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ORIGINAL PAPER

Changes in Soil Phosphorus Fractions and their Relationships with Selected Soil Properties After 14 Years of Combined Fertilization and Cultivation Practices in a Sloping Cropland with Entisols

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Abstract
Understanding the soil phosphorus (P) pool fraction subjected to fertilization and cultivation practices was conducive to improving the effectiveness of P and revealing the changes in and storage of soil organic and inorganic P. However, the changes in soil P fractions caused by long-term fertilization and cultivation remain largely elusive. This study investigated the various soil P fractions and their relationships with selected soil properties in a representative purple soil sloping cropland experiencing long-term fertilization and cultivation. The experiments comprised five treatments: no fertilizer and downslope cultivation (CK); chemical fertilizers and downslope cultivation (T1); 1.5-fold chemical fertilizers and downslope cultivation (T2); manure plus chemical fertilizers and downslope cultivation (T3); and chemical fertilizers and contour cultivation (T4). The soil P fractions were determined at 0–10 and 10–20 cm soil depths using a modified Hedley sequential method. The concentration of soil H_2O-Pi and $NaHCO_3$-Pi in T1 significantly reduced by 49.5–55.0% and 68.0-85.2% than in other treatments (T2 and T3) at the 0–10 and 10–20 cm soil depths, respectively. The P fractions showed nonsignificant differences between T1 and T4 at the 0–10 cm soil depth, while the H_2O-Pi concentration was 253.9% greater in T4 than in T1 at the 10–20 cm depth. The random forest (RF) model indicated that SOC and TN were the key factors for predicting soil P fractions. Our results show that manure plus chemical fertilizer and contour cultivation can be the recommendable agricultural practices for increasing the labile P fractions (H_2O-Pi and $NaHCO_3$-P) in purple soil sloping croplands.

Keywords Long-term experiment · P fractions · Hedley fractionation · Soil properties · P availability · Purple soil

1 Introduction

Phosphorus (P) is an essential nutrient for plant growth and plays an indispensable role in natural ecosystems and agricultural production (Ahmed et al. 2019; Bai et al. 2013). The dynamics and availability of P element in soils commonly depend on the P fractions, which is usually affected by fertilization (Ahmed et al. 2019; de-Bashan et al. 2022). Over the past few decades, fertilization as a supplement to P stocks in fields has become the most important agricultural management practice, leading to considerable increases in inputs of P fertilizer in fields (Vaccari et al. 2019; Zhang et al. 2022). After the application of P fertilizers, most P element could not be directly used by plants due to adsorption, precipitation, and microbial fixation (Weihrauch and Opp 2018; Zhu et al. 2018), leading to the accumulation and low use effectiveness of P element in soils (Liao et al. 2020). Previous study had pointed out that organic fertilizers were considered as a better agroecological strategy compared to inorganic fertilizers (Ma et al. 2022). Organic fertilizers improved the concentration of Olsen-P and total P (TP) in soils (Pizzeghello et al. 2011). Although the impact of fertilizer application on soil P changes is substantial, there is a limited amount of research regarding the response of soil P fractions extracted using the method of Tiessen and Moir (1993) to various combinations of organic and chemical fertilizers.

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Cultivation practices affect the mineralization and decomposition of organic matter by altering the physicochemical properties of soils, which in affects P concentrations and fractions (Redel et al. 2011; Wang et al. 2011). Specifically, cultivation loosens the soil and reduces the diffusion and transport of phosphate ions (Deubel et al. 2011; Sheng et al. 2013). Moreover, contour cultivation, as compared to conventional downslope cultivation, has been found to reduce the runoff rate by increasing soil surface roughness and prolonging nutrient leaching (Stevens et al. 2009; Li et al. 2022). This practice helps retain sediment from slopes and deposit it along beams, thereby reducing soil erosion and nutrient losses from sloping cropland (Guo et al. 2019). While research on contour cultivation mainly focuses on its effect on runoff nutrient loss (Yang et al. 2018), there is limited information available on the effects of different cultivation practices on P fractions in soils. Indeed, there is an urgent need to explore the pattern of change of P fractions in soils under different cultivation practices.

In general, fertilization and cultivation can directly affect soil P concentrations through the input of orthophosphate and organic compounds and indirectly affect soil P concentrations through changes in the microenvironment, which can significantly change soil properties, resulting in changes in P fractions (Khan et al. 2023; Liu et al. 2023; Yan et al. 2016). In other words, the application of fertilization and cultivation practices changes the relationships between soil properties and P fractions, causing differences in the availability and conversion of P fractions in soils (Audette et al. 2016; Ahmed et al. 2019). For example, Soil organic carbon (SOC) was influenced by fertilization and could affect the mineralization and adsorption of soil P fractions (Braschi et al. 2003). SOC improved P availability by emitting organic acids, boosting P mineralization, and diminishing soil P adsorption (Cao et al. 2012). Dissolved organic carbon (DOC), the most dynamic component of SOC, exerted a predominant influence on the leaching of organic P from the soil (Gao et al. 2014; Vaz et al. 1993). Moreover, interactions between soil organic compounds and metal oxides affected phosphate binding pathways and the effectiveness of different P fractions (Sattell and Morris 1992). The nitrification of soil total N (TN) could modify the formation of soil organic P fractions while the presence of soil N could modulate metal ions, enhancing soil adsorption of P (Vitousek et al. 2010; Carreira et al. 2000). These findings highlighted the importance of exploring the effects of different soil properties on the contents of soil P fractions and their chemical features. Nevertheless, the relative importance of soil properties in influencing P fractions under different fertilization and cultivation practices is still not well understood.

In this study, we explored the changes in soil P fractions and their responses to soil properties (i.e., SOC, TN) under different fertilization and cultivation practices. Therefore, the objectives of this study were to (1) quantify the changes in P fractions and select soil properties affected by long-term fertilization and cultivation practices and (2) assess the relative importance of the selected soil properties affecting the changes in soil P fractions.

2 Materials and Methods

2.1 Study Area

The study area was located at the Soil and Water Conservation Experimental Base of Southwest University, Beibei District, Chongqing (106° 24′ 20″ E, 29° 48′ 42″ N). This area has a subtropical monsoon climate with an average annual temperature of 18.7 °C, an average annual sunshine duration of 1047 h, and a frost-free period of 365 days. The soil type in this study area was classified as purple soil according to Chinese soil taxonomy (Liu et al. 2009). Evergreen broadleaf forests dominate the vegetation in this area. The main crops included wheat (*Triticum aestivum* L.), maize (*Zea mays* L.) and sweet potato (*Ipomoea batatas* (L.) Lam.) in this study area. The initial soil properties were determined at the top soil layer (0–20 cm): pH 8.16, SOC 8.75 g kg^{-1}, TN 0.76 g kg^{-1}, TP 0.68 g kg^{-1}, total potassium 8.29 mg kg^{-1}, Olsen-P 18.29 mg kg^{-1}, ammonium nitrogen 24.19 mg kg^{-1}, nitrate nitrogen 19.51 mg kg^{-1}, available potassium 71.39 mg kg^{-1}.

2.2 Experimental Treatments

To investigate the relationships between P fractions and soil properties on purple soil slopes, 15 plots (8 m long × 4 m wide for each plot) were constructed on purple soil slopes with a slope of 15° in 2008. These plots were separated by a 25 cm wide concrete ridge, which was 20 cm above the ground. Based on the conventional local fertilization practices, five treatments were set up in the experiment (three replications for each), namely, CK (no fertilizer and downslope cultivation), T1 (chemical fertilizers and downslope cultivation), T2 (1.5-fold chemical fertilizers and downslope cultivation), T3 (manure plus chemical fertilizers and downslope cultivation) and T4 (chemical fertilizers and contour cultivation).

For each plot, a winter wheat and summer maize rotation was planted as the cropping system. The wheat cultivation season ranged from November to May, during which the base fertilizer was applied before planting and the follow-up fertilizer was applied in late January. The maize season was from March to July, with seeds sown on flat farmlands adjacent to the study area in March and transplanted to plots in early April. Base fertilizer was applied before transplanting, and follow-up fertilizer was applied in late May. Urea, calcium superphosphate, and potassium chloride were used as nitrogen, phosphorus, and potassium fertilizers, respectively. The organic fertilizer used was farm manure (pig feces and urine), which contained 4.31% carbon, 0.24% nitrogen, 0.17% phosphorus pentoxide, and 0.21% potassium oxide, as shown in Table 1. Since the plots were constructed in 2008, the fertilization and cultivation practices were kept the same annually.

2.3 Soil Sampling

Following the summer maize harvest in August 2022, five soil cores from each treatment plot were randomly selected from the two soil profiles (0–10 and 10–20 cm) and mixed into a single composite sample for each replicate using a 2.5-cm diameter auger. A total of 30 samples were collected (5 treatments × 3 replicates × 2 soil depth). Gravel, roots, and other debris were discarded, air-dried, ground and sieved to 0.25 mm, 1 mm and 2 mm.

2.4 Measurements of Soil Properties

The soil pH was determined in a 1:2.5 soil: deionized water (w/v) suspension with a pH meter (PHSJ-5, REX Company, Shanghai, China). SOC was determined by the potassium dichromate method (Nelson and Sommers 1996). DOC concentration in the soil was measured by a total organic carbon analyzer (TOC-V Shimadzu, Japan). Easily oxidized organic carbon (EOC) was measured at 565 nm using the 333 mmol L^{-1} K_2MnO_4 oxidation method (Lefroy et al. 1993). TN was determined by the semiautomatic Kjeldahl digestion method (ISSCAS 1978). Available nitrogen (AN) was determined by the alkalysis diffusion method (Lu 1999). TP was determined by the molybdenum blue colorimetric method (Olsen and Sommers 1982). The Olsen-P content was determined by extraction with 0.5 M $NaHCO_3$ (pH 8.5) according to the Olsen method (Olsen et al. 1954). $CaCl_2$-P was extracted with 0.01 mol L^{-1} $CaCl_2$ solution at a 1:5 soil/reagent ratio (25 °C and shaken for 15 min), after which the concentration was determined via molybdenum blue colorimetry (Bai et al. 2013). The exchangeable calcium (Ca) and exchangeable magnesium (Mg) concentrations were determined at 422.7 nm and 285.2 nm by atomic absorption spectrometry (AAS) using ammonium acetate as an exchanger (Lu 1999). 0.25 mm soils were used for the determination of SOC, TN, TP, DOC, Ca, Mg, and EOC, and 1 mm soils for the determination of Olsen-P and AN, whereas 2 mm soils were used only for the determination of $CaCl_2$-P.

Table 1 Annual nutrient inputs under different long-term fertilization cultivation treatments

Crops	Fertilizers and applied durations	Treatments	Nutrient inputs kg ha^{-1}					
			chemical fertilizers			Farm manure		
			N	P	K	N	P	K
Wheat	Basal fertilizer, early November	CK	0	0	0	0	0	0
		T1	228	75	150	0	0	0
		T2	339	112	225	0	0	0
		T3	140	45	0	0	0	0
		T4	228	75	150	0	0	0
	Topdressing fertilizer, late January	CK	0	0	0	0	0	0
		T1	0	0	0	0	0	0
		T2	0	0	0	0	0	0
		T3	0	0	0	27	19	24
		T4	0	0	0	0	0	0
Maize	Basal fertilizer, early April	CK	0	0	0	0	0	0
		T1	190	90	150	0	0	0
		T2	283	135	225	0	0	0
		T3	223	54	0	0	0	0
		T4	190	90	150	0	0	0
	Topdressing fertilizer, late May	CK	0	0	0	0	0	0
		T1	0	0	0	0	0	0
		T2	0	0	0	0	0	0
		T3	0	0	0	81	57	71
		T4	0	0	0	0	0	0

CK, no fertilizer and downslope cultivation; T1, chemical fertilizers and downslope cultivation; T2, 1.5-fold chemical fertilizers and downslope cultivation; T3, manure plus chemical fertilizers and downslope cultivation; T4, chemical fertilizers and contour cultivation; N, nitrogen; P, phosphorus; K, potassium

2.5 Measurements of Soil P Fractions

The soil P fractions were measured by a modified Hedley sequential fractionation method (Hedley et al. 1982; Tiessen and Moir 1993). In brief, 1 g of air-dried soil (1 mm) from each sample was placed in a 50 mL centrifuge tube. Extraction was conducted with the following extractants sequentially: for H_2O-Pi, extraction was performed with 30 ml of deionized water; for $NaHCO_3$-P, 30 ml of 0.5 M $NaHCO_3$ was used for extraction at pH 8.5; for NaOH-P, 30 ml of 0.1 M NaOH was used for extraction; and for HCl-P, 30 ml of 1 M HCl was used for extraction. The tubes were shaken (200 rpm) for 16 h, centrifuged at 10,000 × g for 15 min before each extraction and filtered with 0.45 µm cellulose membrane filter paper. Finally, the remaining extracts were repeatedly digested with concentrated H_2SO_4 and 30% H_2O_2 to obtain residual-P. The extracted inorganic phosphate was measured at 880 nm using a spectrophotometer (Murphy and Riley 1962). TP was determined in $NaHCO_3$, NaOH and concentrated HCl extracts in an autoclave at 121 °C using concentrated H_2SO_4 and potassium persulfate digestion. The organic phosphate in each extractant was calculated as the difference between the TP and inorganic phosphate.

2.6 Statistical Analyses

The normality of the data was tested using the Shapiro-Wilk test. If the data were not normally distributed, a log transformation (base 10) was conducted to ensure robust statistical analysis. One-way analysis of variance (ANOVA) and least significant difference (LSD) tests were used to determine the effects of long-term fertilization and cultivation on the absolute and relative concentrations (the proportion of each fraction of the TP content) of the soil P fractions. In addition, Pearson correlation analysis was used to determine the relationship between individual P fractions and predictor variables. To determine which predictor variables had the most significant influence on controlling changes in soil P fractions, random forest (RF) analysis was used to quantify the relative importance of individual predictor variables. RF identifies the percentage influence or contribution of a predictor variable (Breiman 2001). The RF model was run based on the scikit-learn library embedded in Python 3.8 (Fig. 1).

3 Results

3.1 Changes in the Concentrations of the Soil P Fractions

At the 0–10 cm soil depth, the H_2O-Pi and $NaHCO_3$-Pi concentrations in the T1 treatment were significantly lower than those in the T2 and T3 treatments ($p < 0.05$), and their concentrations were 36.9–85.2% greater than those in the T1 treatment (Fig. 2). The $NaHCO_3$-Po concentrations in T1 and T2 were 39.4% and 31.5% lower than that in T3,

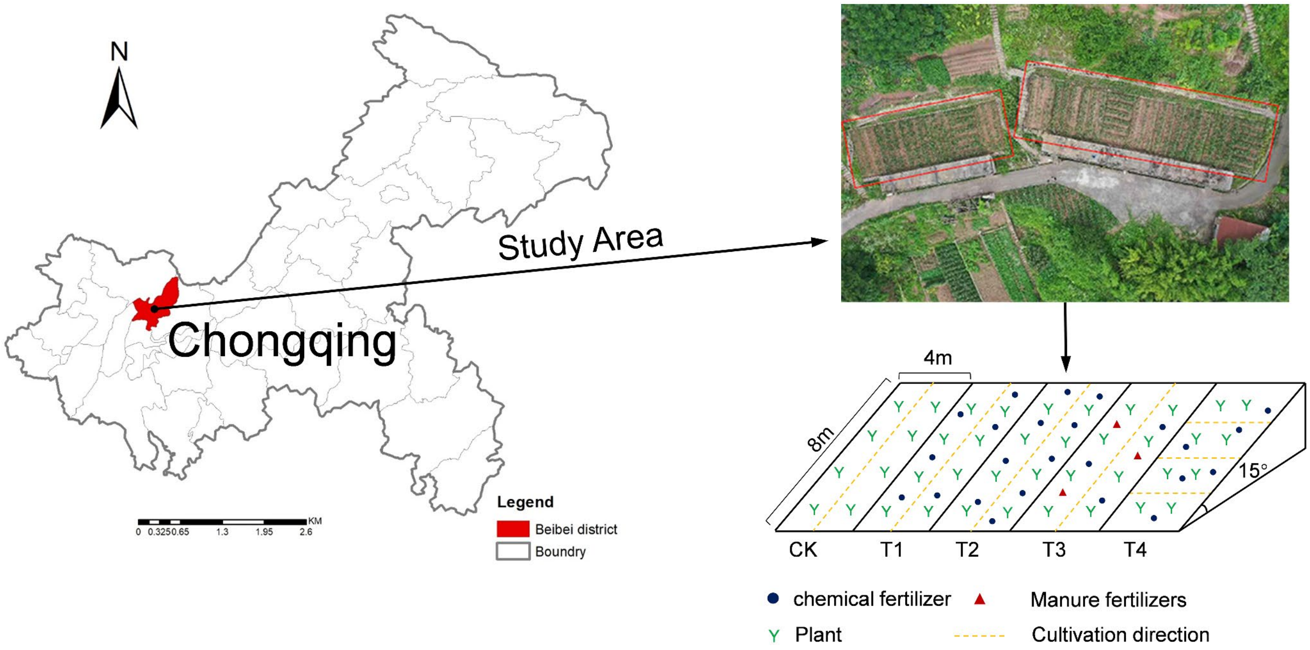


Fig. 1 Location of the experimental site. CK, no fertilizer and downslope cultivation; T1, chemical fertilizers and downslope cultivation; T2, 1.5-fold chemical fertilizers and downslope cultivation; T3, manure plus chemical fertilizers and downslope cultivation; T4, chemical fertilizers and contour cultivation (re-edited from Du et al. 2021)

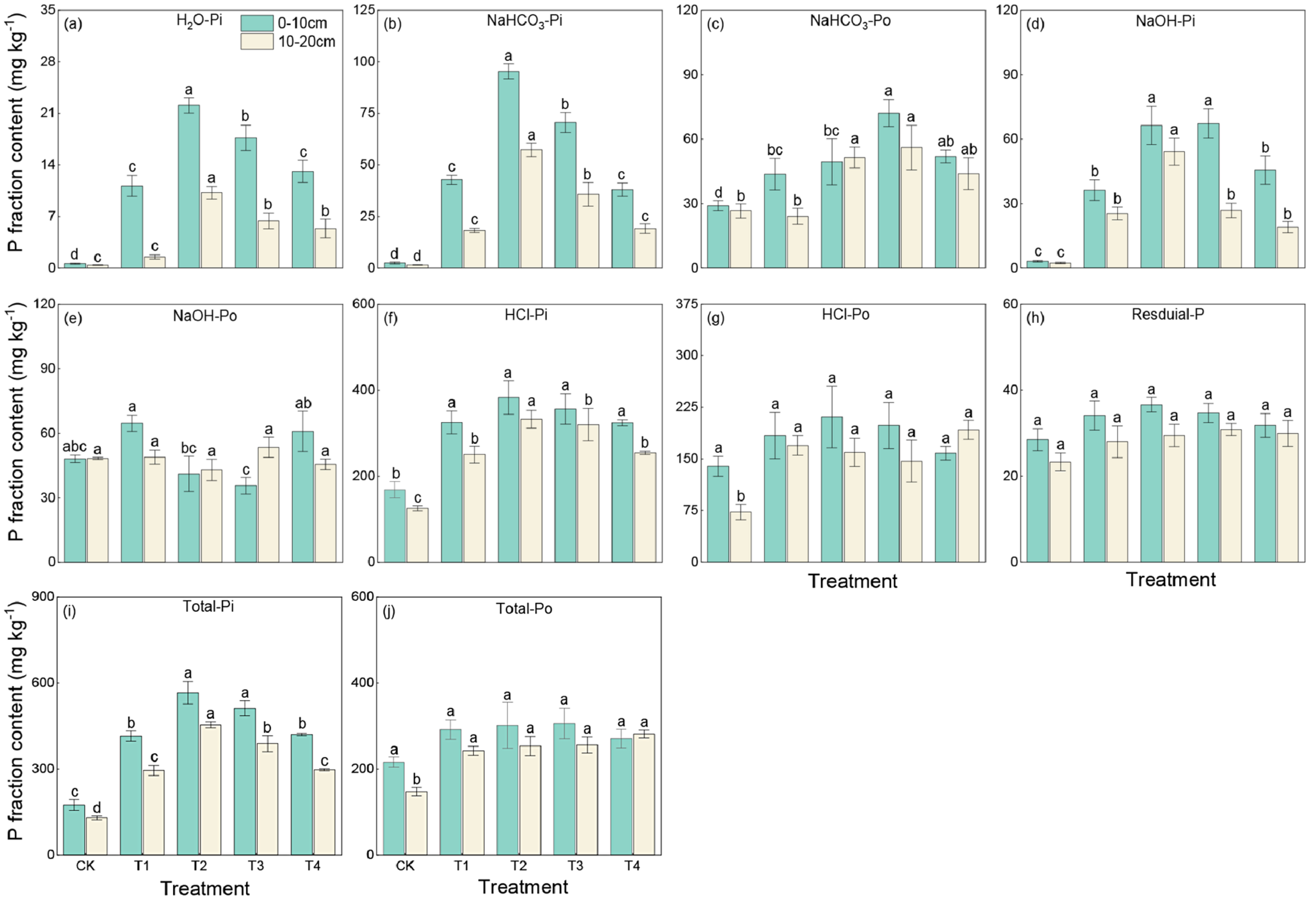


Fig. 2 Content of phosphorus fractions in different soil depth under long-term fertilization cultivation conditions. CK, no fertilizer and downslope cultivation; T1, chemical fertilizers and downslope cultivation; T2, 1.5-fold chemical fertilizers and downslope cultivation; T3, manure plus chemical fertilizers and downslope cultivation; T4, chemical fertilizers and contour cultivation. Different letters above each box indicate significant differences between fertilization and cultivation treatments ($p < 0.05$)

respectively ($p < 0.05$) (Fig. 2). The NaOH-Pi and Total-Pi concentrations were significantly lower in the T1 treatment than in the T2 and T3 treatments (45.4–46.1% and 18.9–26.7%, respectively). The relative concentration of residual-P was significantly different among the five treatments, and the highest concentration was 6.79% in CK (Fig. 3). The HCl-Pi and HCl-Po accounted for 21.5–47.2% of all the P fractions (Fig. 3). Moreover, no P fractions were significantly different between T1 and T4 ($p > 0.05$) (Fig. 2).

At 10–20 cm soil depth, the H_2O-Pi and $NaHCO_3$-Pi in T1 were significantly lower than T2 and T3 ($p < 0.05$), and T2 and T3 were 48.7–85.2% higher than that of T1 (Fig. 2). The NaOH-Pi and HCl-Pi in T2 were significantly higher than T1 and T3 ($p < 0.05$), in which NaOH-Pi was 101.9-112.8% higher than T1, and HCl-Pi was 4.0-32.8% higher than T1 (Fig. 2). The relative concentration of $NaHCO_3$-Pi was significantly different among the five treatments, and the highest concentration was 10.5% in T3 (Fig. 3). The H_2O-Pi concentration in T4 was significantly greater (253.9%) than that in T1 ($p < 0.05$) (Fig. 2). However, the relative concentrations of residual-P in T1 were significantly greater (57.3%) than those in T4 ($p < 0.05$) (Fig. 3).

3.2 Changes in Soil Chemical Properties and Crop Yield

Table 2 shows the variation in soil chemical properties under the different fertilization cultivation patterns at the different soil depths. At the 0–10 cm soil depth, the highest concentrations of SOC and Olsen-P were found in T3, which increased by 39.38% and 52.63%, respectively, compared to those in T2 ($p < 0.001$). The AN concentration in the T1 treatment was significantly lower than that in T2 and T3 ($p = 0.001$), which were lower by 8.54%, and 13.5%, respectively (Table 2).

The maize yield was similar between T1 and T2, which increased by 359.1% and 357.5% ($p < 0.05$) compared to CK, respectively (Fig. 4). The wheat yield increased by 205.2% and 197.7% ($p < 0.05$) in T3 and T4 compared to CK, respectively, (Fig. 4). The maize and wheat yields were

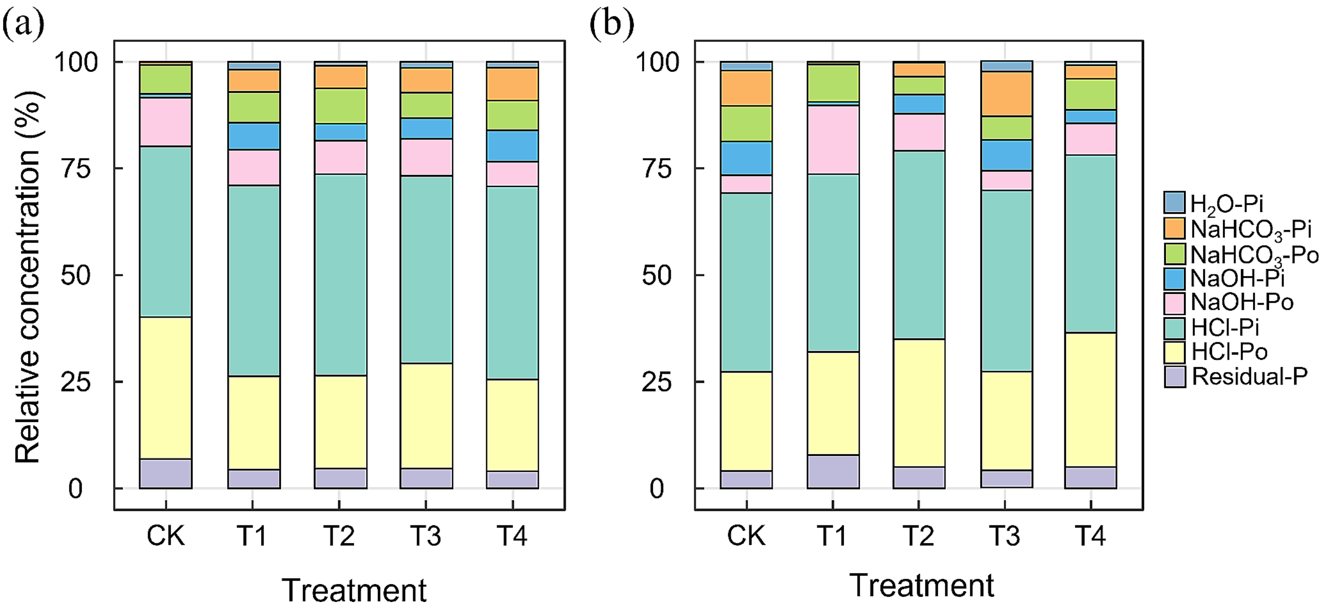


Fig. 3 Changes in the proportions (%) of measured 0–10 cm (a) and 10–20 cm (b) soil inorganic and organic phosphorus fractions in the soil total P content after conversion of different fertilization treatments. CK, no fertilizer and downslope cultivation; T1, chemical fertilizers and downslope cultivation; T2, 1.5-fold chemical fertilizers and downslope cultivation; T3, manure plus chemical fertilizers and downslope cultivation; T4, chemical fertilizers and contour cultivation

not significantly different between T1 and T4 ($p > 0.05$) (Fig. 4).

3.3 Relationships Between P Fractions and Soil Variables and Crop Yields

H_2O-Pi, $NaHCO_3$-Po, NaOH-Pi, HCl-Pi, and residual-P exhibited significant positive correlations with Olsen-P and $CaCl_2$-P (Fig. 5). HCl-P (HCl-Pi, HCl-Po) exhibited significant positive correlations with Ca and TP. HCl-Po had significant negative correlations with pH, Mg, the N: P ratio and crop yield (Fig. 5).

3.4 The Relative Importance of Predictor Variables in Regulating Soil P Dynamics

The RF model further identified the main drivers of variation in different P fractions based on ranking the importance of the influencing factors. Among the four inorganic P fractions, SOC and TN were the most important variables affecting H_2O-Pi, explaining 22.20% and 21.74% of the data, respectively (Fig. 6). TN and SOC were the most important variables affecting NaOH-Pi, which explained 18.29% and 15.17% of the data, respectively. DOC and SOC were the two most important variables affecting $NaHCO_3$-Pi, explaining 18.56% and 17.85% of the data, respectively. SOC and DOC were the most important variables affecting the HCl-Pi concentration, explaining 24.65% and 17.22% of the data, respectively. For the organic P fractions, SOC and DOC were the main variables affecting $NaHCO_3$-Po, explaining of 21.29% and 16.72% of the data, respectively. EOC and Mg were the main variables affecting NaOH-Po, explaining 16.78% and 15.65% of the data, respectively. N: P and TN were the main variables affecting HCl-Po, explaining 13.97% and 13.52% of the data, respectively. TN and AN were the most critical factors affecting residual-P, explaining 24.93% and 14.12% of the data, respectively. Furthermore, SOC and N: P were the two essential factors affecting Total-P, explaining 23.34% and 20.22% of the data, respectively.

4 Discussion

The present study showed that manure plus chemical fertilizer under long-term fertilization and cultivation conditions could significantly increase the concentrations of H_2O-Pi, $NaHCO_3$-Pi, and NaOH-Pi. This result was consistent with previous finding by Wang et al. (2022), who reported that long-term application of organic and chemical fertilizers mainly increased the inorganic P fractions (Resin-P, $NaHCO_3$-Pi, NaOH-Pi, and HCl-Pi) in soils, and attributed this to the high water solubility and colloidal nature of these inorganic P fractions. Indeed, this study also found that the addition of manure fertilizers significantly increased SOC (Table 2), and the increase in SOC might activate the soil inorganic P fractions and elevated the solubility and mineralization of P, which in turn increased the accumulation of

Table 2 Changes in measured soil properties after conversion of different fertilization treatments

Soil variable	Soil depth (cm)											
	0–10						10–20					
	CK	T1	T2	T3	T4	*P*	CK	T1	T2	T3	T4	*P*
SOC (g kg^{-1})	4.51 ± 0.19c	6.56 ± 0.11b	7.31 ± 0.47b	9.13 ± 0.11a	7.09 ± 0.19b	< 0.001	4.08 ± 0.11d	5.59 ± 0.21b	6.56 ± 0.47b	8.06 ± 0.19a	6.13 ± 0.19ab	< 0.001
TN (g kg^{-1})	0.64 ± 0.03b	0.76 ± 0.08ab	0.80 ± 0.04ab	0.95 ± 0.03a	0.76 ± 0.08ab	0.043	0.60 ± 0.05a	0.61 ± 0.06a	0.61 ± 0.06a	0.73 ± 0.07a	0.60 ± 0.03a	0.446
AN (mg kg^{-1})	79.33 ± 12.35ab	77.00 ± 4.04b	106.17 ± 4.21a	86.43 ± 2.87b	74.67 ± 1.17b	0.029	46.67 ± 4.67b	57.17 ± 1.17ab	56.00 ± 4.04ab	64.17 ± 2.87a	64.17 ± 3.09a	0.024
TP (g kg^{-1})	0.44 ± 0.08c	0.83 ± 0.05b	1.03 ± 0.01a	0.82 ± 19.79b	0.86 ± 0.02b	< 0.001	0.40 ± 0.09c	0.80 ± 0.04ab	0.89 ± 0.01a	0.68 ± 0.01b	0.76 ± 0.02ab	< 0.001
Olsen-P (mg kg^{-1})	4.98 ± 0.52c	20.33 ± 0.75b	28.56 ± 1.05a	31.03 ± 1.34a	23.25 ± 0.97b	< 0.001	4.48 ± 1.00c	18.17 ± 0.96b	23.95 ± 0.64a	26.48 ± 1.28a	20.68 ± 0.68b	< 0.001
CaCl$_2$-P (mg kg^{-1})	1.56 ± 0.51c	2.99 ± 0.03b	4.63 ± 0.47a	4.41 ± 0.37a	4.24 ± 0.34a	0.001	1.86 ± 0.08b	2.05 ± 0.03b	3.29 ± 0.38a	2.99 ± 0.26a	2.03 ± 0.08b	0.002
Mg (g kg^{-1})	0.82 ± 0.25a	0.44 ± 0.08a	0.46 ± 0.07a	0.63 ± 0.19a	0.41 ± 0.07a	0.332	0.91 ± 0.27a	0.47 ± 0.05a	0.46 ± 0.10a	0.57 ± 0.16a	0.41 ± 0.10a	0.226
Ca (g kg^{-1})	5.25 ± 0.04b	5.18 ± 0.52b	7.15 ± 0.23a	6.69 ± 0.43ab	8.17 ± 0.69a	0.015	4.96 ± 0.60b	6.11 ± 0.75b	6.95 ± 1.08ab	7.65 ± 0.66ab	9.60 ± 0.17a	0.064
EOC (g kg^{-1})	4.09 ± 0.21c	11.24 ± 0.12a	7.65 ± 1.01b	3.57 ± 0.18c	10.71 ± 1.22a	< 0.001	2.95 ± 0.65c	5.61 ± 0.75ab	4.28 ± 0.66bc	2.56 ± 0.03c	6.73 ± 1.15a	0.012
DOC (g kg^{-1})	5.21 ± 0.73d	7.43 ± 0.58c	9.04 ± 0.16b	12.30 ± 0.76a	4.63 ± 0.18d	< 0.001	3.51 ± 0.25d	5.47 ± 0.07c	7.06 ± 0.15b	9.81 ± 0.24a	4.87 ± 0.19c	< 0.001
pH	7.50 ± 0.17a	7.20 ± 0.06b	7.00 ± 0.06b	7.30 ± 0.06ab	7.10 ± 0.03b	0.028	7.50 ± 0.12a	7.10 ± 0.09b	7.10 ± 0.06b	7.30 ± 0.03ab	7.10 ± 0.03b	0.031
C: P	11.43 ± 0.10a	8.00 ± 0.51 cd	7.08 ± 0.42d	11.83 ± 0.53b	8.28 ± 0.25c	< 0.001	11.83 ± 0.53a	6.98 ± 0.016c	7.35 ± 0.55c	9.41 ± 0.13b	8.05 ± 0.31c	< 0.001
N: P	1.64 ± 0.14a	0.94 ± 0.16b	0.77 ± 0.05b	1.73 ± 0.18b	0.89 ± 0.11b	0.003	1.73 ± 0.18a	0.77 ± 0.19b	0.69 ± 0.07b	0.85 ± 0.08b	0.78 ± 0.02b	< 0.001
Ca: Mg	3.53 ± 3.24a	12.92 ± 5.68a	12.32 ± 10.85a	12.73 ± 6.00a	16.29 ± 14.29a	0.526	3.08 ± 3.05a	13.62 ± 4.96a	17.38 ± 8.80a	12.42 ± 10.82a	20.35 ± 17.64a	0.372

CK, no fertilizer and downslope cultivation; T1, chemical fertilizers and downslope cultivation; T2, 1.5-fold chemical fertilizers and downslope cultivation; T3, manure plus chemical fertilizers and downslope cultivation; T4, chemical fertilizers and contour cultivation. Means (± SE) with different letters indicate significant differences between the five treatments ($p < 0.05$ with one-way ANOVA followed by Duncan test). Soil variables included soil total N (TN), soil total P (TP), soil CaCl$_2$-P (CaCl$_2$-P), soil Olsen-P (Olsen-P), soil organic carbon (SOC), soil dissolved organic carbon (DOC), soil easily oxidized organic carbon (EOC), soil pH (pH), available N (AN), C: P ratio (C: P), N: P ratio (N: P), exchangeable calcium (Ca), exchangeable magnesium (Mg), Ca: Mg ratio (Ca: Mg)

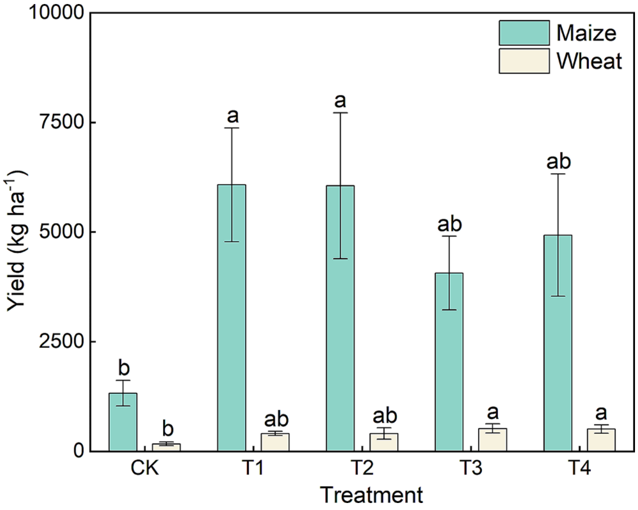
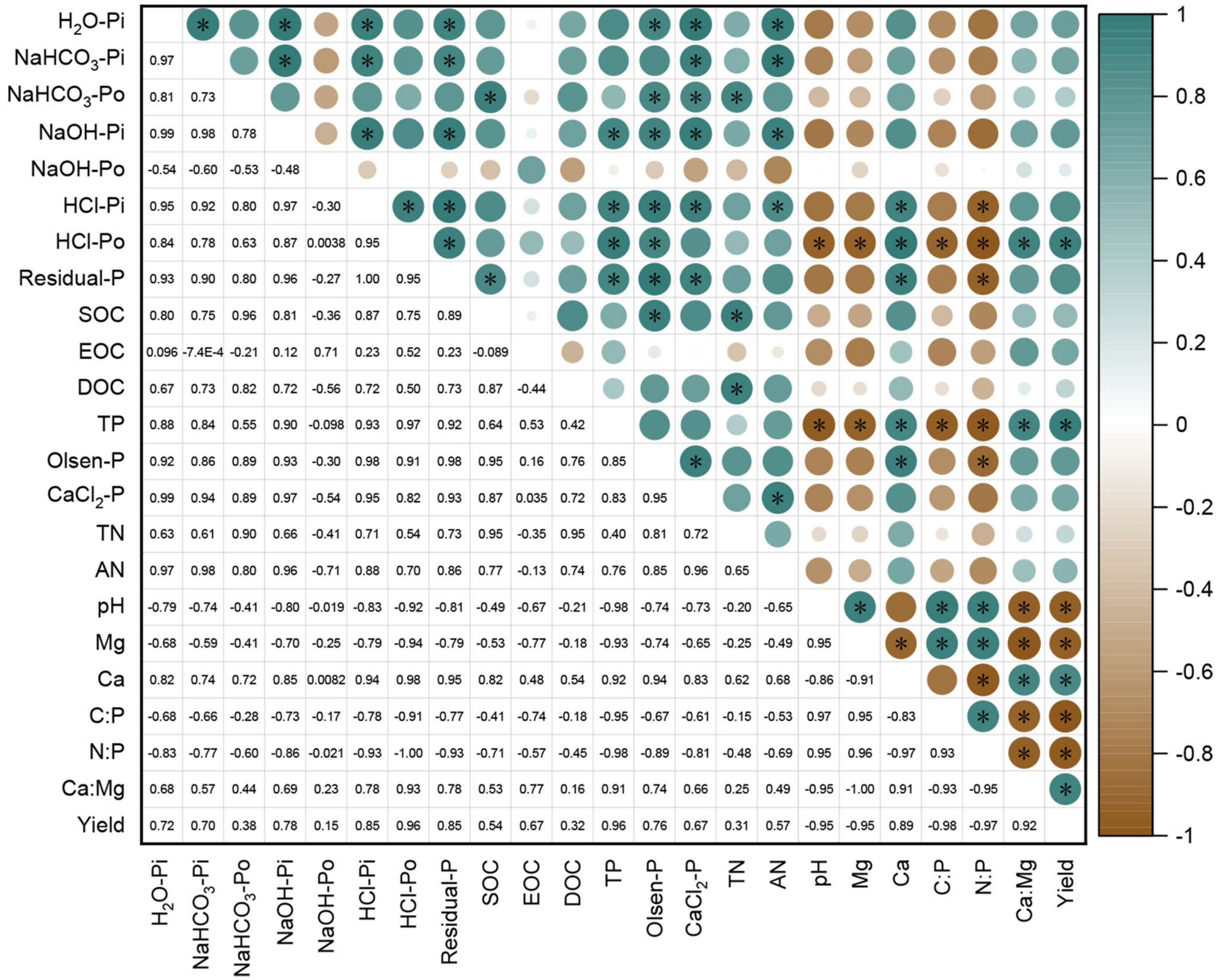


Fig. 4 Crop yields under long-term fertilization cultivation conditions

the inorganic P fractions (Du et al. 2018). On the other hand, long-term application of organic fertilizers increased humus and organic anions in soils, and thus delaying the crystallization and transformation of stable P fractions (Audette et al. 2016; Sato et al. 2005). Moreover, RF results verified that SOC was an important factor influencing H_2O-Pi, $NaHCO_3$-Pi and NaOH-Pi. Labile P (H_2O-Pi and $NaHCO_3$-P) was mostly readily absorbed by plants and was the mostly mineralized and mobile component of the soil P pool (Li et al. 2023). Our study showed that manure plus chemical fertilizer applications could increase the proportion of labile P. Manure fertilizers promoted the dissolving action of phosphatase, catalyzing the hydrolysis of phytate that could increase the accumulation of labile P in soils (Audette et al. 2016). In particular, manure fertilizers increased the accumulation of P in the form of brushite and deoxyribonucleic acid in soils (Lehmann et al. 2005; Liu et al. 2019). In this study, we found that long-term fertilization and cultivation significantly increased the $CaCl_2$-P content in soils, which the $CaCl_2$-P was significantly and positively correlated with the inorganic P fractions (Fig. 5). Herlihy and Carthy (2006) demonstrated that soil $CaCl_2$-P was able to modify the adsorption capacity of P fractions, thereby altering the concentration of H_2O-Pi. This was because that the buffer capacity of soil P decreased as the increased soil $CaCl_2$-P concentration (Recena et al. 2016).

In addition, contour cultivation significantly increased H_2O-Pi at the 10–20 cm soil depth. This was consistent with the findings of Stevens et al. (2009), who found that contour cultivation reduced the P loss of soil particles, thereby preserving P accumulation in the soil, as observed in their field experiments in England. This was because contour cultivation enhanced the interaction between soil and water, and the adsorption in deeper phosphorus-deficient soils, leading to a reduction in H_2O-Pi loss by infiltrating water flows (McDowell et al. 2001; McDowell 2012). Previous studies have shown that the stable P fraction of the soil was not significantly affected by tillage practices (Shi et al. 2013; Wright 2009; Vu et al. 2009). However, our study found that contour cultivation significantly reduced the residual-P fractions at the 10–20 cm soil depth compared to downslope cultivation. This was due to the fact that residual-P in the soil was converted to a more soluble form under long-term continuous cultivation (Tiessen et al. 1992). This suggested that contour cultivation was more favorable as the residual-P pool in the soil was converted to a more soluble form with continuous P depletion. Stable P fractions were the predominant form of P in soils and consisted of HCl-P and residual-P fractions (Fig. 3), which included stable Ca-associated P and Fe-associated P (Khan et al.2021; Xavier et al. 2011). In our study, residual-P level exhibited a significant positive correlation with Ca (Fig. 5). In moderately alkaline soils with abundant calcium ions, phosphates swiftly form calcium phosphate compounds, which were difficult for plant utilization (Strauss et al. 1997). Yin et al. (2018) found that agricultural practices and rainfall may lead to leaching of soil calcium phosphates through runoff. Moreover, contour cultivation considerably enhanced soil Ca levels but significantly reduced the proportion of residual-P. The reason for this phenomenon was that contour cultivation increased the contact time between soil and runoff, which in turn elevated the risk of soil leaching, resulting in residual-P leaching through runoff (USDA-NSCS, 2017; Ricci et al. 2022).

Our findings indicated that SOC and DOC contributed more to labile P. This was consistent with the findings of Khan et al. (2023), who found that SOC had an influence on the dissolution of soil inorganic P and the mineralization of organic P, thus increasing the effectiveness of labile P fractions in soils. DOC, the most dynamic component of SOC, comprises humic acid and a variety of carbon compounds (Gao et al. 2014). Soil phosphatase activity exhibited an increase as the raised SOC and DOC contents (Nannipieri et al. 2011). It was worthy noted that higher soil phosphatase activity facilitated the conversion of stable P to labile P in soils (Yang et al. 2021). However, Guppy et al. (2005) shown that DOC was influenced by the composition and concentration of organic acids in fertilizers and competed with soil P for adsorption sites. TN and AN had a significantly greater impact on the residual-P compared to other factors. Many studies indicated that nitrogen addition appreciably raised the concentrations of TN and AN in the soil, which subsequentially diminished microbial activity (Tian et al. 2016; Wang et al. 2015). This reduction in microbial activity led to a decrease in phosphatase activity, causing augmented levels of plant-unavailable P (Kafle et al. 2019). These findings were consistent with previous studies conducted under different fertilization patterns, where changes



	H_2O-Pi	$NaHCO_3$-Pi	$NaHCO_3$-Po	NaOH-Pi	NaOH-Po	HCl-Pi	HCl-Po	Residual-P	SOC	EOC	DOC	TP	Olsen-P	$CaCl_2$-P	TN	AN	pH	Mg	Ca	C:P	N:P	Ca:Mg	Yield
H_2O-Pi		*		*		*		*					*	*		*							
$NaHCO_3$-Pi	0.97			*		*		*						*		*							
$NaHCO_3$-Po	0.81	0.73							*				*	*	*								
NaOH-Pi	0.99	0.98	0.78			*		*				*	*	*		*							
NaOH-Po	-0.54	-0.60	-0.53	-0.48																			
HCl-Pi	0.95	0.92	0.80	0.97	-0.30		*	*				*	*	*		*			*		*		
HCl-Po	0.84	0.78	0.63	0.87	0.0038	0.95		*				*	*				*	*	*	*	*	*	*
Residual-P	0.93	0.90	0.80	0.96	-0.27	1.00	0.95		*			*	*	*					*		*		
SOC	0.80	0.75	0.96	0.81	-0.36	0.87	0.75	0.89					*		*								
EOC	0.096	-7.4E-4	-0.21	0.12	0.71	0.23	0.52	0.23	-0.089														
DOC	0.67	0.73	0.82	0.72	-0.56	0.72	0.50	0.73	0.87	-0.44					*								
TP	0.88	0.84	0.55	0.90	-0.098	0.93	0.97	0.92	0.64	0.53	0.42						*	*	*	*	*	*	*
Olsen-P	0.92	0.86	0.89	0.93	-0.30	0.98	0.91	0.98	0.95	0.16	0.76	0.85		*					*		*		
$CaCl_2$-P	0.99	0.94	0.89	0.97	-0.54	0.95	0.82	0.93	0.87	0.035	0.72	0.83	0.95			*							
TN	0.63	0.61	0.90	0.66	-0.41	0.71	0.54	0.73	0.95	-0.35	0.95	0.40	0.81	0.72									
AN	0.97	0.98	0.80	0.96	-0.71	0.88	0.70	0.86	0.77	-0.13	0.74	0.76	0.85	0.96	0.65								
pH	-0.79	-0.74	-0.41	-0.80	-0.019	-0.83	-0.92	-0.81	-0.49	-0.67	-0.21	-0.98	-0.74	-0.73	-0.20	-0.65		*		*	*	*	*
Mg	-0.68	-0.59	-0.41	-0.70	-0.25	-0.79	-0.94	-0.79	-0.53	-0.77	-0.18	-0.93	-0.74	-0.65	-0.25	-0.49	0.95		*	*	*	*	*
Ca	0.82	0.74	0.72	0.85	0.0082	0.94	0.98	0.95	0.82	0.48	0.54	0.92	0.94	0.83	0.62	0.68	-0.86	-0.91			*	*	*
C:P	-0.68	-0.66	-0.28	-0.73	-0.17	-0.78	-0.91	-0.77	-0.41	-0.74	-0.18	-0.95	-0.67	-0.61	-0.15	-0.53	0.97	0.95	-0.83		*	*	*
N:P	-0.83	-0.77	-0.60	-0.86	-0.021	-0.93	-1.00	-0.93	-0.71	-0.57	-0.45	-0.98	-0.89	-0.81	-0.48	-0.69	0.95	0.96	-0.97	0.93		*	*
Ca:Mg	0.68	0.57	0.44	0.69	0.23	0.78	0.93	0.78	0.53	0.77	0.16	0.91	0.74	0.66	0.25	0.49	-0.95	-1.00	0.91	-0.93	-0.95		*
Yield	0.72	0.70	0.38	0.78	0.15	0.85	0.96	0.85	0.54	0.67	0.32	0.96	0.76	0.67	0.31	0.57	-0.95	-0.95	0.89	-0.98	-0.97	0.92	

Fig. 5 Correlations between soil properties and soil P fractions. The numerical label and color indicate the strength and sign of the correlation at $p < 0.05$. Soil variables included soil total N (TN), soil total P (TP), soil $CaCl_2$-P ($CaCl_2$-P), soil Olsen-P (Olsen-P), soil organic carbon (SOC), soil dissolved organic carbon (DOC), soil easily oxidized organic carbon (EOC), soil pH (pH), available N (AN), C: P ratio (C: P), N: P ratio (N: P), exchangeable calcium (Ca) and exchangeable magnesium (Mg), Ca: Mg ratio (Ca: Mg), sum of maize and wheat yield (Yield)

in soil P fractions were closely linked to changes in soil properties (Wang et al. 2022, 2023). Therefore, in future agricultural management, it is important to consider the limitation and impact of C and N elements on soil P fractions when applying P fertilizer.

5 Conclusion

Long-term application of manure and chemical fertilizers significantly increased the concentrations of H_2O-Pi and $NaHCO_3$-Pi in the 0–20 cm depth of the soil. The proportion of residual-P in the 0–10 cm soil depth decreased significantly with the long-term input of manure plus chemical fertilizers. Contour cultivation increased the concentration and proportion of H_2O-Pi in 10–20 cm soil depth. In addition, SOC and DOC contributed more to labile P, while AN and TN contributed more to residual-P, validating the hypothesis that different P fractions were more closely related to soil C and N elements. Our study found that manure plus chemical fertilizer and contour cultivation were effective in increasing the labile P fractions in soils, which provided a scientific basis for improving purple soil sloping croplands and efficiently using fertilizers. Further research should be conducted to determine how to fully utilize soil residual-P and reduce the waste of P resources.

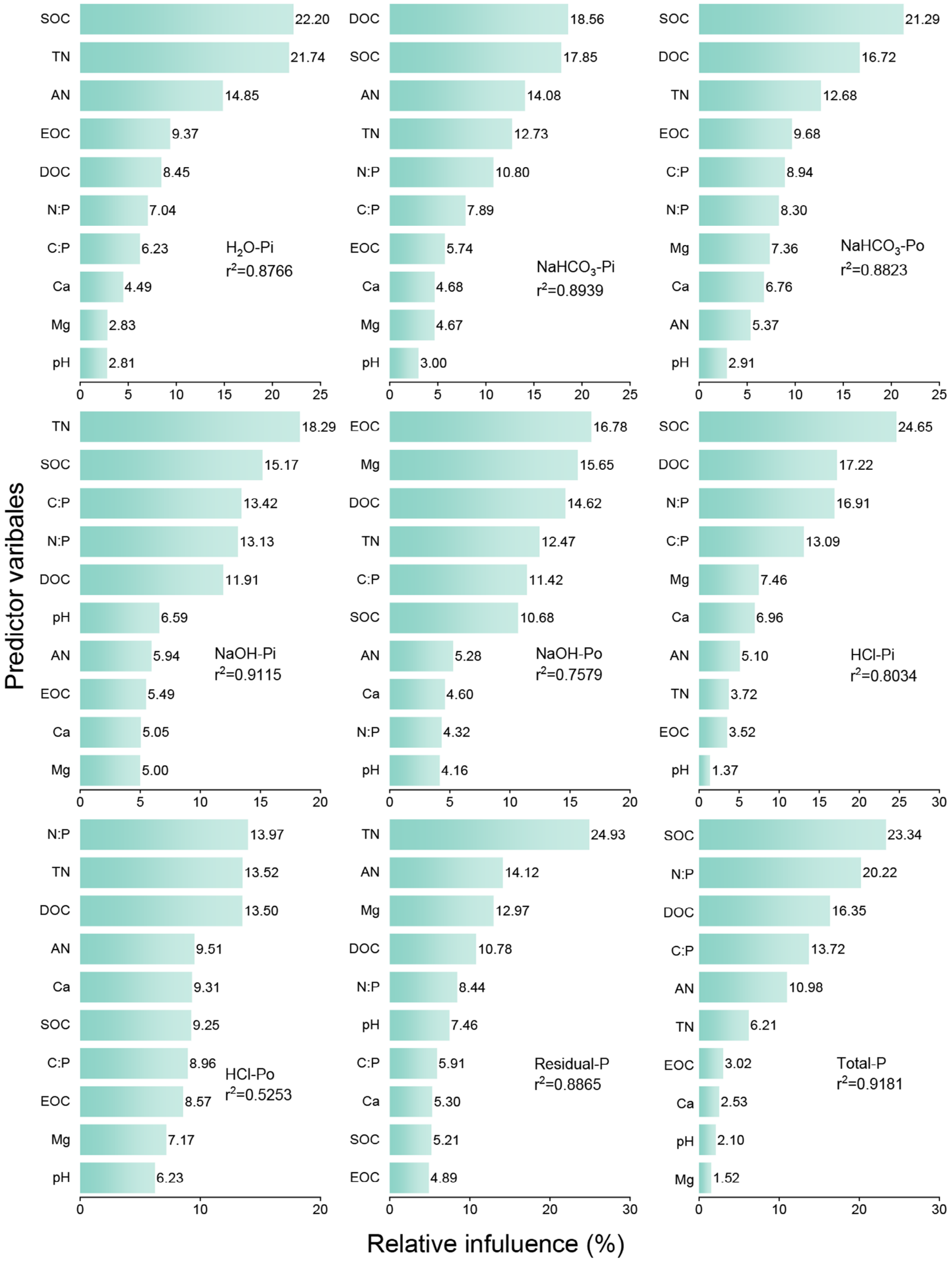


Fig. 6 Relative influences of individual factors to nine measured soil P fractions quantified by the Random Forest model. r^2 values represent the proportion of the variation in each P fraction explained by the model. Soil variables included soil total N (TN), soil total P (TP), soil $CaCl_2$-P ($CaCl_2$-P), soil Olsen-P (Olsen-P), soil organic carbon (SOC), soil dissolved organic carbon (DOC), soil easily oxidized organic carbon (EOC), soil pH (pH), available N (AN), C: P ratio (C: P), N: P ratio (N: P), exchangeable calcium (Ca) and exchangeable magnesium (Mg), Ca: Mg ratio (Ca: Mg)

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Author Contribution Gaoning Zhang: conceptualization, data curation, formal analysis, investigation, methodology, software, visualization, writing–original draft, writing–review & editing. Asif Khan: Investigation, writing–review & editing. Binghui He: conceptualization, funding acquisition, investigation, conceptualization, supervision, resources, project administration, validation, writing– review & editing. Tianyang Li: writing–review & editing.

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Data Availability The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Code Availability Not applicable.

Declarations

Ethics Approval Not applicable.

Consent to Participate Not applicable.

Consent for Publication Not applicable.

Conflict of Interest The authors declare no competing interests.

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