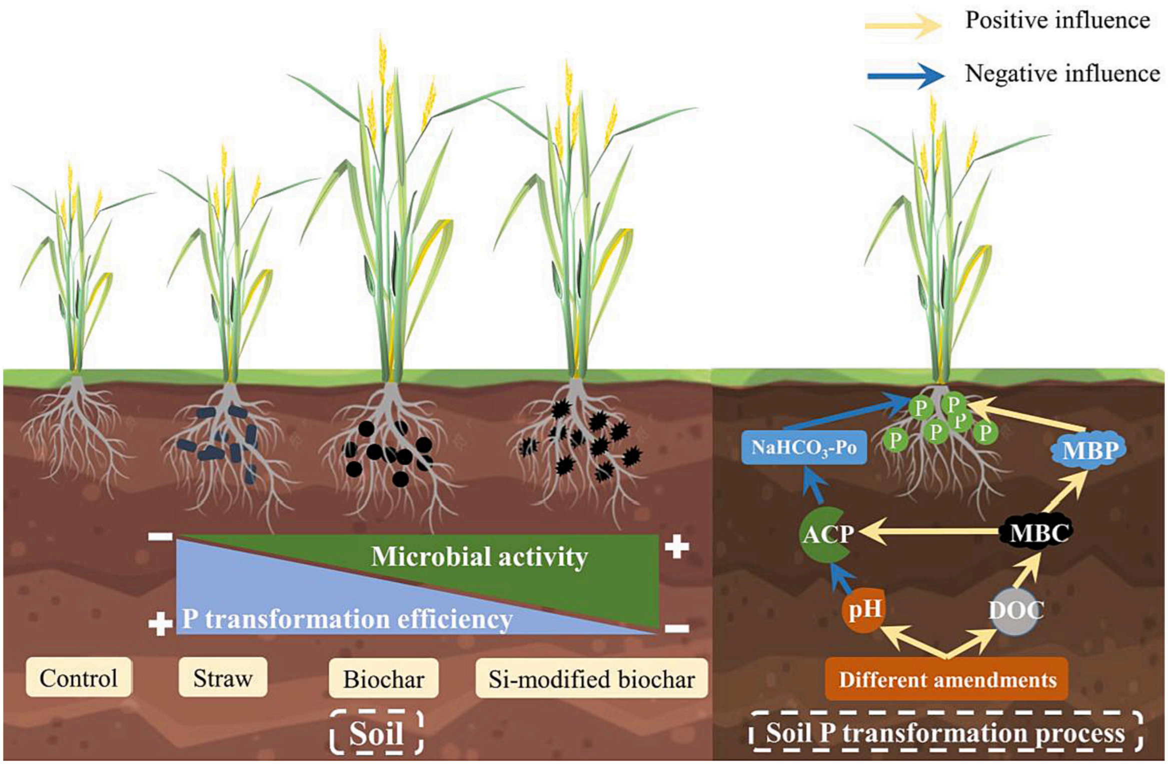

Fig. 8. Conceptual model of the transformation of available P and P fractions in paddy-field soil under the different waste amendment application.

transformation of organic to inorganic P. This is confirmed by the fact that the low P concentrations in straw do not allow for a significant direct input of available P into the soil. Biochar and Si-modified biochar retain external free P via the formation of outer and inner spherical complexes on their surfaces and the co-precipitation of P and biological ash (Yao et al., 2013). As a result, the release of P from the two types of biochar into the soil is a slow, long-term process, and so the increase in soil P is not significant in the short term. Although all three waste amendments promoted the internal transformation of soil P, there were significant differences in their efficiency. Of these, the magnitude of change in the content of each soil component after the application of Si-modified biochar was relatively small, while the RDA also showed that the effects of Si-modified biochar application on the internal transformation of soil P were much less than those of the straw and biochar applications. These results are consistent with the fact that Si-modified biochar contains significantly more cations (Ca^{2+}, Fe^{2+}, K^+, Na^+, Mg^{2+}, etc.) than the other amendments, which significantly increased the soil pH and inhibited acid phosphatase activity and subsequent organic P mineralisation (Colvan et al., 2001; Liu et al., 2017).

4.3. Modulation factors of available P and P fraction transformation in paddy-fields soil under different waste amendment applications

Hou et al. (2018) found that soil physical and chemical properties, soil nutrients and biological effects (plant roots, microbial secretions and their life activities) strongly affected soil P transformation and P availability. The results of the redundancy and SEM analyses show that under the application of different waste amendments, microbial factors (MBC, MBP and ACP) directly influenced soil available P and P transformation, while soil physicochemical and nutrient properties (mainly pH and DOC) indirectly affected soil available P and P transformation by regulating microbial factors. Application of biochar and Si-modified biochar significantly increased soil DOC concentration due to their high activity and solubility, provided nutrients and energy for soil microorganisms, and promoted microbial activity (Cui et al., 2022). With enhanced microbial activity, a large amount of P was assimilated by microorganisms, leading to an increase in soil MBP concentrations, which, as the most active fraction of soil organic P, can rapidly participate in nutrient cycling and become an important source of available plant P due to its rapid turnover rate (Chen et al., 2008; Bing et al., 2016; Anil et al., 2022).

Previous studies have shown that the increased soil pH after biochar application could affect the reduction of soil exchangeable acidity, promote the release of P from metal (hydro) oxides, and reduce the transformation of Fe/Al (hydr)oxide-P to inactive P, thereby increasing the soil available P concentration (Jiang et al., 2015). However, in this study, the pH mainly promoted the transformation of soil P components by regulating ACP and the statistical analyses suggest that these chemical processes did not exert any significant effects on soil available P concentrations. This may be because the soil in this study is neutral to acidic (6–7) and the fixation and transformation of P bounded by Fe/Al oxide is more significant at $pH < 5.5$ (Johan et al., 2021). Therefore, we found that soil pH affects soil available P through chemical and biological processes. P fertiliser management in rice fields needs to be considered on a soil-specific basis and, in particular, the soil pH must be taken into account.

4.4. Different waste amendments as sustainable approaches to phosphate management in paddy fields

Our research showed that different waste amendments used two pathways to increase soil available P concentrations in paddy-field soils and to alleviate the P limitation. The first pathway was the direct input of available P into the paddy field soil, while the second promoted the composition of soil P internal transformation and increased the content of available P in the soil. In each of the three different kinds of waste amendments studied the second pathway was mainly increasing soil available P concentrations. The effects of different waste amendments on soil P transformation were mediated by changes in soil physicochemical and nutrient properties such as soil pH, TC, TN, TP and

DOC, which in turn modulated microbial and ACP activity. Straw application increased soil available P concentrations by stimulating ACP, thereby lowering the soil pH, although less microbial activity compared to biochar application may be detrimental to the long-term sustainability of paddy-field soils. The application of Si-modified biochar significantly improved the microbiological status of the soil and increased the soil available P concentrations somewhat by promoting the transformation from other soil P fractions. However, its transformation from other P fractions was not as efficient as in the other two amendments. Overall, biochar application was more beneficial for P use and sustainable rice production than the straw and Si-modified biochar applications (Fig. 8).

5. Conclusion

This study improves knowledge of how different waste amendments affect soil available P concentrations and P transformation in the distinct soil P fractions in paddy fields. Our results showed that the application of straw, biochar and Si-modified biochar all increased available soil P levels through both the direct input and the promotion of internal transformations of soil P, the latter was the main pathway. The three waste amendments promoted internal transformation of soil P and increased P efficiency by altering abiotic factors (e.g. soil nutrient content, pH, EC and metal oxides) and biotic (e.g. phosphatase and soil microbial activity) factors. Microbial activity and ACP activity are the key factors driving the transformation of P forms in paddy soils. $NaHCO_3$-Po is a sensitive and important P source for available P in paddy-field soils. Of the three waste amendments, the biochar and Si-modified biochar applications were more conducive to the sustainable development of P use and rice production than the application of straw. More than the other two treatments, the application of biochar improved the soil microbial status and most promoted the transformation of soil P fractions. Thus, our results provide evidence that biochar application is more useful than straw and Si-modified biochar in improving the sustainable development of rice P use and production. In the management of rice fields for P fertilisation, the use of biochar is a good mechanism for activating the unavailable P in the soil, thereby reducing the use of chemical phosphate fertilisers.

List of abbreviations

ST	straw
BC	biochar
Si-BC	Si-modified biochar
T	soil temperature
EC	soil electrical conductivity
SWC	soil water content
TC	total carbon
TN	total nitrogen
TP	total phosphorus
C/N	total carbon: total nitrogen ratio
C/P	total carbon: total phosphorus ratio
N/P	total nitrogen: total phosphorus ratio
DOC	dissolved organic carbon
ACP	soil acid phosphatase
ALP	soil alkaline phosphatase
MBC	microbial biomass carbon
MBP	microbial biomass phosphorus
MBC/MBP	microbial biomass carbon: microbial biomass phosphorus ratio
RDA	Redundancy analysis
SEM	Structural equation model
Po	organic phosphorus
Pi	inorganic phosphorus
Resin-P	Resin-extractable phosphorus
$NaHCO_3$-Pi	Sodium bicarbonate-extractable inorganic phosphorus
$NaHCO_3$-Po	Sodium bicarbonate-extractable organic phosphorus
NaOH-Pi	Sodium hydroxide-extractable inorganic phosphorus
NaOH-Po	Sodium hydroxide-extractable organic phosphorus
HCl-Pi	Hydrochloric acid-extractable inorganic phosphorus
HCl-Po	Hydrochloric acid-extractable organic phosphorus
Residual-P	Residual phosphorus

CRediT authorship contribution statement

Conceptualization: Zhuang Huang, Weiqi Wang and Jordi Sardans. Methodology: Zhuang Huang, Weiqi Wang and Jordi Sardans: Software: Zhuang Huang, Chun Wang, Liuming Yang, Yunying Fang, Ziming Li: Data curation: Zhuang Huang, Jordi Sardans, Josep Peñuelas, Weiqi Wang, Qian Jin. Writing - Original draft preparation: Zhuang Huang and Weiqi Wang, Visualization: Zhuang Huang, Investigation.: Zhuang Huang, Josep Peñuelas, and Jordi Sardans, Supervision: Zhuang Huang, Liuming Yang, Yunying Fang, Ziming Li, Weiqi Wang, Validation: Zhuang Huang, Jordi Sardans, Chun Wang, Weiqi Wang, Liuming Yang, Josep Peñuelas, Xiaoqing Zhang, Qian Jin and Ziming Li: Writing - Reviewing and Editing: Zhuang Huang, Chun Wang, Weiqi Wang, Yunying Fang, Xiaoqing Zhang, Jordi Sardans, Qian Jin, Josep Peñuelas.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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