RESEARCH ARTICLE

Effect of long-term fertilization on phosphorus fractions in different soil layers and their quantitative relationships with soil properties

WANG Qiong[1, 2], QIN Zhen-han[1], ZHANG Wei-wei[1], CHEN Yan-hua[1, 3], ZHU Ping[4], PENG Chang[4], WANG Le[1], ZHANG Shu-xiang[1], Gilles COLINET[2]

[1] Institute of Agricultural Resources and Regional Planning, Chinese Academy of Agricultural Sciences/National Engineering Laboratory for Improving Quality of Arable Land, Beijing 100081, P.R.China

[2] TERRA, Gembloux Agro-Bio Tech, University of Liege, Gembloux, 5030, Belgium

[3] Institute of Plant Nutrition, Resources and Environment, Beijing Academy of Agriculture and Forestry Sciences, Beijing 100097, P.R.China

[4] Agricultural Environment and Resources Center, Jilin Academy of Agricultural Sciences, Changchun 130033, P.R.China

Abstract

Investigating the dynamics and distribution of soil phosphorus (P) fractions can provide a basis for enhancing P utilization by crops. Four treatments from a 29-year long-term experiment in black soil with maize cropping were involved in this study: no fertilizer (CK), inorganic nitrogen and potassium (NK), inorganic nitrogen, phosphorus, and potassium (NPK), and NPK plus manure (NPKM). We analyzed soil P fractions in different soil layers using a modified Hedley sequential method. The long-term NPKM treatment significantly increased total P by 0.6–1.6 times in the different soil layers. The Olsen-P concentration far exceeded the environmental threshold for soil Olsen-P (50.6 mg kg^{-1}) in the NPKM treatment in the 0–60 cm soil profile. Moreover, the concentrations and proportion of labile and partially labile inorganic P (Pi) fractions (i.e., NaHCO$_3$-extracted Pi, NaOH-extracted Pi, and dilute HCl-extracted Pi) to the sum of all P fractions (Pt) in the 0–60 cm soil profile were higher in the NPKM treatment than in the NPK treatment, indicating that manure could promote the transformation of non-labile into more labile forms of P in soil, possibly by manure reducing P fixation by soil particles. Soil organic matter, Mehlich-3 extractable iron (Fe), and organic-bound aluminum were increased by fertilization, and were the main factors influencing the differences in the P fractions in the 0–20 cm soil layer. Soil mineral components, i.e., free Fe oxide and CaCO$_3$, were the main factors influencing the P fractions in the subsoil. The soil P transformation process varied with soil layer and fertilization. Application of manure fertilizer can increase the labile (Olsen) P concentrations of the various soil layers, and thus should reduce the mineral P fertilizer requirement for crop growth and reduce potential environmental damage.

1. Introduction

Phosphorus (P) is an essential nutrient element for crop growth and development. In agricultural systems, organic or inorganic fertilizers are typically applied to compensate for P output (uptake by crops, loss by leaching, and surface runoff) and to maintain or increase the amount of P in soil that can be utilized by plants (Ayaga *et al.* 2006; Bauke *et al.* 2018). The total P and available P levels in soil can be maintained or increased when the annual P input rate ranges from 30 to 60 kg P ha^{-1} (Zhang *et al.* 2014; Zhan *et al.* 2015). Analysis of 13 long-term experimental sites in China showed that the concentrations of soil available P was increased by 4.2 mg kg^{-1} yr^{-1} under mineral P plus manure treatment and by 0.9 mg kg^{-1} yr^{-1} under mineral P treatment alone, but was decreased by 0.2 mg kg^{-1} yr^{-1} where no P was applied (Shen *et al.* 2014). It is thus evident that fertilization influences soil available P concentrations in the long term. Therefore, to improve soil P availability, it is necessary to understand how the P status in soil is influenced by different long-term fertilization strategies.

During the 1980–2018 period, the annual P surplus level increased by 10% in China, mostly due to excessive application of P fertilizer (Li *et al.* 2015; Chen and Graedel 2016). The P from excessive fertilizer application may be retained in the surface soil, transferred to deeper soil layers, or leached out from the soil system to groundwater, depending on the amount and fractions of accumulated P in the soil and soil properties (Castoldi *et al.* 2009; Olson *et al.* 2010; Stutter *et al.* 2012; Glaesner *et al.* 2019). Studies have provided valuable insights into the effects of P fertilizer on P in surface soil, but little is known regarding fertilizer effects on the subsoil, which may have huge P reserves, accounting for 25–75% of the total P in the soil profile (Godlinski *et al.* 2004; Kautz *et al.* 2012). Considering the potentially adverse effects of excess P on aquatic environments, investigation of the effects of P fertilizer application on the distribution and migration of P in the soil profile is necessary for evaluation of potential pollution risk from P fertilizer application to soil (Sharpley *et al.* 2015).

The availability of P in soil is directly related to the forms (fractions) in which it is present (Liang *et al.* 2017). Fertilizer application practices are an important factor affecting the P fractions in soil (van der Bom *et al.* 2019). Vu *et al.* (2008) reported that long-term (over 65 years)

use of superphosphate fertilizer significantly increased the concentrations of all inorganic P (Pi) fractions except for Ca-P and had no significant influence on organic P (Po) concentration. Under equivalent P inputs, soil that received long-term manure had a higher proportion of readily available Pi than soil that received only mineral fertilizer (Yan *et al.* 2017, 2018). Some long-term studies have shown that combining mineral with organic fertilizers primarily affected soil Pi concentrations (Ahlgren *et al.* 2013; Annaheim *et al.* 2015; McDowell *et al.* 2016). Fertilizers P could directly influence the concentration of soil Pi through the input of orthophosphate and organic compounds, or indirectly through interaction with soil compounds (Bünemann *et al.* 2008; Yan *et al.* 2016; van der Bom *et al.* 2019). For instance, application of organic fertilizer increased the soil organic matter (SOM) concentration, which influenced the dissolution and desorption of P minerals by changing soil pH (Whalen *et al.* 2000; Yan *et al.* 2018; Nobile *et al.* 2020), and altered the availability of P (McDowell and Sharpley 2003; Sharpley *et al.* 2004). Increased soil pH promoted P desorption from Fe and Al oxides or hydroxides in acidic soil whereas decreased soil pH in calcareous soils contributed to the dissolution and desorption of P minerals, and therefore, increased the concentrations of phosphates in soil solution (Whalen *et al.* 2000; McDowell and Sharpley 2003; Sharpley *et al.* 2004; Eichler-Löbermann *et al.* 2007; Yan *et al.* 2018). Further, the interactions between SOM and metal oxides could also affect the processes wherein phosphate salts bind to soil and influence the availability of different P fractions (Fink *et al.* 2016; Kramer and Chadwick 2018; Sowers *et al.* 2018). Investigation of the contribution of different soil properties (e.g., SOM, pH, and metal oxide contents) to changes in soil P fractions is important for elucidating the influence of different fertilizers and soil layers on the soil P fractions and their availability (Mundus *et al.* 2017; Yan *et al.* 2018; Wang *et al.* 2021). However, until recently, only a few comprehensive quantitative studies have investigated these aspects.

Northeast China is a major grain-producing region that mainly has black soils with higher fertility than most regions of China (Kang *et al.* 2016). A comprehensive understanding of P transformation processes in black soil profiles is important to enhance the utilization efficiency of soil P, to reduce P fertilizer input, and to mitigate soil P losses to the environment. Long-term field experiments provide a resource for investigation of P availability

and the fixing capacity of P fertilizer in soil. Thus, the objectives of the present study were to determine the following: (1) the effect of long-term fertilization on P availability in a black soil and the environmental risk of P loss; (2) the vertical distribution characteristics of different P fractions and soil properties in black soil profile; and (3) the main soil factors affecting the P fractions of different black soil layers by redundancy analysis (RDA) of soil properties and P fractions.

2. Materials and methods

2.1. Study site and experimental design

A long-term field experiment with maize starting in 1990 was conducted at the Chinese National Soil Fertility and Fertilizer Efficiency Monitoring Base for Black Soil (124°48′34′′E, 43°30′23′′N, altitude 222 m above sea level) at Gongzhuling, Jilin Province, China. The local climate is temperate continental monsoon, with an average annual rainfall of 590 mm. The temperature increases from January (minimum average: –35°C) to July (maximum average: 34°C). The soil is a loamy clay (Luvic Phaeozem in the FAO soil system) with 5.5% coarse sand (0.2–2.0 mm), 32.8% fine sand (0.02–0.2 mm), 29.9% silt (2–20 μm), and 31.1% clay (<2 μm). Table 1 shows the soil properties before the establishment of the field trial in 1989.

For the current study, the following four fertilization treatments were selected: no fertilizer (CK), inorganic NK fertilizer (NK), inorganic NPK fertilizer (NPK), and NPK plus manure (NPKM). Urea, diammonium phosphate and potassium sulfate were used as the N, P, and K fertilizers. The organic fertilizers were pig manure (1990–2004) and cattle manure (2005–2018). The precise quantities of fertilizer used in each treatment are shown in Table 2. The complete dose of manure, P, and K, and one-third of the N fertilizer was applied before sowing of the crop, and the remaining two-thirds of the N fertilizer was applied below 10 cm soil depth at the maize jointing stage. Each treatment plot covered 400 m² (57.18 m×7 m). A randomized block design with three replicates for each treatment was used for the experiment. Throughout the experiment, a continuous maize monoculture was used as the cropping system. Maize (60 000 plants ha⁻¹) was

planted by ridge-tilling in late April and harvested in late September in each test year. The grains and straws of maize were manually harvested, air-dried, and weighted to estimate crop yield. No irrigation was provided to the crops in the growth period. The above-ground residues were removed following the harvest.

2.2. Soil sampling

Topsoil samples (0–20 cm) were collected from 1990 to 2017 from each replicate, and deeper soil samples were collected at three depths (0–20, 20–40, and 40–60 cm) in 2018 after crop harvesting. At each sampling, five to seven soil samples were collected with an auger (10 cm in diameter) using an "S" shaped sampling pattern. Field-moist samples were gently broken apart, mixed thoroughly, air-dried, and passed through a 2-mm sieve.

2.3. Soil analysis

SOM content was measured using vitriol acid-potassium dichromate oxidation (Skjemstad and Baldock 2007). Soil pH was measured by a glass electrode meter based on a soil/distilled water (w/v) mixture of 1:2.5 (Lu 1999). Total P content was determined using the H_2SO_4-$HClO_4$ method (Bao 2010). The Olsen method was used to determine the Olsen-P content (Olsen et al. 1954). $CaCl_2$-P content was extracted with 0.01 mol L⁻¹ $CaCl_2$ solution at 1:5 soil/reagent ratio (25°C and shaken 15 min) and determined with the molybdate-ascorbic acid (Bai et al. 2013). $CaCO_3$ content was measured by acid neutralization (Richards 1954). Free Fe and Al oxide (Fe_d and Al_d), amorphous Fe and Al oxide (Fe_o and Al_o), and organic-bound Fe and Al oxide (Fe_p and Al_p) were extracted using $Na_2S_2O_4$-$Na_3C_6H_5O_7$-$NaHCO_3$ (DCB), 0.2 mol L⁻¹ ammonium oxalate (pH=3), and 0.1 mol L⁻¹ sodium pyrophosphate diphosphate (pH=10), respectively, and were then determined using inductively coupled plasma optical emission spectroscopy (ICP-OES) (Lu 1999). Soil samples were extracted using Mehlich-3 extracting solution (0.2 mol L⁻¹ CH_3COOH+0.25 mol L⁻¹ NH_4NO_3+0.015 mol L⁻¹ NH_4F+0.013 mol L⁻¹ HNO_3+0.001 mol L⁻¹ EDTA) by shaking for 5 min in a 1:10 soil/reagent ratio to determine Ca, Mg, Fe, and Al. All elements in Mehlich-3 solutions were determined by

Table 1 Physical and chemical properties of soil samples collected before the establishment of the field trial in 1989

Soil depth (cm)	pH	Bulk density (g cm⁻³)	Soil organic matter (g kg⁻¹)	Total N (g kg⁻¹)	Total P (g kg⁻¹)	Total K (g kg⁻¹)	Olsen-P (mg kg⁻¹)	Available K (mg kg⁻¹)
0–20	7.6	1.19	20	1.34	0.61	16.36	11.8	190
20–40	7.5	1.27	14.4	1.02	0.59	14.94	6.77	181
40–60	7.5	1.33	6.3	0.58	0.44	15.94	3.14	185

Table 2 Mean annual nitrogen (N), phosphorus (P) and potassium (K) inputs under four long-term fertilization treatments in black soil

Treatment[1]	Inorganic fertilizer (kg ha^{-1})[2]			Organic fertilizer (kg ha^{-1})[2]		
	N	P	K	N	P	K
CK	0	0	0	0	0	0
NK	165	0	68	0	0	0
NPK	165	36	68	0	0	0
NPKM	50	36	68	115	39	77

[1] CK, no fertilizer; NK, nitrogen, and potassium fertilizer application; NPK, inorganic nitrogen, phosphorous and potassium fertilizer application; NPKM, NPK plus manure.
[2] The amount of nitrogen (N), phosphorus (P) and potassium (K) contained in the added inorganic or organic fertilizer. Urea, superphosphate and potassium sulfate were the sources of inorganic N, P and K fertilizer, respectively. The organic fertilizers were pig manure (1990–2004) and cattle manure (2005–2018).

using ICP-OES (Mehlich 2008).

A modified Hedley sequential extraction method, based on the assumption that chemical extractants selectively dissolve discrete groups of P compounds, was used to determine the different P fractions (Hedley et $al.$ 1982; Sui et $al.$ 1999; Carter and Gregorich 2007). Briefly, a soil sample (1.00 g) was sequentially extracted with an anion exchange resin membrane (resin-P), 0.5 mol L^{-1} NaHCO$_3$ at pH 8.5 (NaHCO$_3$-P), 0.1 mol L^{-1} NaOH (NaOH-P), 1 mol L^{-1} HCl (dil.HCl-Pi), 10 mL concentrated HCl (conc. HCl-P), and concentrated H$_2$SO$_4$-H$_2$O$_2$ digestion at 360°C (residual P). At each extraction step, the suspension was shaken for 16 h at 200 r min^{-1} at 25°C, centrifuged at 25 000×g for 10 min at 4°C, and filtered through a 0.45-mm filter membrane. The concentrations of Pi extracted by resin, NaHCO$_3$, NaOH, and HCl were determined using a colorimetric method. The concentrations of Pt (sum of Pi and Po) extracted by NaHCO$_3$, NaOH, and concentrated HCl were determined using molybdate colorimetry following digestion with ammonium persulfate (Murphy and Riley 1962; Martin et $al.$ 1999). The contents of Po (NaHCO$_3$-Po, NaOH-Po, and conc.HCl-Po) were calculated as the difference between Pt and Pi. According to the bioavailability of individual P fractions to plants (Motavalli and Miles 2002; Carter and Gregorich 2007; Yang and Post 2011), labile P, the sum of resin-P and NaHCO$_3$-P (Pi+Po), is considered readily available to plants; while partially labile P, the sum of NaOH-P (Pi+Po) and dil.HCl-Pi, which is bound with secondary Fe and Al minerals and primary calcium minerals is less available but may be utilized by plants after it is released by weathering (Cross and Schlesinger 1995; Yang and Post 2011; Hou et $al.$ 2016) . Other P fractions such as conc.HCl-P (Pi+Po) and residual P form the stable P pool

which are the least available to plants because of their particularly low solubility (Hedley et $al.$ 1982; Condron and Newman 2011).

2.4. Calculation

The P uptake and P balance are calculated as follows:
P uptake (kg ha^{-1})=Crop yield (kg ha^{-1})×Crop P content (%)+Straw yield (kg ha^{-1})×Straw P content (%) (1)
P balance=P input–P uptake (2)
The phosphorus activation coefficient (PAC) was used to characterize the availability of soil P and was calculated using the content of total P and Olsen-P as follows (Huang et $al.$ 2016):
PAC (%)=Olsen-P content (mg kg^{-1})/(Total P content (g kg^{-1})×1 000)×100 (3)
The environment threshold was determined by the relationship between Olsen-P (x) and CaCl$_2$-P (y) using a two-segment linear model in Sigma-Plot 10.0. The model was calculated by eqs. (4) and (5) as follows (Bai et $al.$ 2013):
$y_1=a_1x+b_1$ $x<T$ (4)
$y_2=a_2x+b_2$ $x≥T$ (5)
where a_1, a_2, b_1, and b_2 are linear regression coefficients of the equations and T is the critical level for Olsen-P.

2.5. Statistical analysis

The means and standard errors of the crop yield, P parameters and other soil properties were determined All data of measured variables were tested for normality and homogeneity before performing analysis of variance (ANOVA) using the SPSS statistical package (SPSS version 20.0, IBM Institute, USA). For each variable, one-way ANOVA was used to assess whether there were significant differences among different treatments at the same soil depth, or among different soil depths with the same treatment. Multi-way ANOVA was used to assess the significant effects of different fertilizations, soil layers, and their interactions on the measured variables. Mean separation was conducted using Duncan's HSD tests ($P<0.05$). To visualize how common chemical soil properties (SOM, pH, metallic oxides) influence each soil P fraction, RDA (Vegan package in R Software) was used to determine the correlation between soil P fractions and soil properties for different soil depths and fertilization treatments.

3. Results

3.1. Crop yields, P uptake, and apparent P balance

Long-term application of P fertilizer significantly increased

Table 3 Soil total P, Olsen-P, annual plant P uptake, P balance, and crop yield in black soil for the period of 1990–2000, 2001–2010, and 2011–2018 under four long-term fertilization treatments

Year	Treatment[1]	Total P (g kg⁻¹)	Olsen-P (mg kg⁻¹)	P uptake (kg ha⁻¹)	P balance (kg ha⁻¹)	Crop yield (t ha⁻¹)
1990–2000	CK	0.55±0.02 Aa	8.24±0.92 Ca	18±0.9 Ba	–18±1.0 Ca	3.9±0.2 Ba
	NK	0.54±0.03 Aa	9.95±0.76 BCa	39±1.9 Aa	–39±2.1 Da	8.7±0.4 Aa
	NPK	0.56±0.03 Aa	16.05±1.8 ABc	40±2.3 Ab	–5±0.3 Ba	9.2±0.5 Aa
	NPKM	0.62±0.02 Ac	19.30±3.21 Ac	38±2.6 Ac	49±2.9 Aa	8.6±0.6 Ab
2001–2010	CK	0.54±0.03 Ba	5.28±0.65 Cb	14±2.0 Ca	–14±2.0 Ca	3.1±0.4 Ca
	NK	0.49±0.02 Ba	6.01±0.64 Cb	36±1.9 Ba	–36±1.9 Da	8.1±0.4 Ba
	NPK	0.59±0.01 Ba	29.45±3.13 Bb	41±2.4 ABb	–5±0.2 Ba	9.3±0.5 ABa
	NPKM	1.12±0.05 Ab	137±11.54 Ab	44±1.9 Ab	43±2.3 Aab	9.9±0.4 Ab
2011–2018	CK	0.46±0.03 Ca	4.36±0.47 Cb	15±1.3 Ca	–15±1.3 Ba	3.4±0.3 Ca
	NK	0.40±0.04 Ca	5.95±0.27 Cb	32±2.8 Ba	–32±2.8 Ca	7.3±0.7 Ba
	NPK	0.62±0.02 Ba	47.42±2.43 Ba	48±1.3 Aa	–12±1.3 Bb	10.7±0.3 Aa
	NPKM	1.31±0.04 Aa	174±7.11 Aa	52±1.0 Aa	36±1.2 Ab	11.5±0.3 Aa

[1] CK, no fertilizer; NK, nitrogen, and potassium fertilizer application; NPK, inorganic nitrogen, phosphorous and potassium fertilizer application; NPKM, NPK plus manure.
Data are mean±SE (n=3). Within the same sampling period, values with different uppercase letters indicate significant differences among treatments ($P<0.05$). Within the same fertilizer treatment, values with different lowercase letters indicate significant differences among sampling period ($P<0.05$).

P uptake and crop yield (Table 3). Crop yield and P uptake during the fertilization period of 2011–2018 were greater than during 1990–2000 with NPK and NPKM treatments. During the complete fertilization period, the annual apparent P balance was negative in CK, NK, and NPK treatments, the greatest deficit being observed in NK treatment. Combined application of manure and mineral fertilizer resulted in a P surplus, which was significantly decreased with increased fertilization period in the NPKM treatment.

3.2. P availability under the long-term fertilization

Soil Olsen-P concentration tended to increase in NPK and NPKM treatments under long-term fertilization (Table 3),
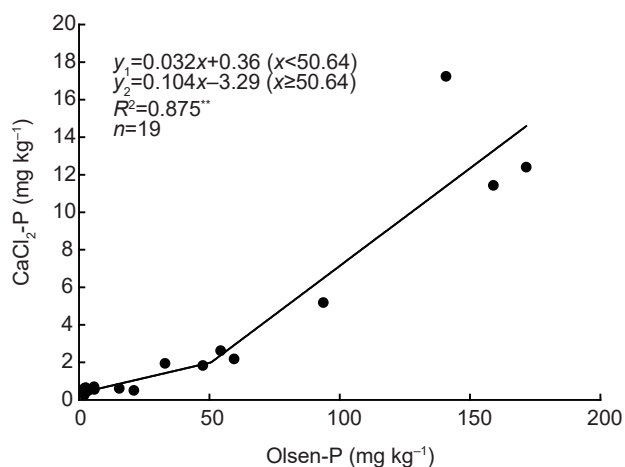

Fig. 1 The change point between soil Olsen-P and CaCl₂-P for black soil at Gongzhuling. **, $P<0.01$.

the increase being greater in the NPKM treatment than in the NPK treatment. The concentration of Olsen-P increased 3.6 and 2.7 times in the NPKM treatment, respectively, compared to that in the NPK treatment during the fertilization period of 2001–2010 and 2011–2018.

A positive correlation was obtained between soil Olsen-P and CaCl₂-P. Further, CaCl₂-P increased rapidly when Olsen-P was greater than 50.6 mg kg⁻¹ (Fig. 1).

3.3. Total P, Olsen-P, and P activation coefficient in the 0–60 cm soil profile

After 29 years of continuous high P input, the concentration of total P was significantly increased, by 1.40 times in the NPKM treatment compared with its initial value in the 0–20 cm soil depth (Fig. 2-A). Soil treated with P had significantly increased Olsen-P and PAC values compared with their initial values in the 0–20 cm soil depth (Fig. 2-B and C). The Olsen-P and PAC values in the NPKM treatment were 1.8–5.9 and 0.6–2.0 times higher, respectively, than those in the NPK treatment over the full soil depth (0–60 cm). For the NPK and NPKM treatments, the concentrations of Olsen-P were 2.6 and 3.0 times, and the PAC values in 0–20 cm depth were 1.7 and 1.3 times those in the 40–60 cm soil depth ($P<0.05$) (Fig. 2-B and C). The Olsen-P concentration in the NPKM treatment ranged from 65 to 195 mg kg⁻¹ and exceeded the critical value of soil Olsen-P at 50.6 mg kg⁻¹ in the 0–60 cm soil profile.

3.4. P fractions in the 0–60 cm soil profile

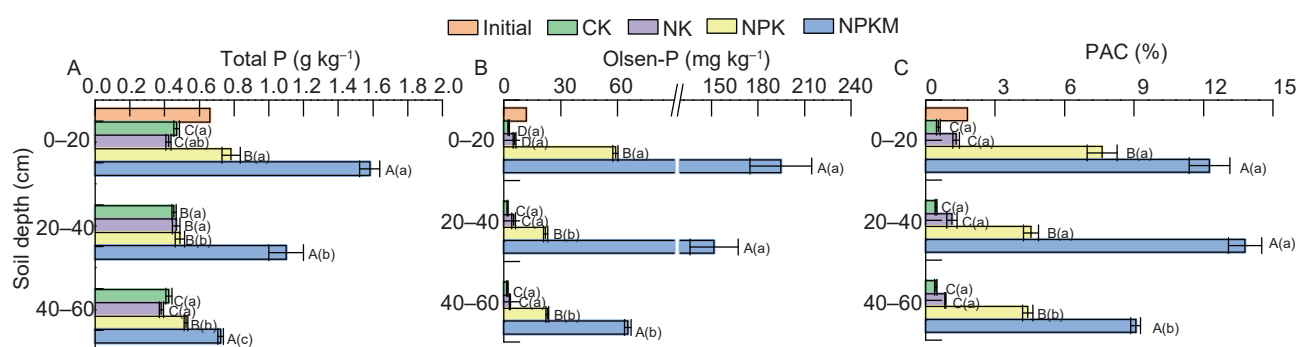The concentrations of labile P and partially labile P in the

Fig. 2 Total P and Olsen-P concentrations, and phosphorus activation coefficient (PAC) values in 1990 (initial) and in 2018 under long-term different fertilization treatments. Initial, soil samples collected in CK treatment in 1990; CK, no fertilizer; NK, inorganic nitrogen, and potassium fertilizer application; NPK, inorganic nitrogen, phosphorous and potassium fertilizer application; NPKM, NPK plus manure (pig manure from 1990 to 2004, and cattle manure from 2005 to 2018). Within the same soil depth, values with different uppercase letters indicate significant differences among treatments (*P*<0.05). Within the same fertilizer treatment, values with different lowercase letters indicate significant differences among soil depths (*P*<0.05). Error bars indicate standard errors of the mean value (*n*=3).
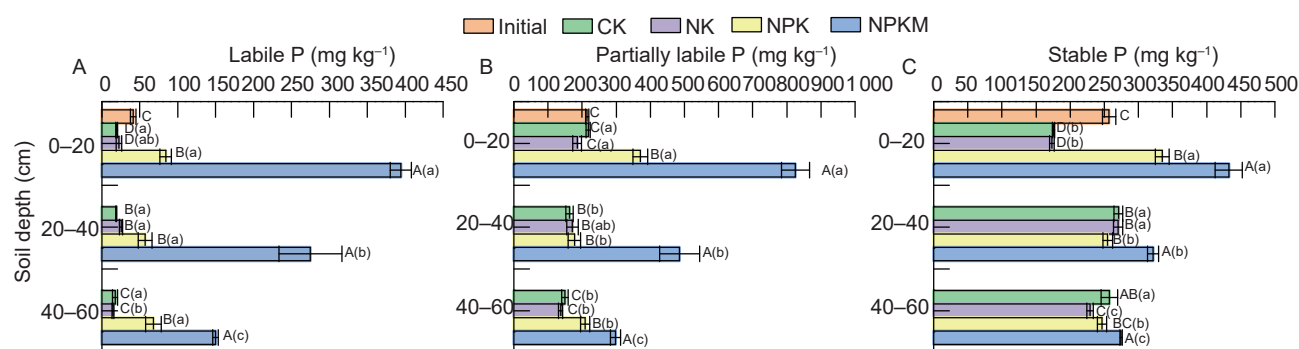

Fig. 3 Concentrations of labile P, partially labile P, and stable P in 1990 (initial) and in 2018 under different long-term fertilization treatments. Initial, soil samples collected in CK treatment in 1990; CK, no fertilizer; NK, nitrogen, and potassium fertilizer application; NPK, inorganic nitrogen, phosphorous and potassium fertilizer application; NPKM, NPK plus manure (pig manure from 1990 to 2004, and cattle manure from 2005 to 2018). Labile P was the sum of resin-P, NaHCO$_3$-Pi, NaHCO$_3$-Po; partially labile P was the sum of NaOH-Pi, NaOH-Po, dil.HCl-Pi; stable P was the sum of conc.HCl-Pi, conc.HCl-Po and residual P. Within the same soil depth, values with different uppercase letters indicate significant differences among treatments (*P*<0.05). Within the same fertilizer treatment, values with different lowercase letters indicate significant differences among soil depths (*P*<0.05). Error bars indicate standard errors of the mean value (*n*=3).

soil treated with P fertilizers were significantly greater than in the CK and NK treatments at the 0–20 and 40–60 cm soil depths, especially in NPKM treatment (Fig. 3-A and B). The concentrations of labile P and partially labile P in the NPKM treatment were 2.2–8.1 and 1.4–2.7 times higher, respectively, than in the NPK treatment in the 0–60 cm soil profile. A significant decreasing trend was observed in the concentrations of labile P, partially labile P, and stable P with increasing soil depth in the NPKM treatment (Fig. 3). The concentrations of labile P, partially labile P, and stable P in the 40–60 cm layer were 62, 64, and 36% lower, respectively, than in the 0–20 cm layer in the NPKM treatment.

Inorganic P (Pi) (sum of resin-P, Pi of each soil P

fraction, and residual P) was the dominant P fraction and accounted for 74–92% of the sum of all P fractions (Pt) in the soil profile (Fig. 4). In the NPK treatment, residual P made up the highest proportion, following by dil.HCl-Pi, whereas in the NPKM treatment, dil.HCl-Pi was the dominant fraction. Compared to the CK and NK treatments, the concentrations of resin-P, NaHCO$_3$-Pi, and NaOH-Pi and their proportion to Pt were greater in soil treated with P fertilizer in each soil depth, especially in the NPKM treatment (Fig. 4-A, B and D; Appendix A). In comparison with NPK treatment, NPKM treatment significantly increased the concentrations and proportions of resin-P, NaHCO$_3$-Pi and dil.HCl-Pi in the 0–60 cm soil profile (Fig. 4-A, B and F; Appendix A). In the
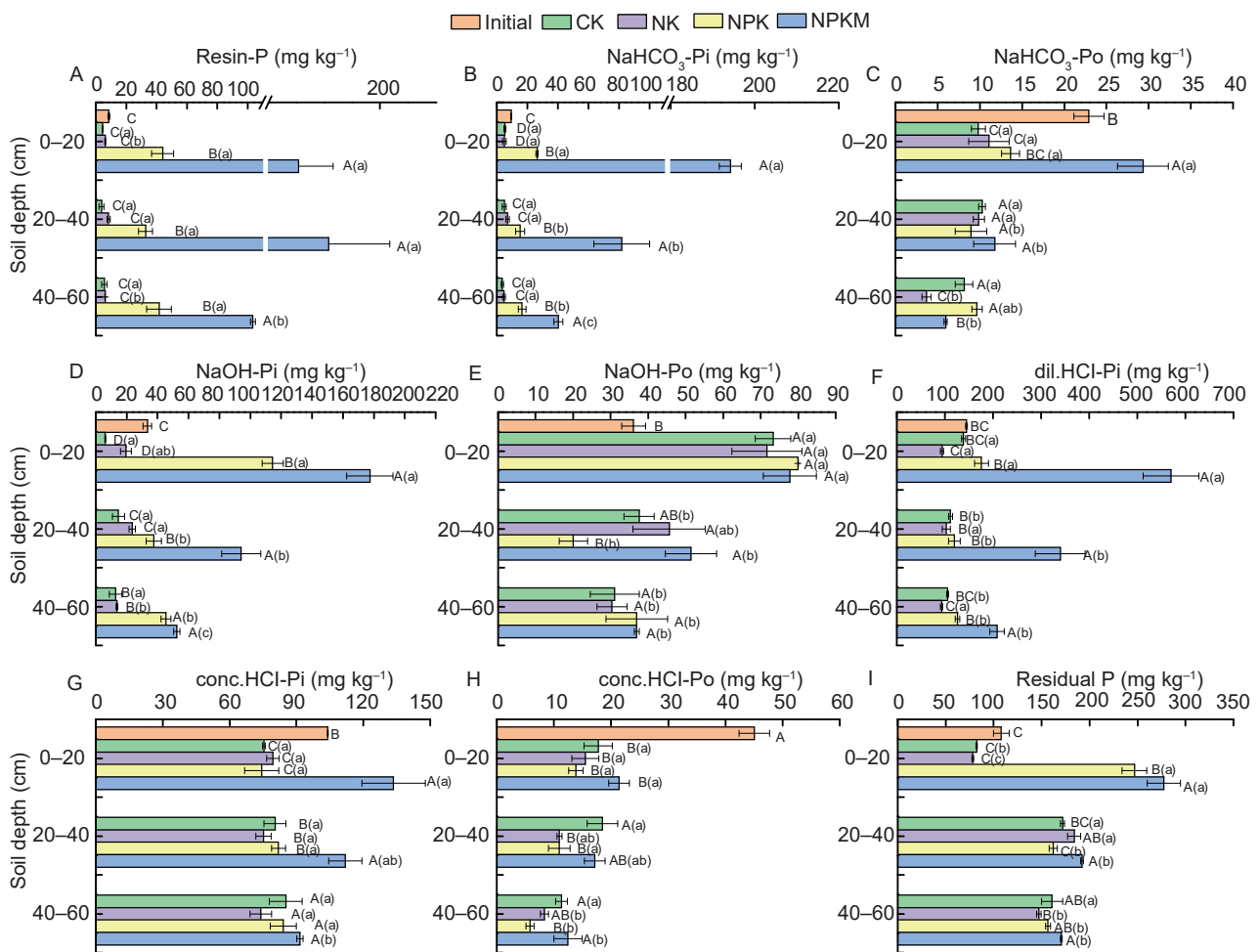
Fig. 4 Concentrations of each P fraction in 1990 (initial) and in 2018 under different long-term fertilization treatments. Initial, soil samples collected in CK treatment in 1990; CK, no fertilizer; NK, nitrogen, and potassium fertilizer application; NPK, inorganic nitrogen, phosphorous and potassium fertilizer application; NPKM, NPK plus manure (pig manure from 1990 to 2004, and cattle manure from 2005 to 2018). Pi, inorganic P; Po, organic P. Within the same soil depth, values with different uppercase letters indicate significant differences among treatments ($P<0.05$). Within the same fertilizer treatment, values with different lowercase letters indicate significant differences among soil depths ($P<0.05$). Error bars indicate standard errors of the mean value ($n=3$).

NPK treatment, with increasing soil depth, a significant decreasing trend was observed in the concentrations of NaHCO$_3$-Pi, NaOH-Pi, NaOH-Po, dil.HCl-Pi, and residual P (Fig. 4-B, D, E, F and I).

3.5. Soil properties in the 0–60 cm soil profile

Different long-term fertilization treatments had a distinct impact on soil properties (Table 4). The concentrations of SOM and M3-Mg in soil treated with NPKM were 0.3–0.9 and 0.1–0.7 times greater, respectively, than in the other treatments in the 0–60 cm soil profile. With increasing soil depth, significant decreases in SOM and M3-Mg concentrations were observed in the NPKM treatment. The concentrations of Fe$_p$, Al$_p$, Fe$_o$, and Al$_o$ in the NPKM treatment were significantly greater by

1.4, 0.2, 0.5, and 0.1 times, respectively, than in the CK treatment in the 0–20 cm soil layer. Compared to the CK treatment, the NPKM treatment had significantly lower concentrations of CaCO$_3$, Fe$_d$, and Al$_d$ in each soil layer, while the pH value was significantly lower in the NK and NPK treatments in the 0–20 and 20–40 cm layers.

The results of multi-way variance analysis indicated that pH, SOM, CaCO$_3$, M3-Ca, M3-Al, M3-Fe, Fe$_d$, Al$_d$, Fe$_o$, and Fe$_p$ were affected by the interaction between soil depth and fertilization. M3-Mg, Al$_o$, and Al$_p$ were only influenced by fertilization ($P<0.05$) (Table 4).

3.6. Influence of soil properties on P fractions

SOM, Fe$_o$, Al$_o$, Fe$_p$, and Al$_p$ showed strong positive correlations with highly active P fractions (resin-P,

Table 4 Soil properties in black soil samples collected in 1990 (initial, 0–20 cm only) and in 2018 under four long-term fertilization treatments at three soil depths[1]

Soil depth (cm)	Treatment[2]	pH	SOM (g kg⁻¹)	CaCO₃ (g kg⁻¹)	M3-Ca (g kg⁻¹)	M3-Mg (g kg⁻¹)	M3-Al (g kg⁻¹)	M3-Fe (g kg⁻¹)	Fe$_d$ (g kg⁻¹)	Al$_d$ (g kg⁻¹)	Fe$_o$ (g kg⁻¹)	Al$_o$ (g kg⁻¹)	Fe$_p$ (g kg⁻¹)	Al$_p$ (g kg⁻¹)
0–20	Initial	7.40±0.3 A	21.5±1.02 C	14.6±0.4 C	4.55±0.04 A	0.35±0.00 B	1.20±0.01 A	0.22±0.01 B	9.83±0.04 A	2.28±0.01 A	2.84±0.03 C	3.04±0.00 D	0.12±0.00 E	0.53±0.00 D
	CK	7.66±0.1 Aa	23.4±0.3 BCa	19.7±0.6 Aa	4.02±0.06 BCa	0.30±0.03 Ba	1.15±0.04 ABa	0.18±0.00 Ca	9.74±0.07 Ab	2.14±0.03 Ba	2.84±0.01 Ca	3.81±0.01 Ba	0.20±0.00 Da	0.58±0.02 Ca
	NK	5.40±0.1 Cc	21.2±2.1 Cab	17.6±0.8 Ba	3.93±0.06 Ca	0.34±0.00 Ba	1.18±0.04 Aa	0.22±0.01 Ba	9.48±0.06 Bc	2.21±0.03 ABb	3.81±0.01 Ba	3.65±0.06 Ca	0.27±0.01 Ca	0.64±0.02 Ba
	NPK	6.11±0.2 Ba	26.7±0.1 Ba	18.3±0.5 ABab	4.17±0.01 Bb	0.28±0.01 Ba	1.18±0.03 Aa	0.25±0.00 Aa	9.54±0.06 Bb	2.12±0.04 Bb	4.42±0.06 Aa	3.80±0.01 Ba	0.36±0.00 Ba	0.68±0.01 ABa
	NPKM	7.41±0.04 Aa	40.3±1.9 Aa	14.5±0.2 Ca	3.89±0.01 Cb	0.47±0.00 Aa	1.04±0.03 Bab	0.24±0.01 Aa	9.12±0.06 Ca	1.66±0.02 Ca	4.36±0.08 Aa	4.09±0.01 Aa	0.48±0.01 Aa	0.71±0.01 Aa
20–40	CK	7.41±0.3 Aa	22.3±1.4 BCa	21.3±0.3 Aa	4.12±0.02 Ba	0.36±0.01 Ba	1.13±0.01 Aa	0.19±0.00 Ba	10.1±0.06 Ba	2.20±0.04 Ba	3.14±0.02 Ba	3.78±0.01 Aa	0.17±0.01 Ca	0.55±0.04 Ba
	NK	6.22±0.2 Bb	24.8±0.2 BCa	18.2±1.0 ABa	3.80±0.1 Ca	0.34±0.00 Ba	1.17±0.04 Aa	0.24±0.02 Aa	10.4±0.07 Aa	2.39±0.03 Aa	3.10±0.05 Bb	3.45±0.2 Aa	0.26±0.01 Ba	0.64±0.01 ABa
	NPK	6.33±0.2 Bab	20.6±1.2 Cb	22.0±1.9 Aa	4.80±0.02 Aa	0.28±0.00 Ca	0.94±0.07 Bb	0.23±0.02 ABa	9.87±0.03 Ca	2.26±0.04 Ba	3.73±0.07 Ab	3.65±0.09 Aab	0.24±0.01 Bb	0.63±0.02 ABab
	NPKM	6.54±0.04 Bb	32.4±0.5 Ab	14.6±0.6 Ba	3.98±0.04 BCab	0.41±0.02 Ab	1.03±0.03 ABb	0.18±0.01 Bb	8.47±0.06 Db	1.70±0.03 Cb	3.97±0.1 Aa	3.89±0.1 Aa	0.36±0.02 Ab	0.71±0.02 Aa
40–60	CK	7.34±0.4 Aa	15.0±0.2 Bb	19.9±0.7 Aa	3.98±0.01 Ba	0.35±0.01 ABa	1.10±0.0 ABa	0.17±0.00 Ba	10.2±0.06 Aa	2.21±0.04 Aa	3.03±0.2 Ba	3.49±0.03 Bb	0.16±0.03 Aa	0.59±0.04 Aa
	NK	6.80±0.2 Aa	17.5±0.6 Bb	18.1±0.3 Ba	4.10±0.1 Ba	0.32±0.03 BCa	1.05±0.01 Ba	0.15±0.00 Bb	10.0±0.05 Bb	2.19±0.04 Ab	3.30±0.1 ABb	3.45±0.2 Ba	0.18±0.01 Ab	0.61±0.01 Aa
	NPK	6.72±0.04 Aa	17.3±0.6 Bc	16.6±0.7 BCb	4.91±0.06 Aa	0.27±0.01 Ca	1.02±0.03 Bab	0.22±0.01 Aa	9.56±0.08 Cb	2.17±0.03 Aab	3.40±0.2 ABb	3.48±0.08 Ab	0.20±0.02 Ab	0.60±0.03 Ab
	NPKM	6.65±0.1 Ab	22.5±1.4 Ac	15.9±0.3 Ca	4.17±0.09 Ba	0.39±0.01 Ab	1.15±0.03 Aa	0.19±0.02 ABb	8.68±0.05 Db	1.85±0.03 Ba	4.05±0.4 Aa	3.99±0.1 Aa	0.23±0.01 Ac	0.65±0.01 Ab
Soil depth		*	*	*	*	NS	*	*	*	*	*	NS	*	NS
Fertilization		**	**	**	**	NS	**	**	**	**	**	NS	**	NS
Soil depth×Fertilization		**	**	**	**	NS	**	**	**	**	**	NS	*	NS

1) SOM, soil organic matter; Fe$_d$, free iron oxide; Al$_d$, free aluminum oxide; Fe$_o$ and Al$_o$, amorphous Fe and Al oxides; Fe$_p$ and Al$_p$, organic-bound Fe and Al oxides; M3-Ca, M3-Mg, M3-Fe and M3-Al, Ca, Mg, Fe and Al extracted by Mehlich-3 extraction.

2) Initial, soil samples collected in CK treatment in 1990; CK, no fertilizer; NK, nitrogen, and potassium fertilizer application; NPK, inorganic nitrogen, phosphorous and potassium fertilizer application; NPKM, NPK plus manure (pig manure from 1990 to 2004, and cattle manure from 2005 to 2018). Data are mean±SE (n=3). Within the same soil depth, values with different uppercase letters indicate significant differences among treatments (P<0.05). Within the same fertilizer treatment, values with different lowercase letters indicate significant differences among soil depths (P<0.05).

NaHCO₃-Pi, NaHCO₃-Po, NaOH-Pi and dil.HCl-Pi), whereas, Fe$_d$, Al$_d$, and CaCO₃ showed negative correlations with these P fractions at each soil depth (Appendix B). The results obtained from RDA showed that the soil properties could explain 95, 92, and 91% of the total variance in the P fraction parameters at the 0–20, 20–40 and 40–60 cm soil depths, respectively (Fig. 5). SOM, M3-Fe, and Al$_p$ at 0–20 cm, Fe$_d$ and pH at 20–40 cm, and CaCO₃, Al$_d$, and M3-Ca at 40–60 cm showed significant effects on the compositions of the P fractions (P<0.05). Specifically, SOM (74%), Fe$_d$ (73%), and CaCO₃ (64%) were the main factors that contributed to the observed differences in the P fractions in the 0–20, 20–40, and 40–60 cm soil depths, respectively (Appendix C).

4. Discussion

4.1. Availability and potential risk of P loss under long-term fertilization

Rational P input is the key to obtaining high-yielding crop production and reducing the risk of P loss (Zhang 2014; Qin et al. 2020). Over 29 years of fertilization higher crop yield and soil Olsen-P levels (but lower the environmental threshold) in the NPK than no-P treatments indicated that a mineral P input of 36 kg ha⁻¹ was acceptable in black soil (Table 3 and Fig. 2). In this study, no significant difference in crop yield was found between NK and NPK treatments during the fertilization periods of 1990–2000 and 2001–2010 (Table 3). A possible reason for this is that N and K addition may increase plant P uptake and root biomass (Yuan and Chen 2012; Liu et al. 2017; Wang et al. 2018; Schleuss et al. 2020). Another reason may be that there was already enough P in the soil and the amount of P applied was not sufficient to change crop yield (Wu et al. 2020). The P input from the NPKM treatment was twice that provided by the NPK treatment, however no significant difference in crop yield was observed between the two treatments during the
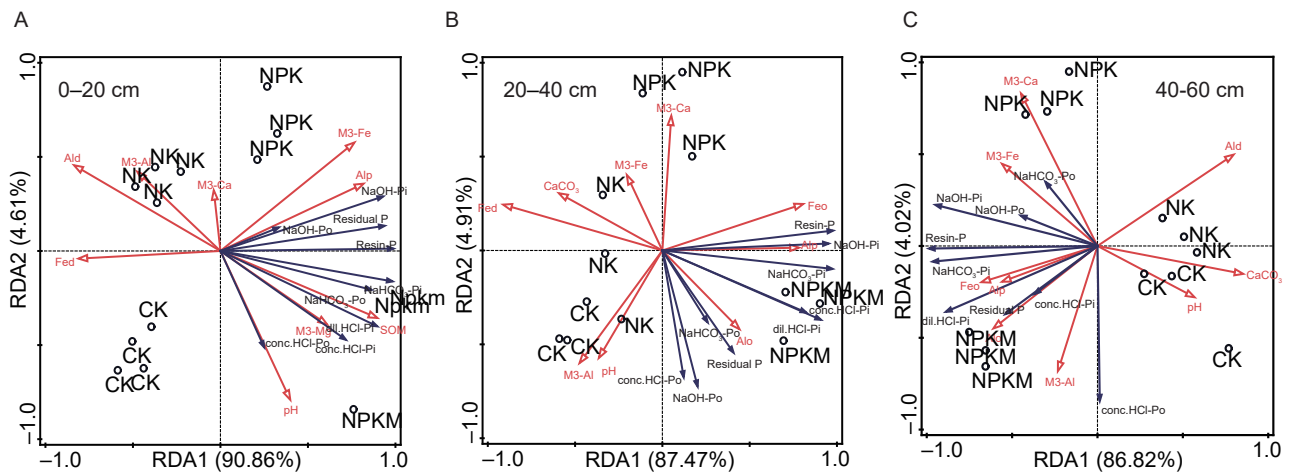
Fig. 5 Redundancy analysis (RDA) triplots showing the relationship between soil properties and P fractions under different long-term fertilization treatments in 2018. SOM, soil organic matter; Fe_d and Al_d, free Fe and Al oxides; Fe_o and Al_o, amorphous Fe and Al oxides; Fe_p and Al_p, organic-bound Fe and Al oxides; M3-Ca, M3-Mg, M3-Fe and M3-Al, Ca, Mg, Fe and Al extracted by the Mehlich-3 extraction. CK, no fertilizer; NK, nitrogen, and potassium fertilizer application; NPK, inorganic nitrogen, phosphorous and potassium fertilizer application; NPKM, NPK plus manure (pig manure from 1990 to 2004, and cattle manure from 2005 to 2018).

three periods (Table 3). This lack of difference may be because the critical value of Olsen-P in the Gongzhuling soil was 13.3 mg kg^{-1}; above this value, crop yield is little influenced by additional P and the extra P would likely remain in the soil (Wu *et al.* 2020). A previous study showed that fertilizer application to black soil with a relatively high Olsen-P could be reduced by 20% and still meet the P demand to achieve high yields, maintain adequate soil Olsen-P levels and an effective P supply to plants, and ensure efficient utilization of P fertilizer (Wu *et al.* 2016).

After 29 years of excessive P input in the NPKM treatment, soil Olsen-P ranged from 65 to 195 mg kg^{-1} in the soil profile layers, levels that were far beyond the threshold for environmental purposes of 50.6 mg kg^{-1} in black soil (Fig. 1). The threshold of 50.6 mg kg^{-1} was similar to the finding of Bai *et al* (2013), who determined a critical value of 52.0 mg kg^{-1} in black soil. The high plant-available P levels retained by the soil, may result in potentially high P leaching losses from soils treated with a combination of manure and mineral fertilizer (Pizzeghello *et al.* 2014; Zhang *et al.* 2019; Qin *et al.* 2020). Labile and partially labile Pi (resin-P, NaHCO₃-Pi, NaOH-Pi, and dil.HCl-Pi) were the main P fractions increased by NPKM treatment (Fig. 3). These Pi fractions are mainly water soluble or colloidal P with strong mobility, and are easily leached into the water (Heathwaite *et al.* 2005; Liu 2013).

Generally, higher PAC values are associated with higher conversion rates of total P to available P (Huang *et al.* 2016). The PAC value in the NPKM treatment was

1.6–3.0 times that in the NPK treatment, indicating that the supply of Olsen-P capacity was better sustained by NPKM than by NPK treatment. This agreed with previous studies showing that a higher P availability was observed in soil with manure than with mineral fertilizer (Nest *et al.* 2016). The possible reasons for the differences between the NPK and NPKM treatments are as follows. The labile and partially labile Pi concentrations and their proportion to Pt were significantly higher in the NPKM than in the NPK treatment, thus increasing the levels of available P. Further, different P fractions in manure are usually used as potential factors to determine the effect of manure on P availability (Pizzeghello *et al.* 2016; Nobile *et al.* 2020). The primary type of P in pig and cattle manures is inorganic P, especially inorganic orthophosphate (54% and 85% in these manures, respectively) (Zhan 2016), indicating that the application of organic fertilizer could lead to a direct increase in soil available P (Qin *et al.* 2020). Furthermore, the long-term addition of manure clearly decreased the soil P sorption strength for mineral soil particles possibly by releasing organic acids as reported previously, thus increasing the soil available P concentration (Lemming *et al.* 2019; Wang *et al.* 2019).

4.2. Change of soil P fractions in response to long-term different fertilization

Resin-P represents the soil solution P pool, which is easily accessed by plants (Tiessen *et al.* 1984). When depleted, it is replenished by NaHCO₃-Pi *via* ligand exchange and mineralization of NaHCO₃-Po (Frossard

et al. 2000; Carter and Gregorich 2007; Yang and Post 2011). The little change in the concentration of resin-P and significantly decreased concentration of NaHCO$_3$-P (Pi+Po) in the 2018 CK and NK treatments in comparison with the initial soil supports this view (Fig. 4). A structural equation model revealed that resin-P was positively and directly influenced by NaHCO$_3$-Pi and NaHCO$_3$-Po (Hou et al. 2016). Furthermore, the decreased concentration of stable P in the CK and NK treatments indicates that stable P could be considered as a potential P source to replenish soil solution P when depleted. Similar results were reported in different soil types by Liu et al. (2017) and Shen et al. (2019). Soil P concentration were higher in the NPK treatment than the NK treatment which increased the concentrations of resin-P, NaHCO$_3$-Pi, and NaOH-Pi and their proportions to Pt (Fig. 4; Appendix A). These results suggest that mineral P addition enriched the plant-available P pool, as observed by Liu et al. (2017, 2019). The buildup of NaOH-Pi under mineral fertilization has been documented and Al-P is considered as a potential P source in black soil (Liu et al. 2017; Yang et al. 2019). Manure is rich in P and Ca (Sharpley and Moyer 2000), and applying manure promotes the formation of soil Ca-associated P (Ca-P) which results in a higher proportion of Ca-P compounds than when manure is not applied (Sato et al. 2005). In the present study, the increased proportion of NaHCO$_3$-Pi and dil.HCl-Pi to Pt in the NPKM treatment indicated long-term application of manure would result in the transformation of crystalline Ca-P species into relatively soluble Ca-P species (Appendix A), as found by Liu et al. (2020) and Yan et al. (2018). Previous study has shown that organic acids in manure could delay the crystallization and formation of hydroxyapatite and result in transformation of relatively soluble Ca-Ps (Sato et al. 2005; Liu et al. 2020).

4.3. Influence of soil properties on P fractions

The transformation of different P fractions in soil is largely controlled by soil organic matter and metal (such as Fe, Al, and Ca) oxide concentrations and pH (Pizzeghello et al. 2011; Yan et al. 2013, 2018). Most previous studies have focused on investigation of the influence of a single soil property on the P fractions in soil (Xu et al. 2018; Fan et al. 2019). However, the influence of soil on P fractions is complex, involving the interaction of multiple factors (Nobile et al. 2020; Sun et al. 2020). In the present study, increased SOM, M3-Fe, and Al$_p$, caused by fertilization, were the main factors influencing P fractions in the 0–20 cm soil depth (Table 4), which may largely be attributed to the fact that SOM can provide a portion of the Pi concentration through mineralization. Organic

matter showed negative relationships with free Fe and Al oxides and positive relationships with amorphous and organic-bound Fe and Al oxides (Appendix B). A possible reason for these relationships is that SOM may be strongly adsorbed on the surface of hydrated oxides, which hinders the formation of crystal nuclei and promotes the transformation of free crystalline Fe and Al oxides into amorphous and organic-bound Fe and Al oxides (Celi et al. 2003; Guo et al. 2007; Abdala et al. 2015). Among Fe and Al (hydr)oxides, poorly crystalline forms show a significantly greater P retention capacity for P compounds; however, when the concentration of P in the soil solution is decreased the reaction is reversible (Celi et al. 1999, 2003, 2020; Yan et al. 2014). NaOH-Pi is thought to be easily adsorbed on the surface of Fe and Al compounds (Hedley 1982), and is affected by the type and concentration of Fe and Al oxides in soil (Li et al. 2013; Barrow et al. 2015; Wang et al. 2017). In our study, the concentration of NaOH-Pi in soil treated with P fertilizer was significantly lower at 40–60 cm than that at 0–20 cm depth, indicating that amorphous and organic-bound Fe and Al oxides could effectively reduce the downward movement of available P into deeper soil layers (Yan et al. 2018). The decomposition products of SOM (organic acids, sulfates, and fluorides) may compete with phosphate radicals in soil solution for specific adsorption sites, or, if previously adsorbed, they may change the surface charge of Fe or Al oxides resulting in the electrostatic repulsion of phosphates (Bayon et al. 2006; von Wandruszka 2006; Antelo et al. 2007; Redel et al. 2007; Zamuner et al. 2008). Soil mineral components and pH were the main factors influencing the P fractions in the subsoil (Appendix C). The concentrations of CaCO$_3$, Fe$_d$ and Al$_d$ in soil treated with P fertilization were lower than in the CK treatment, which increased P availability because of their negative relationships with labile and partially labile Pi in subsoil (Appendix B).

5. Conclusion

Long-term fertilization with combined NPK and manure resulted in high P accumulation in the 0–60 cm profile of a black soil in northern China. The Olsen-P level in the NPKM treatment exceeded the critical value for Olsen-P for environmental safety, and increased the risk of P leaching. The higher PAC value and concentration of each labile Pi and partially labile Pi fraction in the NPKM treatment than in other treatments highlighted a significant increase in the available P in the soil. Redundancy analysis showed that SOM, M3-Fe, and Al$_p$ in the 0–20 cm soil depth, and soil mineral components in the subsoil played crucial roles in promoting the conversion

and release of different P fractions in the black soil. Although we undertook an in-depth investigation into the factors influencing P accumulation and transformation, further research is required to elucidate the influence of organic fertilizer application on the complex mechanisms (physicochemical and biological processes) involved in P cycling. Overall, our study reveals the changes in various P fractions following different fertilizations and quantifies the chemical-associated mechanisms in black soil under long-term fertilization.

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Declaration of competing interest

The authors declare that they have no conflict of interest.

Appendices associated with this paper are available on http://www.ChinaAgriSci.com/V2/En/appendix.htm

References

Abdala D B, Da Silva I R, Vergütz L, Sparks D L. 2015. Long-term manure application effects on phosphorus speciation, kinetics and distribution in highly weathered agricultural soils. *Chemosphere*, **119**, 504–514.

Ahlgren J, Djodjic F, Börjesson G, Mattsson L. 2013. Identification and quantification of organic phosphorus forms in soils from fertility experiments. *Soil Use and Management*, **29**, 24–35.

Annaheim K E, Doolette A L, Smernik R J, Mayer J, Oberson A, Frossard E, Bünemann E K. 2015. Long-term addition of organic fertilizers has little effect on soil organic phosphorus as characterized by ^{31}P NMR spectroscopy and enzyme additions. *Geoderma*, **257–258**, 67–77.

Antelo J, Arce F, Avena M, Fiol S, López R, Macías F. 2007. Adsorption of soil humicacidat the surface of goethite and its competitive interaction with phosphate. *Geoderma*, **138**, 12–19.

Ayaga G, Todd A, Brookes P C. 2006. Enhanced biological cycling of phosphorus increases its availability to crops in low-input sub-Saharan farming systems. *Soil Biology and Biochemistry*, **38**, 81–90.

Bai Z H, Li H G, Yang X Y, Zhou B K, Shi X J, Wang B R, Li D C, Shen J B, Chen Q, Qin W, Oenema O, Zhang F S. 2013. The critical soil P levels for crop yield, soil fertility and environmental safety in different soil types. *Plant and Soil*, **372**, 27–37.

Bao S D. 2010. *Soil Agrochemical Analysis*. 3rd ed. China Agricultural Press, Beijing, China. (in Chinese)

Barrow N J, Feng X H, Yan Y P. 2015. The specific adsorption of organic and inorganic phosphates by variable-charge oxides. *European Journal of Soil Science*, **66**, 859–866.

Bauke S L, von Sperber C, Tamburini F, Gocke M I, Honermeier B, Schweitzer K, Baumecker M, Don A, Sandhage-Hofmann A, Amelung W. 2018. Subsoil phosphorus is affected by fertilization regime in long-term agricultural experimental trials. *European Journal of Soil Science*, **69**, 103–112.

Bayon R C L, Weisskopf L, Martinoia E, Jansa J, Frossard E, Keller F, Föllmi K B, Gobat J M. 2006. Soil phosphorus uptake by continuously cropped *Lupinus albus*: A new microcosm design. *Plant and Soil*, **283**, 309–321.

van der Bom F J T, McLaren T I, Doolette A L, Magid J, Frossard E, Oberson A, Jensen L S. 2019. Influence of long-term phosphorus fertilisation history on the availability and chemical nature of soil phosphorus. *Geoderma*, **355**, 113909.

Bünemann E K, Smernik R J, Marschner P, McNeill A M. 2008. Microbial synthesis of organic and condensed forms of phosphorus in acid and calcareous soils. *Soil Biology and Biochemistry*, **40**, 932–946.

Carter M R, Gregorich E G. 2007. *Soil Sampling and Methods of Analysis*. 2nd ed. CRC Press, Boca Raton.

Castoldi N, Bechini L, Stein A. 2009. Evaluation of the spatial uncertainty of agro-ecological assessments at the regional scale: The phosphorus indicator in northern Italy. *Ecological Indicators*, **9**, 902–912.

Celi L, Lamacchia S, Ajmone-Marsan F, Barberis E. 1999. Interaction of inositol hexaphosphate on clays: Adsorption and charging phenomena. *Soil Science*, **164**, 574–585

Celi L, De Luca G, Barberis E. 2003. Effects of interaction of organic and inorganic P with ferrihydrite and kaolinite-iron oxide systems on iron release. *Soil Science*, **168**, 479–488.

Celi L, Prati M, Magnacca G, Santoro V, Martin M. 2020. Role of crystalline iron oxides on stabilization of inositol phosphates in soil. *Geoderma*, **374**, 114442.

Chen M, Graedel T E. 2016. A half-century of global phosphorus flows, stocks, production, consumption, recycling, and environmental impacts. *Global Environment Change*, **36**, 139–152.

Condron L M, Newman S. 2011. Revisiting the fundamentals of phosphorus fractionation of sediments and soils. *Journal of Soils and Sediments*, **11**, 830–840.

Cross A F, Schlesinger W H. 1995. A literature review and evaluation of the Hedley fractionation: Applications to the biogeochemical cycle of soil phosphorus in natural ecosystems. *Geoderma*, **64**, 197–214.

Eichler-Löbermann B, Köhne S, Köppen D. 2007. Effect of organic, inorganic, and combined organic and inorganic P fertilization on plant P uptake and soil P pools. *Journal of Plant Nutrition and Fertilizers*, **170**, 623–628.

Fan Y X, Zhong X J, Lin F, Liu C C, Yang L L, Wang M H, Chen G S, Chen Y M, Yang Y S. 2019. Responses of soil phosphorus fractions after nitrogen addition in a subtropical forest ecosystem: Insights from decreased Fe and Al oxides and increased plant roots. *Geoderma*, **337**, 246–255.

Fink J R, Inda A V, Tiecher T, Barrón V. 2016. Iron oxides and organic matter on soil phosphorus availability. *Science and Agrotechnology*, **40**, 369–379.

Frossard E, Condron L M, Oberson A, Sinaj S, Fardeau J C. 2000. Processes governing phosphorus availability in temperate soils. *Journal of Environmental Quality*, **29**, 15–23.

Glaesner N, van der Bom F, Bruun S, McLaren T, Larsen F H, Magid J. 2019. Phosphorus characterization and plant availability in soil profiles after long-term urban waste application. *Geoderma*, **338**, 136–144.

Godlinski F, Leinweber P, Meissner R, Seeger J. 2004. Phosphorus status of soil and leaching losses: Results from operating and dismantled lysimeters after 15 experimental years. *Nutrient Cycling in Agroecosystems*, **68**, 47–57.

Guo X M, Wu H H, Luo M, He G P. 2007. The morphological change of Fe/Al-oxide minerals in red soils in the process of acidification and its environmental significance. *Acta Petrologica et Mineralogica*, **26**, 515–521. (in Chinese)

Heathwaite L, Haygarth P, Matthews R, Preedy N, Butler P. 2005. Evaluating colloidal phosphorus delivery to surface waters from diffuse agricultural sources. *Journal of Environmental Quality*, **34**, 287–298.

Hedley M J, Stewart J W B, Changes B S. 1982. Changes in inorganic and organic soil phosphorus fractions induced by cultivation practices and by laboratory incubations. *Soil Science Society of America Journal*, **46**, 970–976.

Hou E Q, Chen C R, Kuang Y W, Zhang Y G, Heenan M, Wen D. 2016. A structural equation model analysis of phosphorus transformations in global unfertilized and uncultivated soils. *Global Biogeochemical Cycles*, **30**, 1300–1309.

Huang J, Zhang Y Z, Xu M G, Gao J S. 2016. Evolution characteristics of soil available phosphorus and its response to soil phosphorus balance in paddy soil derived from red earth under long-term fertilization. *Scientia Agricultura Sinica*, **49**, 1132–1141. (in Chinese)

Kang R F, Ren Y, Wu H J, Zhang S X. 2016. Changes in the nutrients and fertility of black soil over 26 years in Northeast China. *Scientia Agricultura Sinica*, **49**, 2116–2125. (in Chinese)

Kautz T, Amelung W, Ewert F, Gaiser T, Horn R, Jahn R, Javaux M, Kemna A, Kuzyakov Y, Munch J, Pätzold S, Peth S, Scherer H W, Schloter M, Schneider H, Vanderborght J, Vetterlein D, Walter A, Wiesenberg G, Köpke U. 2012. Nutrient acquisition from arable subsoil in temerate climates: A review. *Soil Biology and Biochemistry*, **57**, 1003–1022.

Kramer M G, Chadwick O A. 2018. Climate-driven thresholds in reactive mineral retention of soil carbon at the global scale. *Nature Climate Change*, **8**, 12, 1104–1108.

Lemming C, Oberson A, Magid J, Bruun S, Scheutz C, Frossard E, Jensen L S. 2019. Residual phosphorus availability after long-term soil application of organic waste. *Agriculture, Ecosystems and Environment*, **270–271**, 65–75.

Li W, Feng X H, Yan Y Y, Sparks D L, Philips B L. 2013. Solid-state NMR spectroscopic study of phosphate sorption mechanisms on aluminum (hydr)oxides. *Environmental Science & Technology*, **47**, 8308–8315.

Li Y Y, Yang R, Gao R, Wei H A, Chen A L, Li Y. 2015. Effects of long-term phosphorus fertilization and straw incorporation on phosphorus fractions in subtropical paddy soil. *Journal of Integrative Agriculture*, **14**, 365–373.

Liang X Q, Jin Y, He M M, Liu Y, Hua G F, Wang S, Tian G G. 2017. Composition of phosphorus species and phosphatase activities in a paddy soil treated with manure at varying rates. *Agriculture, Ecosystems and Environment*, **237**, 173–180.

Liu J. 2013. Speciation, mobilization, and control of water-dispersible colloidal phosphorus in agricultural lands. Ph D thesis, Zhejiang University, China. (in Chinese)

Liu J, Han C Q, Zhao Y H, Yang J J, Cade-Menun B J, Hu Y F, Li J M, Liu H, Sui P, Chen Y Q, Ma Y B. 2020. The chemical nature of soil phosphorus in response to long-term fertilization practices: Implications for sustainable phosphorus management. *Journal of Cleaner Production*, **272**, 123093.

Liu J, Sui P, Cade-Menun B J, Hu Y F, Yang J J, Huang S M, Ma Y B. 2019. Molecular-level understanding of phosphorus transformation with long-term phosphorus addition and depletion in an alkaline soil. *Geoderma*, **353**,116–124.

Liu J, Yang J J, Cade-Menun B J, Hu Y F, Li J M, Peng C, Ma Y B. 2017. Molecular speciation and transformation of soil legacy phosphorus with and without long-term phosphorus fertilization: Insights from bulk and microprobe spectroscopy. *Scientific Reports*, **7**, 15354.

Lu R K. 1999. *Soil and Agro-Chemistry Analytical Method*. China Agricultural Science and Technology Press, Beijing. (in Chinese)

Martin M, Celi L, Barberis E. 1999. Determination of low concentrations of organic phosphorus in soil solution. *Communications in Soil Science and Plant Analysis*, **30**, 1909–1917.

McDowell R W, Condron L M, Stewart I. 2016. Variation in environmentally- and agronomically-significant soil phosphorus concentrations with time since stopping the application of phosphorus fertilisers. *Geoderma*, **280**, 67–72.

McDowell R W, Sharpley A N. 2003. Uptake and release of phosphorus from overland flow in a stream environment. *Journal of Environmental Quality*, **32**, 937–948.

Mehlich A. 2008. Mehlich-3 soil test extractant: A modification of Mehlich 2 extractant. *Communications in Soil Science and Plant Analysis*, **15**, 1409–1416.

Motavalli P P, Miles R J. 2002. Soil phosphorus fractions after 111 years of animal manure and fertilizer applications. *Biology and Fertility of Soils*, **36**, 35–42.

Mundus S, Carstensen A, Husted S. 2017. Predicting phosphorus availability to spring barley (*Hordeum vulgare*)

in agricultural soils of Scandinavia. *Field Crops Research*, **212**, 1–10.

Murphy J, Riley J P. 1962. A modified single solution method for the determination of phosphate in natural waters. *Analytica Chimica Acta*, **27**, 31–36.

Nest T V, Ruysschaert G, Vandecasteele B, Houot S, Baken S, Smolders E, Cougnon M, Reheul D, Merckx R. 2016. The long term use of farmyard manure and compost: Effects on P availability, orthophosphate sorption strength and P leaching. *Agriculture, Ecosystems and Environment*, **216**, 23–33.

Nobile M, Bravin M N, Becquer T, Paillat J M. 2020. Phosphorus sorption and availability in an andosol after a decade of organic or mineral fertilizer applications: Importance of pH and organic carbon modifications in soil as compared to phosphorus accumulation, *Chemosphere*, **239**, 124709.

Olsen S R, Cole C V, Watanabe F S, Dean L A. 1954. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. *United States Department of Agriculture Circular*, **939**, 1–19.

Olson B M, Bremer E, McKenzie R H, Bennet D R. 2010. Phosphorus accumulation and leaching in two irrigated soils with incremental rates of cattle manure. *Canadian Journal of Soil Science*, **90**, 355–362.

Pizzeghello D, Berti A, Nardi S, Morari F. 2011. Phosphorus forms and P-sorption properties in three alkaline soils after long-term mineral and manure applications in north-eastern Italy. *Agriculture, Ecosystems and Environment*, **141**, 58–66.

Pizzeghello D, Berti A, Nardi S, Morari F. 2014. Phosphorus-related properties in the profiles of three Italian soils after long-term mineral and manure applications. *Agriculture, Ecosystems and Environment*, **189**, 216–228.

Pizzeghello D, Berti A, Nardi S, Morari F. 2016. Relationship between soil test phosphorus and phosphorus release to solution in three soils after long-term mineral and manure application. *Agriculture, Ecosystems and Environment*, **266**, 214–223.

Qin X C, Guo S F, Zhai L M, Pan J T, Khoshnevisan B, Wu S X, Wang H Y, Yang B, Ji L H, Liu H B. 2020. How long-term excessive manure application affects soil phosphorous species and risk of phosphorous loss in fluvo-aquic soil. *Environmental Pollution*, **266**, 115304.

Redel Y D, Rubio R, Rouanet J L, Borie F. 2007. Phosphorus bioavailability affected by tillage and crop rotation on a Chilean volcanic derived Ultisol. *Geoderma*, **139**, 388–396.

Richards L A. 1954. *Diagnosis and Improvement of Saline and Alkali Soils*. US Salinity Laboratory Staff, US Department of Agriculture, Washington D.C.

Sato S, Solomon D, Hyland C, Ketterings Q M, Lehmann J. 2005. Phosphorus speciation in manure and manure-amended soils using XANES spectroscopy. *Environmental Science & Technology*, **39**, 7485–7491.

Schleuss P M, Widdig M, Heintz-Buschart A, Kirkman K, Spohn M. 2020. Interactions of nitrogen and phosphorus cycling promote P acquisition and explain synergistic plant-growth responses. *Ecology*, **101**, e03003.

Sharpley A, Moyer B. 2000. Phosphorus forms in manure and compost and their release during simulated rainfall. *Journal of Environmental Quality*, **29**, 1462–1469.

Sharpley A N, Bergström L, Aronsson H, Bechmann M, Bolster C H, Börling K, Djodjic F, Jarvie H P, Schoumans O F, Stamm C, Tonderski K S, Ulén B, Uusitalo R, Withers P J A. 2015. Future agriculture with minimized phosphorus losses to waters: Research needs and direction. *AMBIO*, **44**, 163–179.

Sharpley A N, McDowell R W, Kleinman P J A. 2004. Amounts, forms, and solubility of phosphorus in soils receiving manure. *Soil Science Society of America Journal*, **68**, 2048–2057.

Shen P, Xu M G, Zhang H M, Yang X Y, Huang S M, Zhang S X, He X H. 2014. Long-term response of soil Olsen P and organic C to the depletion or addition of chemical and organic fertilizers. *Catena*, **118**, 20–27.

Shen Y, Duan Y H, McLaughlin, N. Huang S M, Guo D D, Xu M G. 2019. Phosphorus desorption from calcareous soils with different initial Olsen-P levels and relation to phosphate fractions. *Journal of Soils and Sediments*, **19**, 2997–3007.

Skjemstad J O, Baldock J A. 2007. Total and organic carbon. In: Carter M R, Gregorich E G, eds., *Soil Sampling and Methods of Analysis*. CRC Press, Florida, US. pp. 225–237.

Sowers T D, Adhikari D, Wang J, Yang Y, Sparks D L. 2018. Spatial associations and chemical composition of organic carbon sequestered in Fe, Ca, and organic carbon ternary systems. *Environmental Science & Technology*, **52**, 6936–6944.

Stutter M I, Shand C A, George T S, Blackwell M S, Bol R, MacKay R L, Richardson A E, Condron L M, Turner B L, Haygarth P M. 2012. Recovering phosphorus from soil: A root solution? *Environmental Science & Technology*, **46**, 1977–1978.

Sui Y B, Thompson M L, Shang C. 1999. Fractionation of phosphorus in a mollisol amended with biosolids. *Soil Science Society of America Journal*, **63**, 1174–1180.

Sun F, Song C J, Wang M, Lai D Y F, Tariq A, Zeng F J, Zhong Q P, Wang F M, Li Z, Peng C L. 2020. Long-term increase in rainfall decreases soil organic phosphorus decomposition in tropical forests. *Soil Biology and Biochemistry*, **151**, 108056.

Tiessen H, Stewart J, Cole C. 1984. Pathways of phosphorus transformations in soils of differing pedogenesis. *Soil Science Society America Journal*, **48**, 853–858.

Vu D T, Tang C, Armstrong R D. 2008. Changes and availability of P fractions following 65 years of P application to a calcareous soil in a Mediterranean climate. *Plant and Soil*, **304**, 21–33.

von Wandruszka R. 2006. Phosphorus retention in calcareous soils and the effect of organic matter on its mobility. *Geochemical Transactions*, **7**, 1–8.

Wang Q, Zhan X Y, Zhang S X, Peng C, Gao H J, Zhang X Z, Zhu P, Colinet G. 2019. Phosphorus adsorption and desorption characteristics and its response to soil properties of black soil under long-term different fertilization. *Scientia*

Agricultura Sinica, **52**, 3866–3877. (in Chinese)

Wang X M, Hu Y F, Tang Y D, Yang P, Feng X H, Xu W Q, Zhu M Q. 2017. Phosphate and phytate adsorption and precipitation on ferrihydrite surfaces. *Environmental Science Nano*, **4**, 2193–2204.

Wang Y, Bauke S L, von Sperber C, Tamburini F, Guigue J, Winkler P, Kaiser K, Honermeier B, Amelung W. 2021. Soil phosphorus cycling is modified by carbon and nitrogen fertilization in a long-term field experiment. *Journal of Plant Nutrition and Soil Science*, **184**, 282–293.

Wang Y, Feng G Z, Yan L, Li C L, Song L X, Liu Z G, Fang J. 2018. N, P and K requirement and fertilizer use efficiencies of spring maize in Jilin Province. *Journal of Plant Nutrition and Fertilizers*, **24**, 306–315. (in Chinese)

Whalen J K, Chang C, Clayton G W, Carefoot J P. 2000. Cattle manure amendments can increase the pH of acid soils. *Soil Science Society of America Journal*, **64**, 962–966.

Wu Q H, Liu X B, Zhang S X, Yin C X, Li G H, Xie J G. 2016. Application of 80% of routine phosphorus rate to keep high yield and P efficiency of maize and P balance in soil. *Journal of Plant Nutrition and Fertilizers*, **22**, 1468–1476. (in Chinese)

Wu Q H, Zhang S X, Feng G, Zhu P, Huang S M, Wang B R, Xu M G. 2020. Determining the optimum range of soil Olsen P for high P use efficiency, crop yield, and soil fertility in three typical cropland soils. *Pedosphere*, **30**, 832–843.

Xu Y, Han F E, Li D P, Zhou J, Huang Y. 2018. Transformation of internal sedimentary phosphorus fractions by point injection of CaO_2. *Chemical Engineering Journal*, **343**, 408–415.

Yan X, Wang D J, Zhang H L, Zhang G, Wei Z Q. 2013. Organic amendments affect phosphorus sorption characteristics in a paddy soil. *Agriculture, Ecosystems and Environment*, **175**, 47–53.

Yan X, Wei Z Q, Hong Q Q, Lu Z H, Wu J F. 2017. Phosphorus fractions and sorption characteristics in a subtropical paddy soil as influenced by fertilizer sources. *Geoderma*, **295**, 80–85.

Yan Y P, F Liu J, Li W, Liu F, Feng X H, Sparks D L. 2014. Sorption and desorption characteristics of organic phosphates of different structures on aluminum (oxyhydr) oxides. *European Journal of Soil Science*, **65**, 308–317.

Yan Z J, Chen S, Li J L, Alva A, Chen Q. 2016. Manure and nitrogen application enhances soil phosphorus mobility in calcareous soil in greenhouses. *Journal of Environmental Management*, **181**, 26–35.

Yan Z J, Chen S, Dari B, Sihi D, Chen Q. 2018. Phosphorus transformation response to soil properties changes induced by manure application in a calcareous soil. *Geoderma*, **322**, 163–171.

Yang X, Post W M. 2011. Phosphorus transformations as a function of pedogenesis: A synthesis of soil phosphorus data using Hedley fractionation method. *Biogeosciences*, **8**, 2907–2916.

Yang X Y, Chen X W, Yang X T. 2019. Phosphorus release kinetics and solubility capacity of phosphorus fractionation induced by organic acids from a black soil in northeast China. *Canadian Journal of Soil Science*, **99**, 92–99.

Yuan Z Y, Chen H Y H. 2012. A global analysis of fine root production as affected by soil nitrogen and phosphorus. *Proceedings of the Royal Society* (B: Biological Sciences), **279**, 3796–3802.

Zamuner E C, Picone L I, Echeverria H E. 2008. Organic and inorganic phosphorus in Mollisol soil under different tillage practices. *Soil and Tillage Research*, **99**, 131–138.

Zhan X Y. 2016. Relationship phosphorus balance and its mechanism under fertilizations in black soil. Ph D thesis, Chinese Academy of Agricultural Sciences, Beijing. (in Chinese)

Zhan X Y, Ren Y, Zhang S X, Kang R F. 2015. Changes in Olsen phosphorus concentration and its response to phosphorus balance in the main types of soil in China. *Scientia Agricultura Sinica*, **48**, 4728–4737. (in Chinese)

Zhang L. 2014. Relationship between change of Olsen-P and phosphorus balance and its mechanism in black soil with long-term fertilization. MSc thesis, Chinese Academy of Agricultural Sciences, Beijing. (in Chinese)

Zhang L, Ren Y, Zhan X Y, Zhang S X. 2014. Soil phosphorus balance and changes of Olsen-P of black soil under long-term conventional fertilization. *Journal of Nuclear Agricultural Sciences*, **28**, 1685–1692. (in Chinese)

Zhang W W, Zhan X Y, Zhang S X, Ibrahima K H M, Xu M G. 2019. Response of soil Olsen-P to P budget under different long-term fertilization treatments in a fluvo-aquic soil. *Journal of Integrative Agriculture*, **18**, 667–676.